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PRIMARY RESEARCH PAPER

Characterization and qualitative changes in DOM chemical characteristics related to hydrologic conditions in a Pampean stream

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Abstract The aim of our study was; (i) to characterize the composition of DOM in stream water and their potential sources (groundwater, overland flow, subsurface flow and rain water) and (ii) to analyze changes in DOM concentration and composition under different hydrological conditions (baseflow and high flow) in a third-order Pampean stream (Argentina). Pampean streams are mainly fed by the shallow aquifer under baseflow conditions and they lack of riparian forest. In addition, water velocity is low due to the gentle slope of the region and nutrient levels are high, favoring the development of rich macrophyte communities. DOM optical properties in the stream and end members were determined by combining absorbance-fluorescence spectroscopy techniques. Our results indicated that DOM chemical characteristics in the stream were mainly modulated by a differential contribution of end members to stream water depending on hydrological conditions. We observed that DOM in groundwater showed a microbial origin while DOM in runoff was terrestrially-derived. DOC concentration and inputs of humic substances from the riparian zone increased with discharge at high flow conditions. Due to the strong link between DOC properties and the riparian environment, structural alterations in the stream channel and changes in riparian vegetation (forestation) may result in changes in DOM composition and dynamics.

Keywords Pampean streams · Dissolved organic matter · High discharge · Base flow condition · Fluorescence spectroscopy · Absorbance spectroscopy

Introduction

Dissolved organic matter (DOM) is a complex mixture of soluble organic compounds that vary in their reactivity and ecological role, and it is the main source of biologically available organic carbon in aquatic ecosystems (Battin et al., 2008; Fellman et al., 2010). The quantity and the composition of DOM in streams is the combined result of different

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sources and in stream biogeochemical processing, including biological production, photochemical degradation and flocculation (Sachse et al., 2005). Depending on its source, DOM can be classified as either allochthonous, autochthonous or anthropogenic. Allochthonous DOM derives from terrestrial ecosystems, and although it is often considered recalcitrant, recent studies showed that it can be degraded by microbial or photochemical activity, fueling net heterotrophy of fluvial ecosystems (Battin et al., 2008; Catalán et al., 2013; Wilson et al., 2016). Allochthonous DOC is generally considered to have a more recalcitrant character than autochthonous DOC because the former is typically derived from vegetation and soil organic matter (Tranvik, 1992; Jaffé et al., 2008). On the other hand, autochthonous DOM is produced within the aquatic system by microbial activity and it is generally rich in biologically reactive compounds such as proteins, lipids and carbohydrates (Bertilsson & Jones, 2003). Anthropogenic DOM derives from human activities such as the direct spillage of sewage effluents to the river (Ejarque Gonzalez, 2014).

The temporal dynamic of stream DOM is usually governed by the discharge regime (Butturini et al., 2005; Neal et al., 2005). During floods, increase of terrigenous inputs from surface runoff causes an increase of DOM concentration in stream water. On the other hand, it has been seen that DOM concentration may also increase during drought periods, due to the accumulation of organic matter on the stream bed (litter, leaves and branches) that derives from riparian vegetation and in stream primary production (Romaní et al., 2006; Ylla et al., 2010). Although DOM concentration increases under both hydrological conditions (droughts and floods), its chemical composition may be different. In a previous research, Ejarque Gonzalez (2014) reported changes in DOM composition from predominantly protein-like fractions during droughts and base flow conditions to predominantly humic-like fractions during floods. Understanding the chemical composition of DOM is important, because chemically different DOM pools have different susceptibility to biogeochemical transformation processes within streams (Cory & Kaplan, 2012; Wollheim et al., 2015).

Most studies relating DOM characterization and hydrological variability have been carried out in forested streams of the north hemisphere (Europe and USA). These studies have reported pulses of DOM during autumn associated to the fall of litter and branches from riparian forests (Romaní et al., 2006; Vázquez et al., 2007; Ylla et al., 2010). However, to our knowledge this topic has not been studied in the Pampas region (Central Argentina), where streams are highly productive and grasses are the characteristic riparian vegetation. Moreover, low current velocity, high irradiance (due to the absence of riparian forest), and elevated nutrients levels favor the development of abundant macrophyte communities and in stream production (García et al., 2017). Thus, a higher contribution of DOM more degradable may be expected in Pampean streams compared to forested streams, where riparian vegetation mainly provides litter and branches. In addition, soils in the region are rich, with an organic matter content that varies between 3 and 3.9% in the northern Buenos Aires province (Sainz Rozas et al., 2011). Consequently, it should be expected elevated DOM levels in stream water, and a larger proportion of DOM originated from autochthonous sources (derived from epiphytic and benthic biofilms and macrophytes) with low molecular weight and higher bioavailability, compared to forested streams.

The characterization of the main sources (or end members) to stream DOM, jointly with the analysis of DOM changes with flow in Pampean streams may help to understand DOM dynamics in non-forested fluvial systems. In addition, it will serve to establish baseline conditions in a region that is undergoing a process of agricultural intensification. In the last few years, the riparian zone of Pampean streams is being altered through the replacement of the original herbaceous riparian vegetation by cropland or through the impact of cattle breeding. Cattle with unrestricted access to streams impacts on watercourses thought, grazing near the stream and the trampling of stream banks. This provides sediments, associated nutrients, and bacteria with a direct route to the stream (Osmond et al., 2007). The knowledge of stream DOM characteristics and its dynamics may allow us to determine the effects of these changes on DOM quantity and composition.

The aims of our study were; (i) to characterize DOM composition in stream water and their potential sources (groundwater, overland flow, subsurface flow and rain water) by combining absorbance-fluorescence spectroscopy techniques, and (ii) to analyze changes in DOM concentration and composition under different hydrological conditions (baseflow and high flow) in a Pampean stream. Our hypotheses are that (i) DOM composition in stream water depends on the contribution of different autochthonous and allochthonous DOM sources, and that (ii) the predominance of the different sources varies with the hydrological conditions. Hence, we expected (i) an increase in DOC concentration during high flow, which will mainly derive from soil and plant material and characterized by a high humic content, in contrast with (ii) DOM derived from in stream production and macrophyte decomposition under baseflow conditions. To our knowledge, this is the first study that characterized DOM composition in Pampean fluvial environments.

Methodology

Study site

The pampa is a vast grassland system, covering an area of 500,000 km^2 in central Argentina. The climate is temperate humid, with mean annual temperatures between 14 and 20°C. The mean annual precipitation oscillates between 600 and 1200 mm, and is evenly distributed throughout the year, with maximum levels in spring and fall (Gantes, 2000; Vilches & Giorgi, 2010). Pampean streams begin in small depressions with emergent plants, such as *Schoenoplectus californicus* (C. A. Mey) Soják or *Typha latifolia* L. (Vilches & Giorgi, 2010) and are mainly fed by the shallow aquifer under baseflow conditions (unpublished results). Water velocity is low and discharge is laminar due to the gentle slope of the region. The stream bed consists of fine sediments (primarily silt and clay) without stones or pebbles. High nutrient levels favor the development of rich and dense macrophyte communities that give substrate to biofilms (epiphytic and benthic communities), and food and refuge to macroinvertebrates and fishes (Giorgi et al., 2005). Although, water flow is usually low, it can drastically increase during extreme storm events, which are frequent at the Pampas region (Vilches & Giorgi, 2010).

