UNIVERSITAT DE BARCELONA

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Alba Guarch Ribot

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Memòria presentada per Alba Guarch Ribot
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Vist-i-plau del director de tesi

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Agraïments

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Resum

La matèria orgànica dissolta (MOD) és una important font de carboni per als microorganismes aquàtics i regula molts processos biogeoquímics. Per tant, els canvis en la concentració i propietats de la MOD en els rius afecten notablement el funcionament dels ecosistemes fluvials i costaners i alteren el cicle global del carboni. La MOD en els rius de capçalera està modelada principalment per la hidrologia: durant les crescudes, els vessants de la conca són rentats i la MOD terrígena és transportada als rius. A la regió mediterrània, el règim de precipitació i evapotranspiració modula fortament la hidrologia fluvial, que mostra cabals baixos a l'estiu i pot arribar fins i tot a la seva desaparició.

En aquesta tesi hem analitzat un sèrie temporal a llarg termini de cabal i MOD a Fuirosos, un riu de capçalera intermitent al NE de la Península Ibèrica. El nostre objectiu era examinar la relació entre la MOD i la hidrologia en diferents escales temporals. Primer, vam caracteritzar el règim hidrològic d'aquest riu mediterrani. Al llarg de l'estudi, es va revelar una disminució del cabal, encara que les tendències de la temperatura i la precipitació no van ser significatives. Per altra banda, no vam trobar una tendència temporal clara en la durada de la sequera. En canvi, el retorn del cabal en el període de transició sec–humit s'ha endarrerit significativament de setembre a octubre. La freqüència de les crescudes va disminuir en l'interval 1998–2015, tot mostrant una relació positiva significativa amb l'activitat solar, amb un decalatge de dos anys.

La concentració de carboni orgànic dissolt (COD) ha patit una lleugera disminució durant el període d'estudi, cosa que contrasta amb el que s'ha observat en sistemes boreals. Aquest patró podria respondre a la minva de l'aportació de COD terrígen dels vessants forestats, com a conseqüència de la disminució dels episodis de rentat. La dinàmica temporal del COD durant el període de transició va ser regulada per la durada del període sec. Les oscil·lacions de cabal van explicar fins al 50% de la variabilitat total del COD

durant el període humit. Cal destacar que el pes del factor cabal va augmentar de forma significativa al llarg dels anys.

La qualitat de la MOD també va ser explorada, i descrita en termes de propietats d'absorbència i fluorescència. La majoria de les propietats de la MOD van ser clarament relacionades amb el cabal, i revelen una entrada de MOD al·lòctona, degradada, aromàtica, húmica i de mida molecular gran sota condicions de cabal alt. No obstant, aquestes relacions van ser alterades durant els períodes de fragmentació i de transició. La regressió lineal múltiple i l'anàlisi de comunitats van mostrar que, a més de la magnitud dels episodis de crescuda, les condicions hidrològiques prèvies (en concret, el cabal basal abans de l'episodi i la magnitud de l'episodi anterior) juguen un paper significatiu perquè regulen les tendències i formes de les histèresis MOD–cabal.

Per acabar, vaig identificar les diferències i semblances en les relacions MOD–cabal entre el riu mediterrani intermitent analitzat i un riu perenne alpí amb un cabal mitjà superior (Oberer Seebach). La MOD Fuirosos va ser significativament més concentrada, més terrígena, més degradada, més aromàtica i més humificada. El signe de la resposta global MOD-cabal va ser el mateix en els dos rius. Ara bé, el cabal era un predictor més robust de la variabilitat de la MOD a Oberer Seebach. En realitat, els períodes de cabal baix i de transició a Fuirosos van introduir una dispersió considerable en la relació. Durant el desgel a Oberer Seebach, la sensibilitat al cabal també va disminuir o desaparèixer. Els patrons de rentat/dilució van ser associats essencialment amb la magnitud dels episodis de crescuda a Fuirosos. Per contra, a Oberer Seebach, el canvi de qualitat de la MOD estava més lligat a les condicions de cabal basal, mentre que les precipitacions explicaven les oscil·lacions del COD.

Aquest estudi testifica la importància de generar i analitzar sèries biogeoquímiques de llarga durada i alta freqüència, que permeten explorar les relacions entre la MOD i la hidrologia en rius de capçalera intermitents que estan subjectes a règims hidrològics extrems.

Abstract

Dissolved organic matter (DOM) is an important source of carbon for aquatic microorganisms and it regulates many biogeochemical processes. Therefore, changes in river DOM concentration and properties could notably affect the functioning of fluvial and coastal ecosystems and alter the global carbon cycle. The DOM in headwater streams is strongly influenced by hydrology, as a consequence of the modification of catchment flow paths with high discharges. During storm events, the catchment hillsides are washed and terrigenous DOM is transported to rivers. In the Mediterranean region, the precipitation regime and evapotranspiration strongly modulate fluvial hydrology, which shows low discharges in summer and even flow disappearance. These dry–wet cycles of conditions affect many ecological and biogeochemical processes.

In this thesis, I analyse a long time series of discharge and DOM data from Fuirosos, an intermittent headwater stream in NE Spain. My aim is to examine the relationship between DOM and hydrology at different temporal scales. First, I characterise the hydrological regime of this Mediterranean stream. A decrease in discharge was revealed, although trends in temperature and precipitation were not significant. In contrast, I did not find a clear temporal trend in dry period duration. However, rewetting has been significantly delayed, moving from September to October. The mean magnitude of the storm events that occurred in autumn was lower in the years with *El Niño* phases in those months. The frequency of storm events decreased over the interval 1998–2015, showing a significant positive relationship with solar activity with a 2-year lag.