This study was carried out in Las Flores stream, a third-order stream located in the Luján River basin in the northeast of the Buenos Aires province, Argentina. This stream is considered representative of most Pampean streams. It has been affected by human activities only to a small extent because it does not receive inputs from point sources of pollutants, with the exception of one tributary (ST_2) that receives effluents from the wastewater treatment plant of a dairy industry (Fig. 1).

Sampling design

We selected a 2.2 km reach of Las Flores stream, which originates at the confluence of two tributaries (ST_1 and ST_2) with different subcatchment areas (18.6 km^2 for ST_1 and 13.3 km^2 for ST_2). Tributary ST_2 receives effluent of the wastewater treatment plant of an industry that produces cheese and caramel. At the end of the reach, we installed collectors for sampling the different end members. Groundwater (GW) was sampled from a piezometer situated 1 m apart from the stream channel. The piezometer consisted of a PVC tube (0.11 m diameter and 4 m depth) with slots in the last 3 m. Groundwater was sampled with a peristaltic pump, and prior to sample collection the piezometer was purged with a minimum of 3 piezometer volume. Overland flow (OF) was collected using a PVC gutter (2 m long) situated parallel to the channel and covered with a sheet to avoid the entrance of rainwater. The gutter was connected by a plastic tube to a 20 l tank, from which samples were collected. Subsurface flow (SF) was collected in a PVC tank (0.15 m diameter and 0.30 m depth) with slots in the upper 0.15 m, and buried with the slots located just over the limit between the organic-rich surface soil and the clay subsoil to collect rainwater that percolates through the superficial horizons and then flows on the top of subsoil to the stream. Subsurface water samples were sampled from the tank with a peristaltic pump. Rainwater (*R*) was collected using a pluviometer situated in an open area close to the stream. We also collected stream water (*S*) samples at the end of the reach and at both tributaries (ST_1 and ST_2) just before their confluence (Fig. 1).

Sampling was conducted from 2013 to 2015 under different hydrological condition, from baseflow to high flow (after storm events) to include natural variation of stream discharge. Water samples were collected the next day after the storm, remaining less than 12 h in the different sampling devices. After

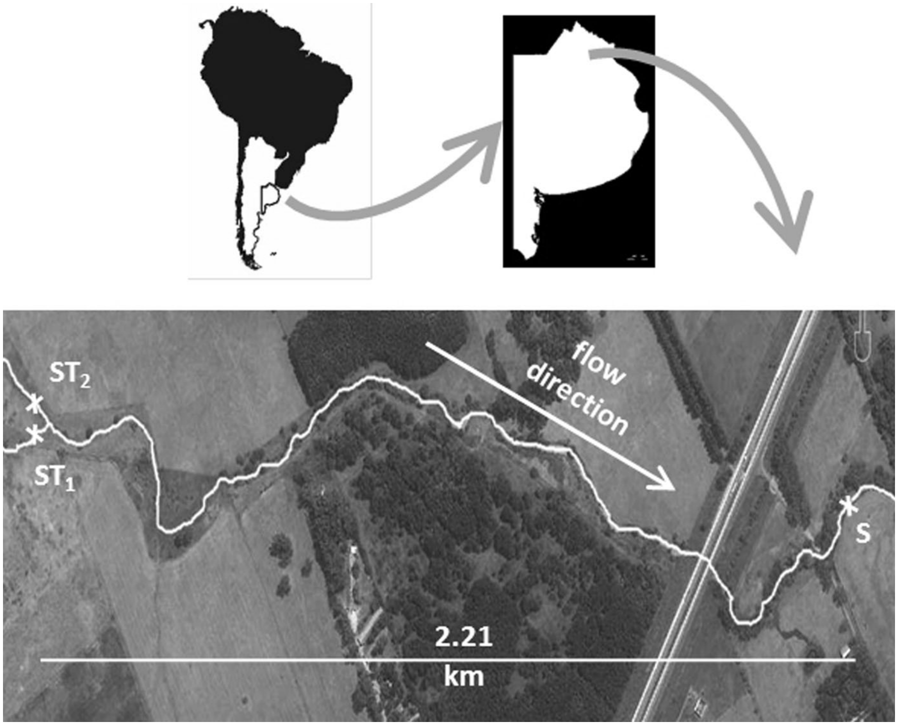

Fig. 1 Location of the studied reach at Las Flores stream. S: stream sampling point. ST$_1$ and ST$_2$: upstream tributaries. Collectors of the different end members (groundwater, rainfall, subsurface flow and overland flow) were located in S

sample collection, sampling containers were emptied and cleaned. To minimize sample contamination, samples were stored in an ice chest to keep them cold and in dark condition until being transported to the laboratory. Samples were filtered within 3 h from collection. In addition, three storm events were intensively monitored in May 2014 during 8 days, in January 2015 during 3 days, and in July 2015 during 7 days. During storm events water samples were taken at regular intervals, every 2 h until the hydrograph peak was reached, and then at longer intervals until attaining baseflow conditions again.

At each sampling date, stream discharge (Q) was determined by the velocity-area method (Gordon et al., 1994) at the end of the stream reach and both tributaries using a multiprobe anemometer (Schiltknecht MiniAir20). Water level was measured using a levelogger (Solinst 3001 LT F15/M5) installed at the end of the reach, which was compensated for atmospheric pressure by a barologger Edge (Solinst 3001 LT FE/M15) located close to the sampling point. The relationship between water level and measured Q (Eq. 1) was used to obtain a continuous record of discharge using stream water depth data throughout the whole study period:

$$Q = 0.0656 \times h^{2.443}\left[\text{volume time}^{-1}\right] \tag{1}$$

where Q is discharge (in l s^{-1}) and h is stream water level (in m) ($R^2 = 0.94$). This empirical relationship was used to estimate discharge during the three monitored storm events, when high flows hampered direct measurements of discharge. In each water sample, we measured temperature (T, °C), pH, and electrical conductivity (EC, µS cm^{-1}) using a Hach multiprobe (HQ40D).

Sample preparation

Cleaning procedures

All glass and plastic material were cleaned with diluted acid (HCl 10%) and rinsed with Milli-Q ultrapure water. All containers were rinsed several times with sample before filling.

Dissolved organic carbon (DOC) and spectrometric analysis

In this work, DOC concentration is considered a proxy for DOM quantity. Water samples for DOC analysis were collected in 25 mL amber glass bottles after filtration through precombusted glass fiber filters (nominal pore size = 0.7 µm, Whatman GF/F). All DOC samples were acidified with HCl 10% and preserved at 4°C until analysis. DOC concentration was measured through high-temperature catalytic oxidation on a Shimadzu TOCV CSH analyzer (Shimadzu Corporation, Japan.). Water samples for absorbance-fluorescence analysis were filtered through 0.7 µm, and then through 0.2 µm nylon membrane filters, collected in 20 ml bottles, kept in cool and dark conditions until analysis.