Dissolved organic carbon (DOC) concentration saw a slight decrease during the study period, which was opposed to that observed in boreal systems. This pattern might respond to a reduction of terrigenous DOC input from forest hillsides as a consequence of the decrease in flushing episodes. The DOC temporal dynamics during the rewetting was regulated by dry period duration. Discharge oscillations explained up to 50% of total DOC variability during the wet period. Notably, this weight of discharge increased significantly over the years.

DOM quality was also explored, and described in terms of absorbance and fluorescence properties. Most of the DOM properties were strongly related to discharge, revealing the input of allochthonous, degraded, aromatic, humic and large-molecular DOM under high flow conditions. However, these relationships were altered during drying and rewetting periods. The DOM responses at the individual storm event scale were highly heterogeneous. Multiple linear regression and commonality analyses showed that, in addition to the magnitude of storm episodes, antecedent hydrological conditions, namely pre-event basal flow and the magnitude of the previous storm event, played a significant role in regulating the trends and shapes of DOM–discharge hysteresis.

Finally, I identified the differences and similarities in the DOM–discharge relationships between the intermittent Mediterranean stream analysed herein and a perennial Alpine stream with higher mean discharge (Oberer Seebach). The DOM in Fuirosos was significantly more concentrated, more terrigenous, more degraded, more aromatic and more humified. The sign of the global DOM–discharge response was the same in both streams. However, discharge was a more robust predictor of DOM variability in Oberer Seebach. In fact, low flow and rewetting periods in Fuirosos introduced considerable dispersion into the relationship. During snowmelt in Oberer Seebach the sensitivity to discharge also decreased or disappeared. The flushing/dilution patterns were essentially associated with the magnitude of storm events in Fuirosos. In contrast, the DOM quality change was more coupled to basal flow conditions in Oberer Seebach, while the storms were behind the DOC oscillations.

This study attests to the importance of generating and analysing long-term and high-frequency biogeochemical series, which allow relationships between DOM and hydrology to be explored in intermittent headwater streams that are subjected to extreme hydrological regimes.

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General introduction

La Guingueta d'Àneu, Núria Ribot i Rius 1984

Rivers and dissolved organic matter

Lotic systems connect continents to oceans. Under pressure from the water cycle, gravity and hydraulic gradients, rivers move material from emerged land to the seafloor. However, rivers do not merely act as conveyor belt structures (Cole et al. 2007); they are active reactor systems that continuously transform the matter they transport. In a biogeochemical context, inland waters play an active role in the carbon cycle at the local, regional and global scales (Battin et al. 2009, Aufdenkampe et al. 2011). An important proportion of the total carbon, about 3.6–5.7 Pg C yr^{-1} that reaches fluvial networks from terrestrial environments (Raymond et al. 2013, Wehrli 2013) is processed in those river systems. It has been estimated that a total of 2.1–4.2 Pg C yr^{-1} is emitted in the form of CO_2 from inland waters (Raymond et al. 2013, Wehrli 2013) and that carbon burial in sediments is approximately 0.6 Pg C yr^{-1} (Tranvik et al. 2009). Finally, rivers and groundwater discharge about 0.9 Pg C yr^{-1} into the oceans (Cole et al. 2007), of which half is organic carbon (Schlünz and Schneider 2000). The export of the dissolved fraction of organic carbon (DOC) ranges between 0.17 and 0.33 Pg C yr^{-1} (Alvarez-Cobelas et al. 2012, Dai et al. 2012).

Dissolved organic matter (DOM) is the most important source of organic carbon in aquatic ecosystems (Wetzel 2001): it supports the food web providing energy and nutrients to heterotrophic microorganisms (Findlay et al. 1992, Stepanauskas et al. 1999) and therefore affecting the nutrient balance (Findlay and Sinsabaugh 2003). Not only does DOM stimulate bacterial production, but it is related to higher density of zooplankton, which are key organisms for the transfer of carbon to higher trophic levels, and its quality can modulate their community structures (Mitrovic et al. 2014). Even some algae can use DOM as a source of carbon and nitrogen, which might enhance algal blooms (Glibert et al. 2001, Loureiro et al. 2009).

While flowing from headwaters to the ocean, DOM influences the physical and biogeochemical conditions of the aquatic environment. DOM is optically active and contributes to the vertical attenuation of visible light and ultraviolet radiation through the water column (Brooks et al. 2005, Foden et al. 2008). Therefore, light absorption by DOM may protect aquatic organisms from potentially harmful radiation, but can also reduce the amount of photosynthetically active radiation available for autotrophs (Blough and Del Vecchio 2002).

Moreover, DOM can interact with metal ions to form organometal complexes (Buffle 1984). Complexation with DOM decreases the ionic concentration of metals in water and thereby reduces its toxicity to aquatic biota. Conversely, such binding prevents precipitation in the form of inert particles (Maranger and Pullin 2003). Both the quantity and quality of DOM modulate its potential as a chelating agent and thus affect the transport and bioavailability of trace metals (Baken et al. 2011). DOM also regulates pH due to its content of different acidic groups, buffering against acidity or contributing to it depending on the ionic strength of the water (Kerekes et al. 1986, Kuliński et al. 2014).

Chemical characteristics of DOM

In aquatic systems, as well as the DOM there is also particulate organic matter (POM). This difference is defined operationally using a filter with a certain pore size through which DOM pass while POM is retained. That size is not standardised; the most usual is 0.45 µm but also 0.2 µm, 0.7 µm and 1.2 µm have been used in many studies (Filella and Rodríguez-Murillo 2014). DOM is usually quantified in terms of dissolved organic carbon (DOC); in natural waters, around half the DOM weight consists of carbon (Allan and Castillo 2007). DOM is a heterogeneous mixture of compounds that can be divided into a humic fraction and a non-humic fraction (Thurman 1985).

Non-humic substances are well-known molecules of low molecular weight comprising lipids, proteins and carbohydrates (Schnitzer and Khan 1972). In contrast, humic substances are molecules with complex chemical structures, high molecular weight and a high aromatic content (Schnitzer and Khan 1972, MacCarthy et al. 1990) and they are the main component of DOM, representing 50%–75% (Aiken et al. 1985, Volk et al. 1997). Humic substances in aquatic systems can be partitioned based on their differing degrees of solubility: humic acids are not soluble below a water pH of 2 , while fulvic acids are soluble in all conditions (McDonald et al. 2004). Fulvic acids account for 45%–65% of the DOM and they have lower apparent molecular weights than humic acids: 600–1000 Da in contrast to 1500–5000 Da (Malcolm 1990).

The characterisation of the exact chemical composition of DOM is extremely difficult due to its high heterogeneity (Hertkorn et al. 2008). Fourier transform infrared spectroscopy, nuclear magnetic resonance and mass spectrometry are analytical techniques that have been applied to this task (Nebbioso and Piccolo 2013, Minor et al. 2014). They can provide information regarding functional groups, compound classes and elemental formulas of DOM. However, only a few compounds can be identified at the molecular level and the techniques to do so usually require previous isolation and concentration of samples. In contrast, spectroscopic techniques provide information on the chemical characteristics of DOM in a simpler, less expensive and faster way (Jaffé et al. 2008). For instance, absorbance can indicate DOM aromaticity and its relative molecular weight (Weishaar et al. 2003, Helms et al. 2008). However, through optical properties, absorbance and fluorescence, only the chromophoric DOM is analysed (the fraction that absorbs UV–visible light) or fluorescent DOM.

Fluorescence occurs when a molecule has absorbed energy causing the excitation of an electron to a higher energy level and then the electron drops back down to its original energy level emitting the excess energy in the form of light. DOM has optimal characteristics that allow its fluorescence to be studied: it has a high content of aromatic compounds, which present a structure of unpaired electrons sharing energy in the carbon rings that are easily excited (Hudson et al. 2007). The wavelength of excitation and fluorescent emission is characteristic of each molecule or fluorophore (Lakowicz 2006). Nevertheless, it is difficult to identify the individual chemical structure corresponding to each fluorophore. DOM fluorophores can be divided in 2 groups: those presenting fluorescent properties similar to proteins, specifically tryptophan and tyrosine; and those similar to humic substances (Coble 1996). Fluorescence properties can be useful in indicating DOM source, its freshness or the degree of humification (Fellman et al. 2010, Coble et al. 2014).

DOM sources

Sources of aquatic DOM can be autochthonous or allochthonous, usually with a predominance of the latter, especially in forested headwater streams with dense canopy cover and low light availability (Fisher and Likens 1973). Autochthonous DOM is produced in-stream, mainly by aquatic primary producers in the form of exudates and cell lysis from algae and macrophytes (Bertilsson and Jones 2003). It consists in non-humic substances such as monomeric sugars and amino acids and therefore it is considered highly bioavailable (Chen and Wangersky 1996). However, autochthonous DOM might also include humic substances, which have lower aromatic carbon content than allochthonous DOM (McKnight et al. 1994).

Allochthonous DOM is terrestrially derived: it originates in the leaching of degraded organic matter from the catchment: throughfall, root exudate, leaf and root litter, and the primary and secondary metabolites of microorganisms (Aitkenhead-Peterson et al. 2003). The composition of allochthonous DOM is dominated by humic substances derived from the humification of structural plant compounds such as lignin and cellulose. These aromatic structures are recalcitrant and inhibit enzyme activity (Marschner and Kalbitz 2003). Nevertheless, allochthonous DOM may contain a highly bioavailable fraction (Guillemette et al. 2013). The amount of DOM in soils is related to temperature (Dawson et al. 2008) and land use, which could also influence its quality (Williams et al. 2010). The transport of DOM from the terrestrial environment to rivers is mainly mediated by storm events (Buffam et al. 2001, Wiegner et al. 2009).

Hydrology and DOM

In running waters, the DOM concentration typically increases under high discharge conditions. This pattern has been reported in all biomes and with any land use (Austnes et al. 2010, Bass et al. 2011, Oeurng et al. 2011, Roig-Planasdemunt et al. 2017). Furthermore, in headwater streams storm events are responsible for most DOC export (Hinton et al. 1997, Raymond and Saiers 2010). During storm events, the catchment hillsides are washed and terrigenous DOM is transported to rivers by overland flow and rising groundwater leading to saturation of the soil horizons (Dhillon and Inamdar 2014). Riparian flushing is the predominant input in the rising limb of the storm hydrograph, while hillside runoff arrives later in the falling limb (McGlynn and McDonnell 2003).

Storm events also influence DOM quality. Higher discharge causes the elevation of the water table and the flushing of terrestrial surface and subsurface soil horizons (Boyer et al. 1997, Hinton et al. 1998). Fresh litter leachates in shallow soil layers present distinguishable characteristics from organic matter in deeper soil layers, which has been exposed to microbial degradation and extended sorption to mineral surfaces (Michalzik et al. 2003). Therefore, the change in flow path causes higher humic-like content, aromaticity, degree of humification and DOM molecular weight (Li et al. 2005, Hood et al. 2006, Duan et al. 2007, Vidon et al. 2008, Fellman et al. 2009, Nguyen et al. 2010, 2013, Inamdar et al. 2011, Pellerin et al. 2012).