The absorbance spectra (190–800 nm) from filtered water samples were measured on an Agilent 8453 diode array spectrophotometer (Agilent Technologies, Germany) using a 1-cm quartz cuvette. Milli-Q water was used as a blank. The average sample absorbance between 700 and 800 nm was subtracted from the spectrum in order to correct for offsets due to instrument baseline drift (Green & Blough, 1994). We calculated the specific UV absorbance at 254 nm ($SUVA_{254}$, L mg^{-1} m^{-1}) by dividing the UV absorbance measured at 254 nm by the DOC concentration (Weishaar et al., 2003). SUVA index is associated with bulk aromaticity in the sample, with higher values being indicative of a high content of aromatic carbon. The spectral slopes for the interval 275–295 and 350–400 nm ($S_{275–295}$ and $S_{350–400}$, respectively) were determined by fitting the single absorbance spectra to an exponential decay function. The slope ratio (S_R) was calculated as the ratio of $S_{275–295}$ to $S_{350–400}$. Helms et al. (2008) demonstrates that $S_{275–295}$ and S_R are inversely related to the molecular weight of DOM.

Excitation-Emission matrices (EEMs) were obtained using a fluorescence spectrophotometer (F-7000, Hitachi, Japan) with a 1-cm quartz cuvette. EEMs were obtained by measuring fluorescence intensity across the excitation range set from 200 to 449 nm (3 nm increments) and the emission range set from 250 to 598 nm (3 nm increments). Before measuring the samples, fluorometer was calibrated with a Rhodamine B solution to correct instrument-specific biases. Water samples were allowed to warm to room temperature prior to measurements. EEMs were blank subtracted using the EEM of Milli-Q water, determined every ten samples. Spectra were corrected for inner filter effects using UV–Vis absorbance spectra as described in Kothawala et al. (2013). The intensity of the main fluorescence peaks (A, C, M, B, and T; Coble, 1996) used for DOM characterization was obtained from EEMs (Table 1). Peaks A and C exhibit emission at long wavelengths and are related to aromatic humic-like fluorophores that derive from terrestrial sources. Peak M is also related to humic-like substances, although it exhibits emission at shorter wavelengths, and it is considered to be less aromatic and likely of lower molecular weight. Peaks B and T are related to tyrosine-like and tryptophan-like substances, respectively, and have been associated to protein-like materials of different origin (Table 1). Although it is assumed that the presence and proportion of this type of fluorophores are indicative of labile organic carbon (Fellman et al., 2009a, b; Hood et al., 2009), a recent study indicates that majority of the tryptophan-like FDOM was recalcitrant, while tyrosine-like FDOM was 100% biodegraded and the majority was classified as labile (Cory & Kaplan, 2012).

We also calculated the following spectral indices: humification index (HIX), biological index (BIX) and fluorescence index (FI). HIX was calculated by dividing the area of fluorescence intensity between 435 and 480 nm by that between 300 and 345 nm, at a fixed excitation wavelength of 254 nm (Zsolnay et al., 1999). HIX is associated with an increase in the degree of the humification of organic matter (Zsolnay et al., 1999). High HIX values correspond to maximal fluorescence intensity at longer wavelengths and thus to the presence of complex molecules like high molecular weight aromatic compounds (Senesi et al., 1991). BIX was calculated as the ratio between the emitted fluorescence intensity at 380 nm and the emitted fluorescence intensity at 430 nm for an excitation at 310 nm. An increase in BIX is related to an autochthonous origin of DOM and to the presence of freshly released DOM (Huguet et al., 2009). FI index was calculated as the ratio of the emitted fluorescence intensity at 470 nm and the emitted fluorescence intensity at 520 nm for an excitation of 370 nm. The FI indicates the origin of precursor material, that is DOM derived from microbial (FI ~ 1,8) or terrestrial (FI ~ 1,2) sources (Cory & McKnight, 2005).

Table 1 Wavelength and description of the main fluorescence peak used in this study

Peak	Wavelength	Interpretation
A	250 Ex–450 Em	Humic substances and recent materials (Stedmon & Markager, 2005; Fellman et al., 2010, UVA-humic-like)
C	350 Ex–450 Em	Humic substances from terrestrial sources (Stedmon & Markager, 2005; Fellman et al., 2010, UVC-humic-like)
M	310 Ex–400 Em	Autochthonous production, low molecular weight (Stedmon & Markager, 2005; Fellman et al., 2010, UVC-humic-like)
T	280 Ex–330 Em	Protein-like material (resembling the aminoacid Tryptophan signal) (Stedmon & Markager, 2005; Fellman et al., 2010, Tryptophan-like)
B	270 Ex–300 Em	Protein-like material (resembling the aminoacid Tyrosine signal) (Stedmon & Markager, 2005; Fellman et al., 2010, Tryptophan-like)

Data treatment and analysis

Data are reported as mean ± SE for every variable. Differences between variables were tested with non-parametric Kruskal–Wallis tests, due to variables do not fit to a normal distribution even after log transformation. We applied Spearman correlation tests to analyze the relationship between variables. Then we analyzed the way in which correlated variables were related. The model that best describe the relationship between DOC concentration and fluorimetric and spectrometric indexes with discharge (Q) was a power model ($C = aQ^b$) (Godsey et al., 2009; Moatar et al., 2017). Relationships were considered significant at $P < 0.05$.

Results

Stream and end members' physicochemical characterization

We found that temperature values were similar among stream and end members (Table 2). pH varied from 7.4 to 8.02, showing similar values in the stream and tributaries (S, ST_1 and ST_2) but different values in the other end members (GW, OF, SF and R). EC was lower in R samples (33 µS cm^{-1}) and higher in GW samples (700 µS cm^{-1}). The stream, their tributaries and the rest of the end members showed intermediate values.

DOM chemical characterization

DOC concentration was higher in runoff samples (OF and SF) and lower in GW and R samples (Fig. 2). DOC concentrations were intermediate and similar in S, ST_1 and ST_2. SUVA did not vary between S and their end members, except for R samples that showed the lowest values (Kruskal–Wallis test, $P < 0.0001$) Fig. 3). The S_R was higher in GW samples, while similar values were observed in S and the other end members (Fig. 3).

Relative contribution of humic (A, C and M) peaks to total fluorescence were higher in S, ST_1 ST_2 and in runoff samples (OF and SF), with peak A contributing almost 40% to total fluorescence and the others peaks representing a 20% each one. On the contrary, peaks B and T, related to protein-like compounds, showed a higher contribution in GW and R samples (~ 20%), while no differences were observed between the other end members (Kruskal–Wallis test, $P < 0.0001$) (Table 3).

With regard to fluorimetric indexes, we observed that end members could be separate in two groups according to HIX; GW and R samples with lower and significantly different values (Kruskal–Wallis test, $P < 0.0001$), and the other end members with higher values that did not differ among them (Fig. 3). However, BIX and FI showed the opposite pattern with the highest values in GW and R (Kruskal–Wallis test, $P < 0.0001$) (Fig. 3).