Moreover, storm events have a controversial effect on heterotrophic DOM consumption. On one hand, high discharge reduces the retention time of water in sediment, thus diminishing the time when DOM is in contact with biologically active surfaces (Battin et al. 2008) and decreasing ecosystem respiration (Acuña et al. 2004). On the other hand, the extra input of allochthonous DOM carried by storm events can enhance DOM turnover (Roberts et al. 2007).

Mediterranean streams and DOM

The Mediterranean climate is characterised by a high inter-annual and intra-annual variability in precipitation, with high levels of precipitation in autumn and spring and low levels in summer together with high temperatures; this combination causes a considerable evapotranspiration in summer (Woodward 2009). The precipitation regime and evapotranspiration strongly modulate fluvial hydrology, which shows low discharges in summer and high discharges in autumn. In summer the flow can even cease totally. Therefore, in the Mediterranean region it is common for rivers to have an intermittent character (Gasith and Resh 1999). During drought, the hydrological connectivity is disrupted and transport downstream, exchange between the river and riparian interfaces and the influence of groundwater are all hampered (Lake 2011). These dry–wet cycles of conditions affects many ecological and biogeochemical processes in these streams. Allochthonous inputs of DOM from the catchment are reduced during drought (Dahm et al. 2003). Moreover, longer water residence times may provide more opportunities for the biophysical retention of DOM (Battin et al. 2008). Therefore, the quantity and quality of DOM is altered (von Schiller et al. 2015). Furthermore, the isolated pools caused by hydrological fragmentation increase the heterogeneity of biogeochemical conditions (Vázquez et al. 2011).

During the successive autumnal rewetting, discharge suddenly increases and the streams are reconnected to groundwater and riparian zones, restoring the solute exchange between them (Butturini et al. 2003, Vázquez et al. 2007). Due to the mobilisation of the leaf litter accumulated on the stream bed and the flushing of the hillsides, DOM concentration greatly increases during this rewetting, showing an allochthonous character (von Schiller et al. 2015). Those DOM inputs are bioavailable and reactivate heterotrophic microbial activity (Romaní et al. 2006). The rewetting period can contribute up to 20% of the total annual DOM export (Bernal et al. 2005).

Time series and DOM

In this thesis, I analyse a hydrological and biogeochemical time series from an intermittent Mediterranean stream. Recently rich and outstanding research has proliferated focusing on DOM quantity and quality along river networks (Ejarque-Gonzalez 2014, Casas-Ruiz 2017). These studies are profoundly connected to the river continuum concept (Vannote 1980) and the development of the spiralling length metric (Newbold et al. 1981). Thus, this literature strongly emphasises DOM transport, retention, processing and release along the hierarchical structure of fluvial systems and takes advantage major analytic advances in the description of DOM. One consequence of these advances is that much less effort is focused on temporal biogeochemical studies.

In northern boreal regions there is a longstanding tradition of generating long-term DOC studies (Filella and Rodríguez-Murillo 2014). In those regions, the impact of acid precipitation motivated the development of accurate long-term biogeochemical monitoring programmes in small and medium sized catchments starting in the 1970s (Likens et al. 1972). However, that tradition is almost absent from Mediterranean countries. In addition, the strong pressure to publish as quickly as possibly reinforces the development of short-term studies and establishing long-term biogeochemical monitoring programmes in not seen as a good strategy. Therefore, it is not surprising that long-running biogeochemical studies are far less frequent.

Nevertheless, long-term time series are considered essential for hydrological systems with high inter-annual hydrological variability, such as Mediterranean streams (Woodward 2009). In these systems, long-term biogeochemical series are fundamental to capture significant temporal trends. And last but not least, temporal changes associated with hydrological oscillations have been reported to have a greater impact on DOM variability than the spatial axis along the fluvial system (Mulholland 2003, Ejarque et al. 2017). Consequently, a full understanding of the biogeochemical functioning of lotic systems cannot be achieved while excluding the temporal axis.

Objectives

Tavelles, Francisca Rius i Sanuy 1984

This thesis focuses on the temporal dynamics of DOM quantity and quality in Fuirosos, an intermittent Mediterranean headwater stream. Temporal DOM variability has been related to stream hydrology. The link between DOM and discharge is assessed, with special emphasis placed on the annual, seasonal and storm event temporal scales. Environmental and climatic drivers that modulate the DOM–discharge relationship are studied in depth and results are compared with a similar data set from an alpine stream.

In the first chapter, entitled *Hydrology of an intermittent headwater stream: results of a decade of high-frequency monitoring*, I describe the hydrological regime of Fuirosos: the stream that is the object of study in this thesis. I analyse a 15-year high-frequency time series of stream discharge with the following specific objectives:

- To describe the variability in the annual discharge regime in terms of the distribution of discharge values, duration of dry episodes and magnitude of storm events.
- To detect temporal trends at the decadal scale in the aforementioned hydrological variables.
- To relate the long-term hydrological trends to climatic drivers.

The second chapter, entitled *Long-term temporal dynamics of dissolved organic carbon concentration in the Fuirosos stream*, analyses the temporal dynamics of stream DOC concentration and its relationship with discharge. The main goals when analysing the 13 years of stream biogeochemistry are:

- To explore long-term trends in DOC concentration.
- To analyse seasonal changes in DOC and their inter-annual variability.
- To dissect the relationship between DOC and discharge during the distinct hydrological seasons.
- To compare DOC dynamics with that of the nitrate concentration.