Table 2 Physicochemical parameters electrical conductivity (EC), temperature and pH in the stream (S), both tributaries (ST_1: and ST_2) and their end members: subsurface flow (SF); overland flow (OF); groundwater (GW) and rain (R)

End member	EC (µS cm^{-1}) Mean (± SE)	*T* (°C) Mean (± SE)	pH Mean (± SE)
S	574.69 (± 55.95)	17.87 (± 0.97)	7.82 (± 0.1)
ST_1	466.27 (± 62.99)	18.51 (± 1.22)	7.92 (± 0.09)
ST_2	674.98 (± 54.7)	17.21 (± 0.96)	8.02 (± 0.09)
SF	201.81 (± 39.64)	16.11 (± 1.35)	7.08 (± 0.19)
OF	124.18 (± 18.56)	17.99 (± 2.01)	7.37 (± 0.14)
GW	770.56 (± 3.54)	18.2 (± 037)	7.67 (± 0.02)
R	33.75 (± 8.19)	19.02 (± 1.34)	7.4 (± 0.48)

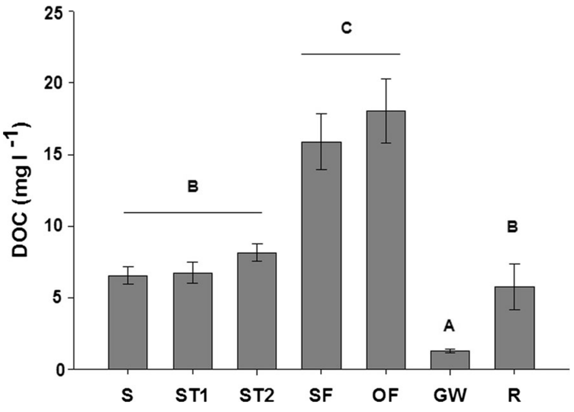

Fig. 2 DOC concentration for the stream (S), both tributaries (ST_1: and ST_2) and their end members: subsurface flow (SF); overland flow (OF); groundwater (GW) and rain (R)

Hydrological characterization and changes in DOM with discharge

Stream flow in the sampling point S was highly variable, with a mean value of 240 l s^{-1} and ranging from 23 to 1451 l s^{-1}. Comparing the tributaries, ST_1 had a higher flow than ST_2 (89 ± 1.84 and 64 ± 1.4 l s^{-1}, respectively). Stream DOC concentration in S increased with stream discharge ($R^2 = 0.56$; $P = 0.0005$) and the same trend was observed in tributaries ST_1 and ST_2 ($R^2 = 0.50$; $P = 0.0013$ and $R^2 = 0.21$; $P = 0.0408$, respectively) (Fig. 4.).

Focusing on optical indexes, we observed no significant relationships between SUVA and S_R with discharge in S and the tributaries, except for SUVA in ST_1 that increased with discharge ($R^2 = 0.41$; $P = 0.0047$). Fluorescence intensity of peaks related to humic fluorophores expressed in raman units (peaks A, C and M) increased with discharge, both in S (*peak A*: $R^2 = 0.47$ and $P = 0.0021$; *peak C*: $R^2 = 0.46$ and $P = 0.0023$; and *peak M*: $R^2 = 0.36$ and $P = 0.0081$) and ST_1 samples (*peak A*: $R^2 = 0.26$ and $P = 0.025$; *peak C*: $R^2 = 0.30$ and $P = 0.018$; and *peak M*: $R^2 = 0.28$ and $P = 0.021$, Table 4). However, no significant relationships were observed between these fluorophores and discharge in ST_2. No relationships were either observed between peak B or peak T and discharge in S, ST_1 and ST_2. HIX increased with discharge ($R^2 = 0.24$; $P = 0.03$) for S, but was unrelated to discharge in ST_1 and ST_2. BIX and FI for S samples decreased with discharge ($R^2 = 0.41$ and $P = 0.0046$ and $R^2 = 0.36$ and $P = 0.0078$, respectively) (Table 4). The same tendencies for BIX and FI were observed in ST_1 ($R^2 = 0.52$ and $P = 0.0009$ and $R^2 = 0.30$ and $P = 0.017$, respectively) (Table 4). Although, FI decreased with increasing discharge in ST_2 ($R^2 = 0.45$; $P = 0.0018$), no relationship were found between BIX and discharge for this tributary. Higher slopes of the relationships between humic peaks (A and C) and discharge indicate a stronger response of these peaks to flow changes compared to the other DOM descriptors (Table 4).

Description of changes in DOM chemical composition during storms event

In general, stream baseflow increased between 2 and 300 times and stream level raised tenfold (between 0.19 and 2.0 m high) during storm events (Table 5). However, it should be noted that these values may be