In the third chapter, entitled *Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis* (Guarch-Ribot and Butturini 2016), the quality of stream DOM is analysed over 32 months. I describe the diversity of spectroscopic DOM properties and their relationship with hydrology at the seasonal and storm event scales. Moreover, the potential legacy of antecedent hydrological, climatic and biogeochemical conditions on the variability of DOM response to changes in discharge is studied. Therefore, the particular objectives of this chapter are:

- To describe the seasonal relationship between DOM quality and discharge.
- To analyse the response of DOM properties to storm events.
- To reveal the main drivers of DOM changes during storm events.

The fourth chapter, entitled *Response of DOM dynamics in two headwater streams with contrasting hydrological regimes*, focuses on identifying the differences and similarities of the relationship between DOM properties and discharge, for an intermittent Mediterranean and a perennial Alpine streams, which have clearly different hydrological regimes. The specific goals are:

- To characterise the differences in the contrasting hydrologies.
- To compare the slopes of the relationship between DOM and discharge.
- To analyse the distinct response of DOM quality in each stream to storm events during the rising limb and the recession limb.

General methods

Fuirosos stream, Alba Guarch Ribot 2013

Study site

Fuirosos is a headwater stream that drains a 15 km^2 granitic catchment in Catalonia, in the north-east of the Iberian Peninsula (Fig. M.1). It is located in a mountainous area in the Montnegre–Corredor Natural Park (41° 42’ N; 2° 34’ E) with an elevation of 50–700 m above sea level. This third-order stream has a main stem of 10 km long and it is a tributary of La Tordera river.

The Fuirosos catchment is highly forested (90%) and mostly undisturbed, with the presence of some isolated agriculture fields. The predominant vegetation is cork oak (*Quercus suber*) and pine tree (*Pinus halepensis*). In the valley head it appears a deciduous woodland of chestnut (*Castanea sativa*), hazel (*Corylus avellana*) and oak (*Quercus pubescens*). The riparian vegetation is dominated by plane tree (*Platanus hispanica*) and alder (*Alnus glutinosa*). The closed canopy limits the light reaching the streambed of this oligotrophic stream (Sabater et al. 2011). The climate is Mediterranean, with mild winters (mean of 7 °C in January and February) and warm summers (mean of 22 °C in August and July). Annual precipitation ranges between 500 mm and 900 mm, with intense storms in spring and autumn and a severe summer drought. The strong seasonality of the precipitation regime determines a severe water-deficit stress and the flow cessation in summer. In summary, Fuirosos represents a typical semi-pristine intermittent stream with dry-wet cycles. It has been intensively studied since 1998 becoming a reference site for fluvial ecology and biogeochemistry in the Mediterranean area (Vázquez et al. 2013).

The streambed is composed of riffles, dominated by boulders and cobbles, and pools with accumulated gravel and sand. The riparian sediments are constituted by a gravel–sandy soil layer of 0.8–2.8 m thickness and a weathered granite layer of 2–11 m thickness. The groundwater level ranges from 0.5 m depth with respect to the ground surface in winter to 3.4 m depth in summer. Groundwater never saturates the upper soil organic layer, and soil–water volumetric content ranges from 8% in summer to 25% in winter (Butturini et al. 2002). The high hydraulic conductivity favours the stream water infiltration into the aquifer, with a maximum peak of specific discharge of 1.5 m^{-1} d^{-1}. The mixing area of the infiltrating stream water and the hillside groundwater expands 3–10 m into the riparian area (Butturini et al. 2003).

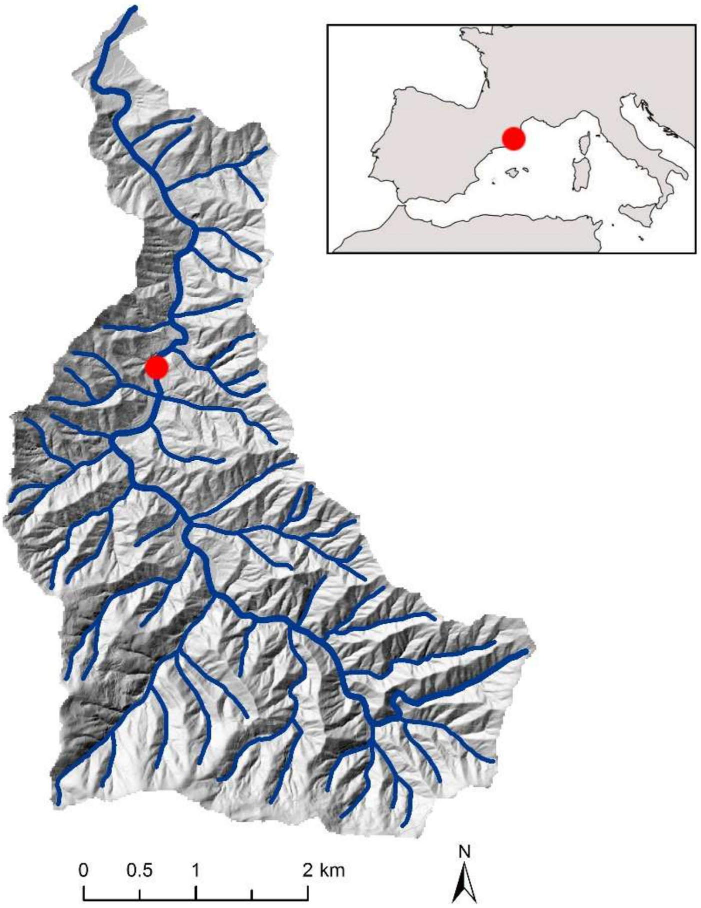

Fig. M.1 Location of the sampling point (red dot) in Fuirosos catchment. The hillshade is shown in grey colouring.