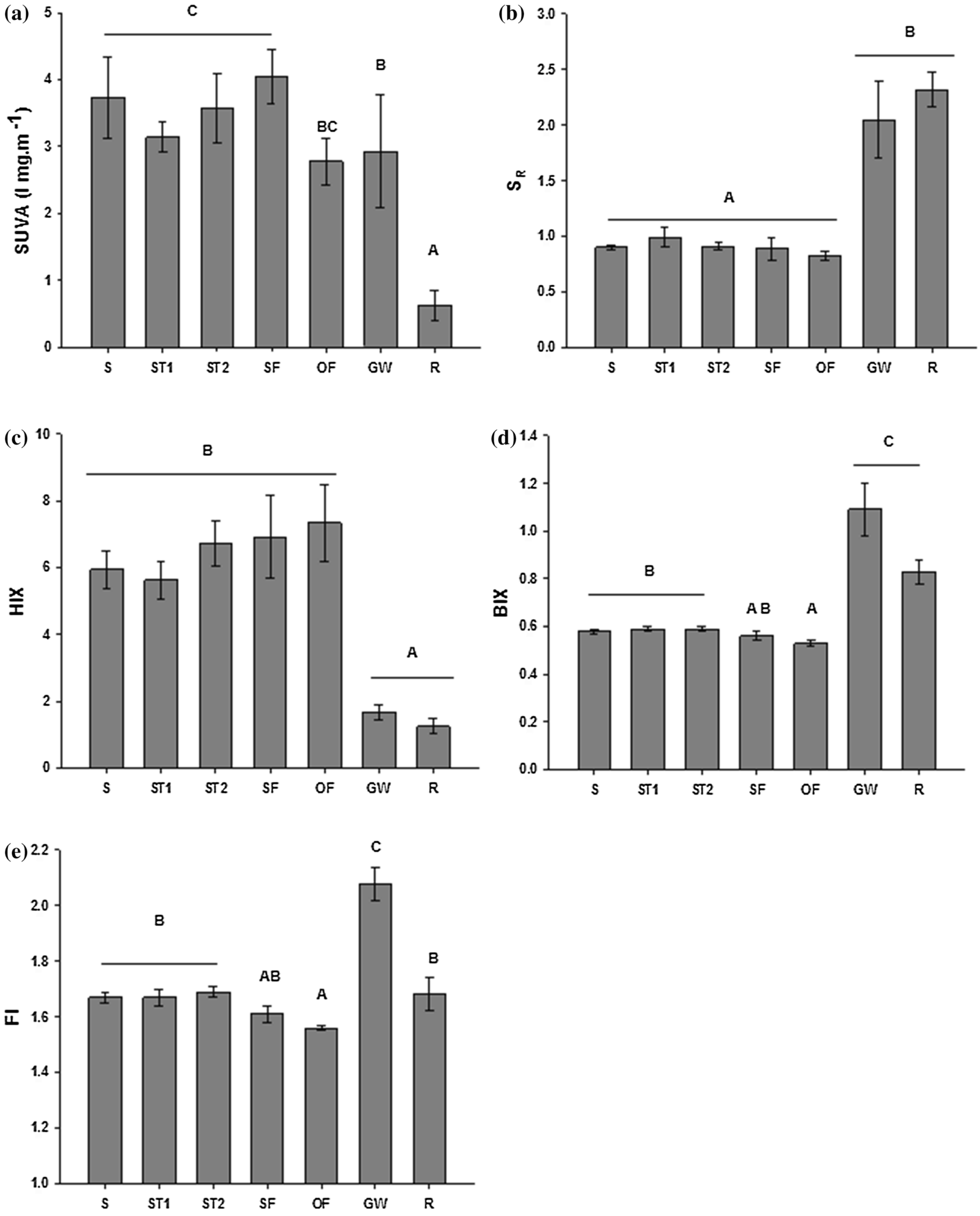

Fig. 3 **a** SUVA, **b** SR, **c** HIX, **d** BIX and **e** FI indexes for the stream (S), both tributaries (ST_1: and ST_2) and their end members: subsurface flow (SF); overland flow (OF); groundwater (GW) and rain (R)

Table 3 Fluorescence peaks expressed as mean ± SE for the stream (*S*), both tributaries (ST_1: and ST_2) and their end members: subsurface flow (SF); overland flow (OF); groundwater (GW) and rain (*R*)

End member	Peak A (%) Mean (± SE)	Peak C (%) Mean (± SE)	Peak M (%) Mean (± SE)	Peak B (%) Mean (± SE)	Peak T (%) Mean (± SE)
S	38.22 (± 1.62)	18.77 (± 0.78)	19.88 (± 0.45)	9.11 (± 1.22)	14.02 (± 1.62)
ST_1	38.17 (± 1.41)	18.31 (± 0.78)	19.76 (± 0.82)	9.60 (± 1.40)	14.16 (± 1.44)
ST_2	38.89 (± 1.27)	19.40 (± 0.69)	20.12 (± 0.55)	8.14 (± 1.23)	13.46 (± 1.27)
SF	36.14 (± 3.97)	19.31 (± 1.58)	24.17 (± 3.02)	8.10 (± 1.99)	11.96 (± 1.32)
OF	39.97 (± 1.03)	21.21 (± 0.57)	21.47 (± 0.50)	6.79 (± 1.28)	11.00 (± 0.71)
GW	26.74 (± 1.36)	12.43 (± 0.57)	16.76 (± 1.35)	20.69 (± 1.59)	23.38 (± 1.64)
R	22.91 (± 1.76)	12.20 (± 0.78)	16.23 (± 0.93)	22.68 (± 1.77)	26.38 (± 2.34)

Fluorescence peaks are reported as percent contribution of each peak to the sum of fluorescence intensity by all peaks

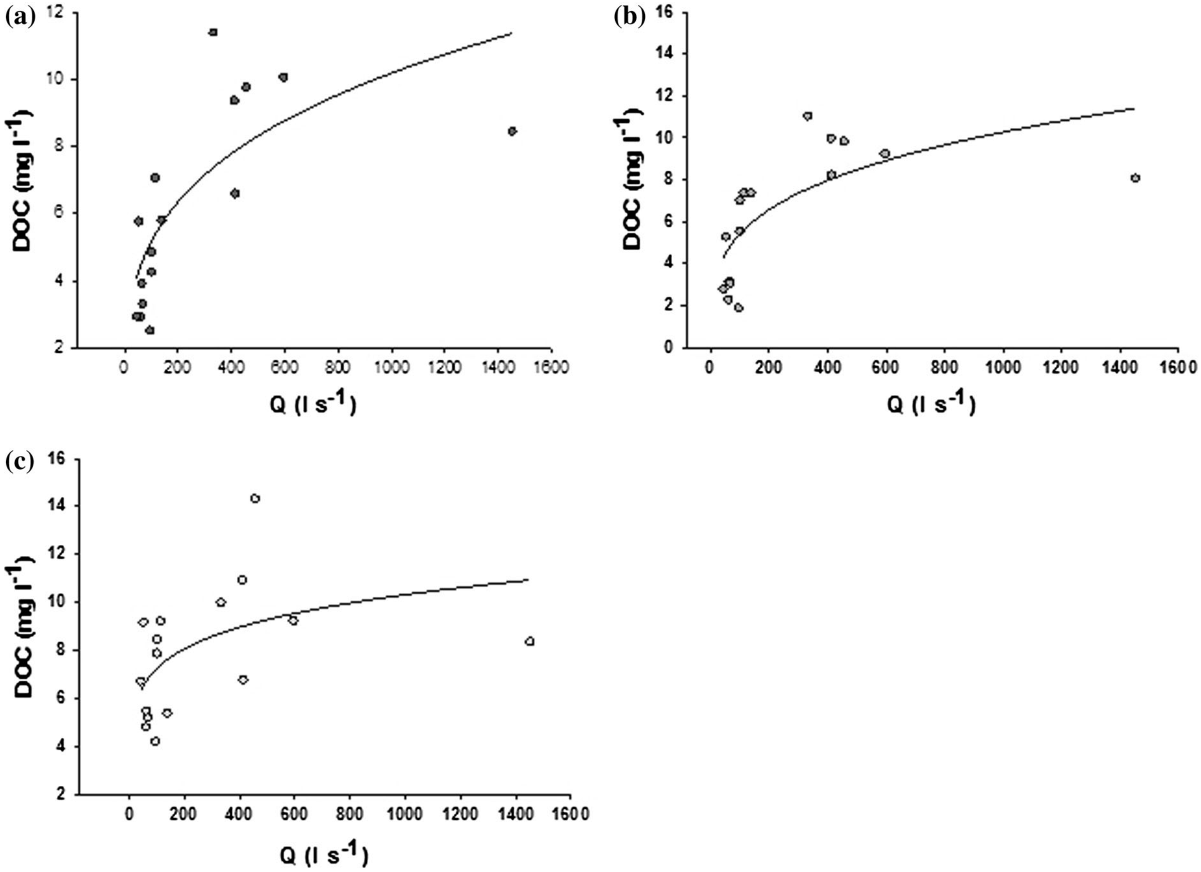

Fig. 4 Relationship between DOC concentration (mg C l^{-1}) and Q (l s^{-1}) for **a** stream (S), **b** stream tributary 1 (ST_1) and **c** stream tributary 2 (ST_2)

interpreted with caution because in two of the three monitored storm events, maximum discharge exceeded the range considered in the empirical relationship between depth and discharge. Although DOC concentration increased during events, no clear patterns were detected between DOC concentration and discharge. We observed that SUVA and HIX increased with discharge ($R^2 = 0.50$; $P = 0.0013$ and

Table 4 Relationship between discharge (expressed as log) and several optical indexes in the stream (*S*) and both tributaries (ST_1 and ST_2)

End member	*S*	ST_1	ST_2
HIX	$r = 0.64$ $R^2 = 0.24$ $b = 0.20$ $P = 0.034$ $N = 19$	NR	NR
BIX	$r = -0.52$ $R^2 = 0.41$ $b = -0.047$ $P = 0.0046$ $N = 19$	$r = -0.79$ $R^2 = 0.52$ $b = -0.046$ $P = 0.0009$ $N = 17$	
FI	$r = -0.68$ $R^2 = 0.36$ $b = -0.03$ $P = 0.0008$ $N = 19$	$r = -0.75$ $R^2 = 0.30$ $b = -0.034$ $P = 0.016$ $N = 17$	$r = -0.80$ $R^2 = 0.45$ $b = -0.029$ $P = 0.0019$ $N = 18$
Peak A	$r = 0.83$ $R^2 = 0.47$ $b = 0.32$ $P = 0.0021$ $N = 19$	$r = 0.62$ $R^2 = 0.26$ $b = 0.16$ $P = 0.0025$ $N = 17$	NR
Peak C	$r = 0.84$ $R^2 = 0.47$ $b = 0.31$ $P = 0.0023$ $N = 19$	$r = 0.61$ $R^2 = 0.30$ $b = 0.17$ $P = 0.018$ $N = 17$	NR
Peak M	$r = 0.77$ $R^2 = 0.36$ $b = 0.27$ $P = 0.008$ $N = 19$	$r = 0.63$ $R^2 = 0.28$ $b = 0.16$ $P = 0.021$ $N = 17$	NR

Peaks are reported here as fluorescent intensities. Correlation coefficient (*r*), determinant coefficient (R^2), slope (*b*), significance levels and number of cases are indicated. NR no relationship between variables

Table 5 Discharge (Q, l s^{-1}) and stream level (m) for the tree storm event

	May 2014		January 2015		July 2015	
	Q (l s^{-1})	Level (m)	Q (l s^{-1})	Level (m)	Q (l s^{-1})	Level (m)
Mean (± SE)	3615.25 (± 144.8)	58.21 (± 0.01)	117.48 (± 144.8)	0.21 (± 0.001)	1482 (± 86.6)	0.38 (± 0.01)
Max	27,748.9	2.01	227.77	0.28	20,359.98	1.77
Min	89.62	0,19	57.61	0.16	57.4	0.16
Median	260.19	0.30	108.29	0.21	132.04	0.23

$R^2 = 0.536$; $P = 0.0009$, respectively) for May and July events ($R^2 = 0.80$; $P = 0.0001$ and $R^2 = 0.43$; $P = 0.0046$, Fig. 5), whereas no significant relationship was observed in January event. BIX, FI and S_R did not show any relationship with the increase of discharge during the events. We also observed that fluorescence intensity of peaks related to humic compounds (peaks A; C and M) increase with increasing discharge both in May (*peak A*: $R^2 = 0.52$ and $P = 0.0009$; *peak* C: $R^2 = 0.52$ and $P = 0{,}0010$ and *peak* M: $R^2 = 0.52$ and $P = 0.0010$) and in July (*peak A*: $R^2 = 0.765$ and $P < 0.0001$; *peak* C: $R^2 = 0.80$ and $P < 0.0001$ and peak M: $R^2 = 0.78$ and $P = < 0.0001$) (Fig. 6), but no relationship were observed in January. The slopes of the relationship between peaks A and C (humic) and discharge in July event were stronger than (higher slopes) the other DOM descriptor. This indicates that the response of humic peaks to flow changes is higher than the response of other DOM descriptor. Also, we observed that in May event, slopes of the relationship between humic peaks and discharge and the slope of the relationship between S_R and HIX with discharge were similar indicating that parameters respond in the same way to the flow changes.

Discussion

DOM characterization in the stream and end members

The integration of the spectroscopic methods with detailed hydro-biogeochemical monitoring during extreme hydrological conditions provides an excellent challenge to capture a more complete perspective

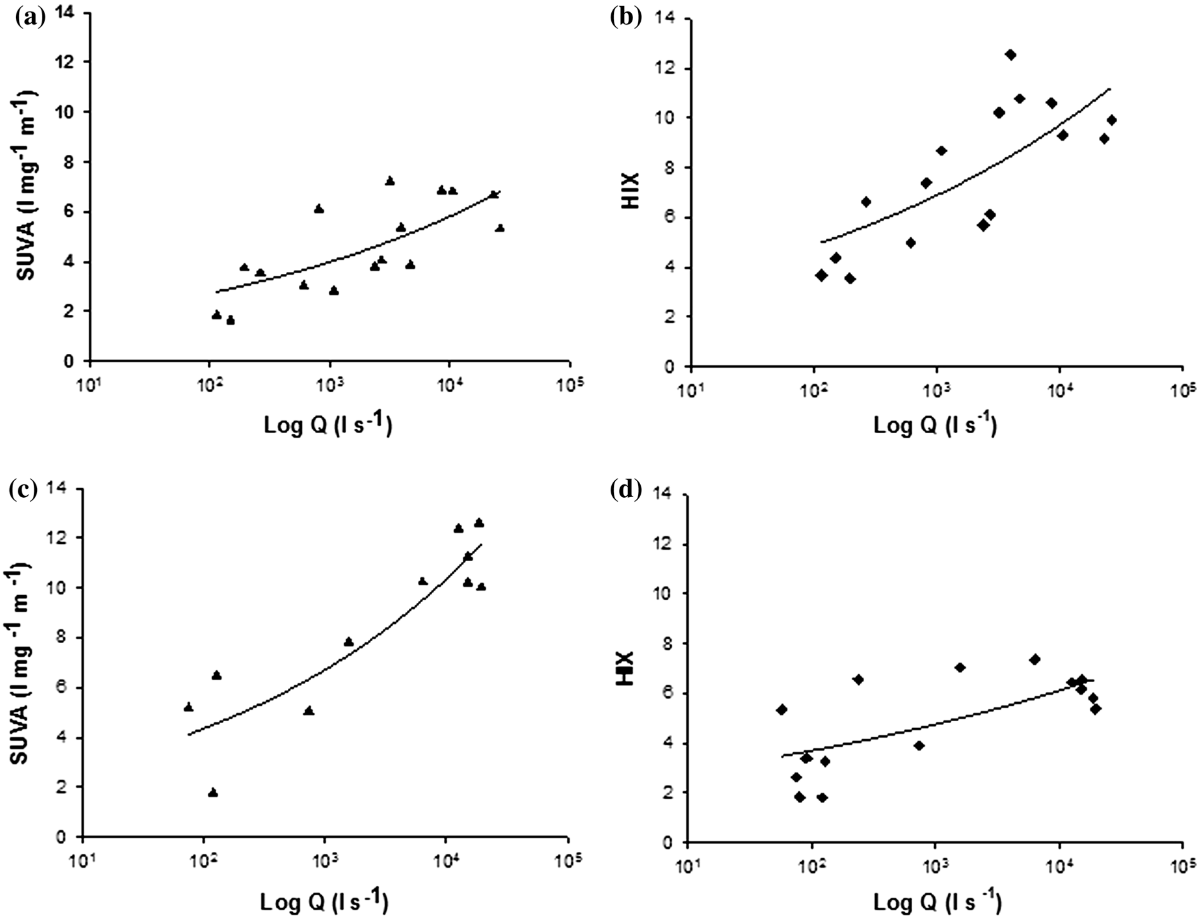

Fig. 5 Relationship between SUVA and HIX and log discharge for May (**a**, **b**) and July (**c**, **d**) storm event