Monitoring and water analysis

Stream level was recorded every 30 minutes using a water pressure transducer (Druck PDCR 1830). The relationship between water level and discharge was assessed performing weekly discharge measurements by mass balance calculation using the *slug* chloride addition method (Gordon et al. 2004). These potential equations ($R^2 > 0.95$) were recalculated every time that the level sensor was moved for maintenance or by a high flood (Fig. M.2).

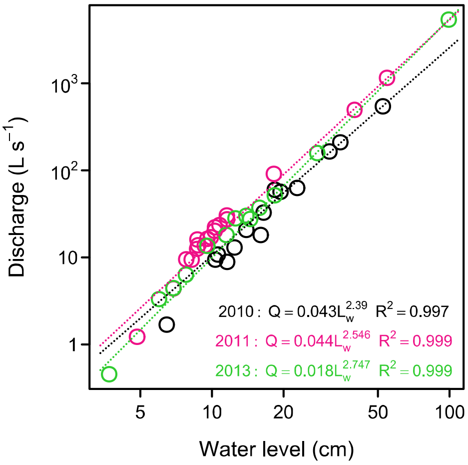

Fig. M.2 Example of the water level–discharge relationship in Fuirosos for 2010 (black), 2011 (pink) and 2013 (green).

A stage–actuated automatic sampler (Sigma 900 max) was used to collect a stream sample every 4–6 hours. Water samples were filtered with precombusted GF/F 0.7-µm filters (Whatman), acidified (pH=2) and kept in precombusted vials in the dark at 4 °C pending analysis. DOC concentration was determined by oxidative combustion and infrared analysis using a Shimadzu total organic carbon analyser coupled to an inorganic carbon removal unit. Qualitative properties of DOM were inferred using spectroscopic techniques. Samples for the optical analysis were filtered just before their analysis with 0.22-µm-pore nylon membranes to avoid any possible impurities, and they were analysed at room temperature.

Chromophoric DOM was measured by using the absorbance spectrum from 200 to 800 nm with a UV–Visible spectrophotometer UV1700 Pharma Spec (Shimadzu) and a deionised water blank was subtracted from each sample. Specific ultraviolet absorbance (SUVA) was calculated as the absorbance at 254 nm divided by DOC and by the cuvette path length. SUVA has been related to DOM aromaticity (Weishaar et al. 2003). Spectral slopes ratio (S_R) was obtained dividing the spectral slope for the interval of 275–295 nm of the absorbance spectrum to that of 350–400 nm. High S_R values indicates low apparent DOM molecular weight (Helms et al. 2008).

Fluoromophoric DOM was estimated performing emission–excitation matrices (EEMs). To obtain the EEMs we measured 21 synchronous fluorescence spectrums for each sample with a fluorescence spectrophotometer RF-5301 PC (Shimadzu) and a 1-cm quartz cell. Excitation wavelength range was 230–390 nm. Initial emission wavelength range was 310–540 nm and it increased in 10 nm every scan. The bandwidths for both excitation and emission were 5 nm, with a wavelength increment of 1 nm. EEMs were standardised following Goletz et al. 2011. We applied excitation corrections using Rhodamine 101 as quantum counter (Lakowicz 2006) and emission corrections measuring reference spectra of quinine sulphate and tryptophan provided by the National Institute of Standards and Technology (Gardecki and Maroncelli 1998). EEMs were normalized dividing by the area of Raman peak of deionised water at 350 nm excitation wavelength and 371–428 nm emission wavelength (Lawaetz and Stedmon 2009). Inner filter effects were corrected using the absorbance spectrum at 200–800 nm (Lakowicz 2006). Finally, we subtract a blank EEM of deionised water measured the same day from the EEM of each sample. EEMs were corrected and analyzed using Mathematica (Wolfram Research) software.

Humic fractions were obtained from EEMs (Coble et al. 1990, Mopper and Schultz 1993). Fluorescence peaks were identified by peak picking. Considering that an EEM is a bivariate matrix (f(xy)), we detected global and local maxima in the f(xy) with the Nelder–Mead optimisation algorithm under constrained conditions (Horst and Pardalos 1995, Butturini and Ejarque-Gonzalez 2013). We classify each found peak in one of the regions of interest: C (330–370 nm excitation wavelength, 430–460 nm emission wavelength) and A_C (230–250 nm excitation wavelength, 420–460 nm emission wavelength). These peaks have been the basis for fluorescence comparisons in numerous studies (Coble et al. 1990, 2014, Fellman et al. 2010). Peak A_C is related to fulvic acids —more soluble and slighter in molecular size (McDonald et al. 2004)—, while peak C is linked to humic acids (Chen et al. 2003).

Three fluorescence indices were analysed in this thesis: the fluorescence index (FI), the biological index (BIX) and the humification index (HIX). FI has been proposed to assess DOM sources (McKnight et al. 2001). It is the ratio of emission intensities at 470 nm and 520 nm that characterizes the slope of the emission curve at an excitation of 370 nm (Cory and McKnight 2005). High values (≈1.8) suggest an autochthonous origin of DOM and low values (≈1.3) an allochthonous origin.

BIX is based on the broadening of the emission fluorescence spectrum due to the presence of the β fluorophore, characteristic of autochthonous biological activity in water samples (Parlanti et al. 2000). This index was calculated at an excitation of 310 nm as the ratio of the fluorescence intensity emitted at 380 nm, corresponding to the maximum of intensity of the β band when it is isolated, and that emitted at 430 nm, which corresponds to the maximum of the humic fraction (Huguet et al. 2009). High values of BIX (>1) suggest a predominantly autochthonous origin of DOM and the presence of organic matter freshly released into water, whereas a lower DOM production in natural waters will lead to a low value of BIX (0.6–0.7).

HIX estimates the extent of humification by quantifying the extent of shifting of the emission spectra towards longer wavelengths (due to lower H:C ratios) with increasing humification (Zsolnay et al. 1999). HIX was calculated as the sum of the fluorescence intensities between 300–345 nm divided by the sum of the intensities between 300–345 nm and 435–480 nm, for an excitation wavelength of 254 nm (Ohno 2002). As such, HIX values range from 0 to 1 with higher values indicating a greater degree of humification of DOM.

Chapter 1

Hydrology of an intermittent headwater stream: results of a decade of high-frequency monitoring.

Gorg dels Banyuts, Josep Ribot i Calpe 1926

Introduction

Stream discharge is a major driver of multiple biological and physical processes in fluvial ecosystems and it acts at all scales: from small-scale microhabitats to the whole Earth system scale, passing through the habitat, reach, segment and fluvial network scales (Table 1.1). Therefore, the analysis of discharge variability is an essential step to understanding the functioning of running water ecosystems.

Climate change and human water consumption will exacerbate hydrological alteration worldwide: obviously in Mediterranean areas as well (IPCC 2013, Wada et al. 2013). Focusing on climate-hydrology coupling in Mediterranean rivers, most attention converges on two key hydrological factors: droughts and floods. Drought severity is expected to increase as a consequence of a reduction in annual precipitation, an increase of evaporative stress due to an increase of temperatures (Vicente-Serrano et al. 2014, Spinoni et al. 2015) and increase of water withdrawal (Wada et al. 2014). Thus, a scenario is plausible where the start of drying phases is brought forward and their duration is extended. On the other hand, extreme precipitations events are also expected to increase and the "flashiness" of hydrological regimes might increase in the near future (Giorgi and Lionello 2008). Nevertheless, caution is necessary in making forecasts because the increase int the frequency of extreme precipitations events in north-east Iberian Peninsula is not clear (Barrera-Escoda and Llasat 2015).

Temporal trends in stream hydrology have been analysed in Mediterranean basins. Most of the analysis reveals a decrease in the mean monthly or annual discharge (Stahl et al. 2010, Gallart et al. 2011, Lorenzo-Lacruz et al. 2012, Martínez-Fernández et al. 2013, Vicente-Serrano et al. 2014, Baahmed et al. 2015). Low flows, measured as the seven-day annual minimum streamflow and the 10th percentile of the yearly flow duration curve, also decreased (Stahl et al. 2010, Coch and Mediero 2016). In the central Pyrenees the contribution of low

Table 1.1 List of fluvial processes modulated by hydrology. Processes are ordered according to a hierarchical scale. The list was generated according to the references cited in the last column.

Ecosystem scale	Processes	References
Microhabitat	Gravel–sand–mud deposits Organic matter deposition Surface–subsurface microbiota/macrobenthic communities	Battin et al. 2008
Habitat	Surface–hyporheic hydrologic interactions Debris accumulation Organism colonisation–refuge	Lowe et al. 2006 Lake 2000 Rolls et al. 2012
Reach	River–riparian interactions Surface–groundwater hydrologic interactions Pool–riffle–pond–bar structures Tributary confluences Anthropogenic inputs Water abstraction	Lowe et al. 2006 Rolls et al. 2012 Hupp and Osterkamp 1996
Segment	Meanders Active–abandoned channels Alluvial terraces Food web structures	Lowe et al. 2006 Hupp and Osterkamp 1996 Naiman et al. 2008
Fluvial network	Catchment erosion Fluvial continuum–discontinuum Fluvial order Aquifer recharge Network configuration Riparian corridor diversity Solute transport–transformation–retention Organism migration Human settlements Energy for humans Dams–water abstraction Disease dispersion	Rolls et al. 2012 Naiman et al. 2008 Poole 2002 Naiman et al. 1993 Thorp et al. 2006 Rodriguez-Iturbe et al. 2011
Planet	Continents–Ocean link Global nutrient cycles Carbonate–Silicate cycle Earth climate	Aufdenkampe et al. 2011 Gaillardet et al. 1999

flows to annual runoff increased, while the contribution of high flows decreased (López-Moreno et al. 2006). Trends in high flows have been studied less in the Iberian Peninsula and with no consensus emerging. López-Moreno et al. (2006) and Mediero et al. (2014) found a decrease in the magnitude and frequency of floods. Meanwhile, extraordinary floods increased in number in Catalonia, whereas the most catastrophic floods did not show any significant trend (Barrera-Escoda and Llasat 2015). It should be taken into account that the Barrera-Escoda and Llasat (2015) study covered seven centuries (1301–2012) and the magnitudes of floods were estimated not in terms of discharge, but in terms of their impact on river channels, human activities and infrastructures.

Global climate parameters could influence local meteorological variables and therefore flow variability. El Niño–Southern Oscillation (ENSO) is an irregular periodic fluctuation in sea surface temperature and air pressure in the equatorial Pacific Ocean. ENSO teleconnections have been associated with precipitation and temperature in the Iberian Peninsula (Frías et al. 2010) and its oscillations partially explained the leaf input from riparian zones into the stream that is object of this study (Sanpera-Calbet et al. 2016). In parallel, solar radiation fluctuations at the century temporal scale are considered an important climatic force and have been related to flooding in the Tajo headwaters (Moreno et al. 2008). At shorter temporal scales, the solar activity cycle (with an 11–year period) has been related to flooding frequency in rivers of central Europe (Czymzik et al. 2016), the Alps (Peña et al. 2015) and north-eastern Iberian Peninsula (Barrera-Escoda and Llasat 2015). However the top–down climatic link between hydrology and solar activity is controversial and under scrutiny (Lockwood 2012).