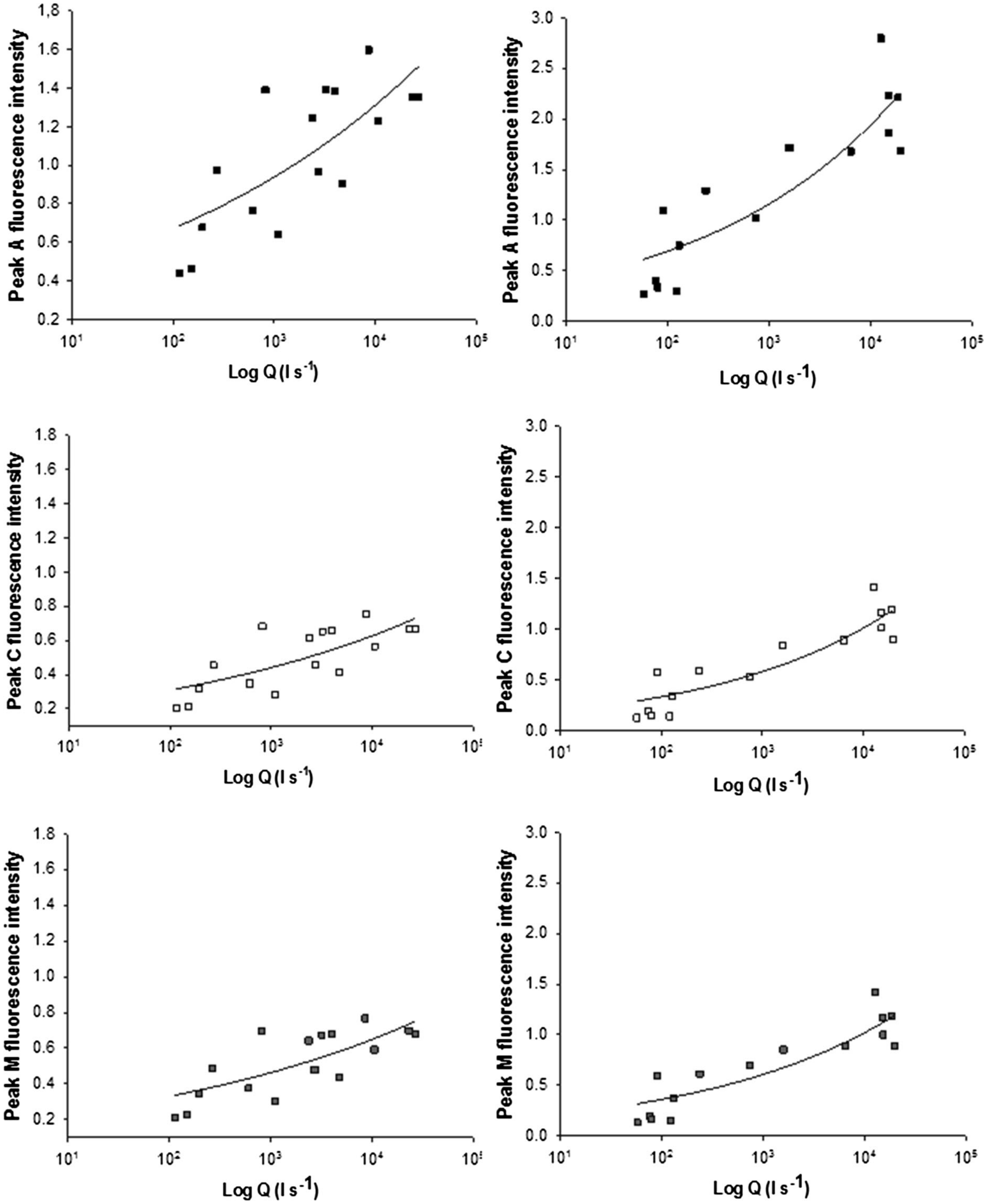

Fig. 6 Relationship between peaks A, C and M and discharge for May (left) and July (right) events

on heterogeneity of DOM composition (Hood et al., 2006; Vidon et al., 2008). We hypothesized that stream DOM optical properties may be associated to the combined contribution of the different end members to stream flow. In this study, we found that stream DOM show FI values that might be the result of both vegetal and microbial DOM release (Vázquez et al., 2011), while BIX and HIX suggest a more degraded humic material, which consist of aromatic and high molecular weight compounds, as it is also indicated by the SUVA and S_R values. The dominant fluorescence contribution of peak A and relevant contribution of peak C to total fluorescence, also suggest the presence of terrestrial DOM of high molecular weight. Peaks M and T additionally contributed to total fluorescence, even though to a lesser extent. As it was mentioned previously, peak T is usually related to protein-like components while, peak M is commonly reported to DOM of low molecular weight, derived from mixed-terrigenous, autochthonous, and microbially reworked source (Fellman et al., 2010; Stubbins et al., 2014). It is possible that peak M is indicative of DOM derived from macrophytes, which are abundant in Las Flores stream. DOC originated from macrophyte degradation would be more similar, in terms of molecular composition and presumably of reactivity, to DOC from terrestrial vascular plants than to autochthonous DOC derived from algal biomass (Catalán et al., 2013). However, vascular macrophytes and specially the submerged ones usually contain low or no lignin, even in vascular tissues, and have thin cuticles and leaves with only a few cells in thickness (Wetzel, 1983). All these features could be reflected in a more labile humic-like material of lower molecular weight than those derived from terrestrial vascular vegetation (Catalán et al., 2013), which is usually associated to peak M.

DOC concentration in GW was lower than in stream water and in their tributaries (ST_1 and ST_2). These results are in agreement with previous research that reported low DOC concentration in groundwater related to superficial waters (Sachse et al., 2005; Vázquez et al., 2007; Inamdar et al., 2012), possibly due to the sorption to mineral surface as DOM percolates through the soil (Qualls & Haines, 1991; Inamdar et al., 2012). Considering DOM optical properties, high S_R, BIX and FI, and the relevance of fluorescence peaks B and T in GW, we suggest that groundwater DOM has an autochthonous origin, and consists of compounds of low molecular weight and low content of aromatic carbon. However, Cory & Kaplan (2012) found that peak T includes mostly less degradable compounds. Previous studies also reported high FI and low HIX values and a high fluorescence intensity of peak B in groundwater (Hood et al., 2006; Romaní et al., 2006; Vázquez et al., 2007; Vázquez et al., 2011; Inamdar et al., 2012). Our results suggest that groundwater DOM mainly derived from microbial activity within the aquifer, possibly associated to the degradation of ancient soil organic matter (Fellman et al., 2014). The autochthonous origin of groundwater DOM was also reported by other authors (Inamdar et al., 2012). We also observed that SUVA showed intermediate values and peak A was the most important contributor to total fluorescence in GW samples. Consequently, we cannot dismiss that humic-like materials of terrestrial origin also contribute to groundwater DOM (Coble et al., 2014).

DOM in runoff samples (OF and SF) may derive from plant material and the organic matter of rich Pampean soils given the high values of HIX and SUVA and low values of S_R, which are indicative of an elevated content of aromatic compounds of high molecular weight (Helms et al., 2008). Low values of the FI and BIX also support this interpretation of DOM origin. We also observed increases in DOC concentration, HIX, and fluorescence intensities of humic-like peaks with increasing discharge, which denote an input of allochthonous DOM during storm events. In agreement with our results, Inamdar et al. (2012) reported higher values of HIX and SUVA in leachate and soil water. In addition, Hood et al. (2006) and Vidon et al. (2008) showed that during storm episodes, DOM inputs from near surface soil organic layer presented high SUVA values.

We found that DOC concentration in rainwater samples was high, but within the range reported in previous studies. For instance, Liu & Sheu (2003) found that DOC concentration in the rainfall was 4.7 mg l^{-1}, while Siudek et al. (2015) observed 5.10 ± 7.46 mg l^{-1} in an urban place and 4.72 ± 4.21 mg l^{-1} in a forested area. We think that the high values observed in our study are probably due to the predominance of weak winds, leading to an enrichment of organic material in the atmosphere, with secondary formation of organic carbon and increase of DOM in rain samples (Santos et al., 2009). This also could explain the presence of humic and protein components in rain samples (Kieber et al., 2006; Muller et al., 2008). Despite its high DOC levels, rain as direct deposition should not be a relevant DOC source to the stream because rainwater contribution to stream discharge is negligible (data not shown).

Hydrological characterization and changes in DOM with discharge

In this study, we found that DOC concentration in stream water increased with increasing discharge. Our results are in agreement with previous studies in streams of the Northern hemisphere that reported an increase in DOC concentration with increasing flow (Buffam et al., 2001; Bernal et al., 2002; Butturini et al., 2005; Vidon et al., 2008; Raymond & Saiers, 2010; Guarch-Ribot & Butturini, 2016). We also observed that DOC concentration-discharge relationship follow a power-law function. Different explanations have been proposed for this kind of DOC concentration and discharge relationship. Godsey et al. (2009) assumed that power–law relationships are due to a variable solute flux and the mixing of waters of different ages. But Bernal et al. (2002) proposed that DOC accumulates in soils during drought periods and that it may be leached during storm events, increasing DOC concentration in stream water. Vidon et al. (2008) hypothesized that the increase of DOC concentration during storms is due to a shift in the dominant source of DOC, from mineral soil DOC poor in aromatic substances at baseflow, to near surface soil DOC rich in aromatic substances during storms. In concordance with this, in our study, the increase in DOC concentration with discharge may be attributed to wash processes that release the organic matter accumulated in the superficial soil. These processes may be favored by the flat relief of the region that increases contact time between water and the soil in terrestrial flowpaths, as it was observed in other plain stream systems (Giling et al., 2014). The influence of wash processes on DOC concentration has been reported earlier in other Pampean stream (Arreghini et al., 2005).

At baseflow conditions, half of stream discharge was provided by groundwater while the other half was provided by stream tributaries (ST_1 and ST_2), with a similar contribution each one (data not shown). Under high flow conditions, end members that contributed to stream discharge were the same (groundwater, ST_1 and ST_2) plus overland flow. But during storm events, ST_1 contribution was higher than ST_2 and represented nearly half of stream flow, and overland flow contribution became a significant water input. Hence, end members contribute differentially to stream flow depending on hydrological conditions. Our results indicate that at baseflow conditions, when stream flow is mainly maintained by groundwater inflow, DOC is predominately composed by a mixture of compounds derived from microbial activity (protein-like components) and those derived from the terrestrial landscape that is transported to the stream during storm events. We also found that HIX and florescence intensity of peaks related to humics compounds (peaks A, C and M) increased with discharge, while BIX (related to a freshly produced DOC) and FI (indicative of microbial DOC sources) decreased with discharge, suggesting a shift in DOC chemical character from an autochthonous to a more allochthonous humic material during storm events (Hood et al., 2006; Wilson et al., 2016). Changes in the chemical character of DOC during storm events were previously reported in the literature. For example, Hood et al. (2006) and Vidon et al. (2008) found an increase in SUVA values indicating an increase in aromaticity during storm events, with lower SUVA values before and after the storm event, when the stream flow was mainly maintained by groundwater input. Change in DOM properties toward a more humic composition during storm events is also supported by the fact that HIX, SUVA and the fluorescence peaks related to humic compounds also increase with discharge.

Concluding remarks

Our results indicate that DOM chemical characteristics in Las Flores stream are mainly modulated by a differential contribution of end members to stream water depending on hydrological conditions. Stream DOM consists of a mixing of proteinaceous and humic compounds. Protein-like compound mainly derived from GW contribution at baseflow and in stream production derived from epiphytic communities (Bertilsson & Jones, 2003), while humic-like fractions derived from materials washed out during storm events. However, part of humic-like fluorescence could originate from the breakdown of highly productive macrophyte communities. It is often assumed that lotic DOC is dominated by terrestrial sources, with a clear prevalence of humic-like materials (Stanley et al., 2012; Stedmon & Cory, 2014), and that autochthonous DOM is almost exclusively derived from microbial and phytoplanktonic activities (Catalán et al., 2013). In the case of Las Flores stream, protein-like components seems to have a more relevant contribution to the total DOC pool than in forested systems. Moreover, in this stream, macrophytes could provide an additional and significant source of DOM, which is more bioavailable than DOM derived from terrestrial higher plants. Our results highlight the importance regional characteristics like relief, type of riparian vegetation, soil organic content and presence of aquatic macrophytes in modulating DOM chemical properties in open-canopy streams.

As we mention before, Pampas region is undergoing a process of agriculture intensification that impacts on the riparian zone of streams and rivers through the replacement of the herbaceous original vegetation by crops or the introduction of cattle. Agricultural activities increase dissolved nutrient levels in water, stimulating in stream degradation of labile materials and even facilitating the decomposition of more recalcitrant compounds (Guenet et al., 2010; Bodmer et al., 2016). In addition, cattle trampling increase erosive processes in the riparian zone and the input or organic soil particles into the stream (Osmond et al., 2007). Consequently, the impact of agricultural activities should be reflected in a higher input of terrestrial DOM and acceleration of the aquatic carbon cycle, altering DOM chemical composition and dynamics. Considering the prominent role of DOM on energy flows across trophic levels, the implementation of management practices in the riparian zone may be key measures to maintain DOM dynamics and chemical properties in Pampean streams.

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