This study focuses on the temporal dynamics of hydrology in a Mediterranean headwater stream over 18 years. From October 1998 to September 2016, discharge was measured at hourly intervals. Fuirosos is a near-pristine forested catchment that did not suffer substantial changes in land use over the study period. Furthermore, water abstraction for human consumption is almost non-existent. Therefore, its temporal hydrological patterns are mainly influenced by climate drivers. In this regard, the main objective of this study consisted of describing the hydrological regime at four different temporal scales:

- At the storm event scale, analysing the frequency and magnitude of storm episodes
- At the seasonal scale, monitoring the beginning and ending of each summer drought episode
- At the annual scale, estimating the proportion of low, median and high flows
- At the decadal scale, analysing the temporal pattern of the aforementioned hydrological parameters.

Methods

Discharge values were monitored in the Fuirosos stream from October 1998 to September 2016 at an hourly frequency. The data were split into hydrological years from the 1st October to the 30th September of the following year, which were used to name them. Three years' data were discarded due to the large gaps in the time series of discharge (2004, 2005 and 2016). Thus, the data from 15 hydrological years were analysed. Beside stream discharge, environmental data including local and more global climate parameters were registred. The local climate parameters were air temperature and precipitation at daily intervals; while the global ones were ENSO and solar activity.

Daily precipitation and temperature data were obtained from weather stations within the natural park: Pla de La Tanyada (3.5 km from the sampling point), Hortsavinyà (5.3 km away), Collsacreu (8.5 km) and Dosrius (18.5 km). Precipitation data were not available for the first year of monitoring.

In the present study ENSO was quantified using the Southern Oscillation index (SOI) defined as the normalised pressure difference between Tahiti and Darwin (Ropelewski and Jones 1987). The monthly SOI values were downloaded from the Climatic Research Unit, University of East Anglia. Five-month running mean values of the SOI remaining below −0.5 standard deviations for 5 months or longer indicate El Niño phases; whereas those over +0.5 standard deviations for 5 months or longer indicate La Niña events (Ropelewski and Jones 1987).

Solar activity can be estimated from solar radio flux at 10.7 cm (2800 MHz) in solar flux units (1 sfu = 10−22 W m−2 Hz−1). Monthly data were obtained from the Space Weather Prediction Center of the National Oceanic and Atmospheric Administration. The relationship between solar activity and hydrological parameters was explored at 0–4 years of delay because, if it exists, it is expected that this link should emerge with some delay (Czymzik et al. 2016).

Daily mean discharge was used to analyse long-term patterns, annual runoff, probability distribution of discharge and peaks-over-threshold (POT). In order to assess the existence of a significant monotonic trend in the time series we used the Mann–Kendall test (Mann 1945, Kendall 1975): a rank-based test suitable for non-normally distributed data that is widely used in hydro-climatic studies. The magnitude of the trend was then calculated using Sen's slope (Sen 1968). Serial correlation should be removed before applying these tests, and this was achieved applying the trend-free pre-whitening method (Yue et al. 2002). Moreover, we made a correction to avoid the underestimation of the lag-1 autocorrelation (Serinaldi and Kilsby 2016).

Annual runoff was calculated by integrating the area under the curve of daily discharge using Simpson's rule. We analysed the frequency of extreme events using the POT approach (Lang et al. 1999), wich accounts for daily discharge values that exceed a given truncation level in each hydrological year. We set the threshold at an average of 3 events per year, that is, $160\ \mathrm{L\ s^{-1}}$. Storm events were characterised by their magnitude (ΔQ), the difference between the pre-event base discharge and the maximum peak of the event. For some periods of time we calculated the cumulative magnitude of the storm events ($\sum \Delta Q$), that is, the sum of the magnitudes of all such events that occurred during that period. The probability distributions of daily discharges and of the magnitude of storm events were obtained with logarithmic bins. The quartiles of the whole daily discharge time series and the storms magnitude data were calculated. We determined the probability of those values in each hydrological year to explore any temporal trend at the decadal scale.

All the analyses were performed with R version 3.3.0 (R Core Team, 2016), using the packages “lubridate” (Grolemund and Wickham 2011), “plyr” (Wickham 2011), “Hmisc” (Harrell Jr 2015), “Bolstad2” (Curran 2013) and “zyp” (Bronaugh and Werner 2013). The significance level for the statistical tests was set at a p-value < 0.05.

Results

Environmental parameters

Annual precipitation in Fuirosos (Fig. 1.1a) varied widely between 508 L m^{-2} and 912 L m^{-2} (Table 1.2) and did not show a significant long-term pattern (Mann–Kendall test, $\tau = -0.01$, p-value > 0.1). Nevertheless, the distribution of precipitation showed some tendency to change. For instance, before 2008, in August–September typically more than 100 L m^{-2} precipitation accumulated. After that year, the precipitation only surpassed this threshold in 2014 and 2015. Air temperature showed the typical seasonal pattern (Fig. 1.1b) with a summer maximum (21.5 °C in July and August) and a winter minimum (6.7 °C in January and February). At the decadal temporal scale, air temperature saw a slight increase, although it was not significant (Mann–Kendall test, $\tau = 1.3 \times 10^{-3}$, p-value > 0.5).

Table 1.2 Annual values of the environmental and hydrological parameters during the study period. Solar activity is expressed in solar flux units (1 sfu = 10−22 W m−2 Hz−1).

Year	Precipitation ($L\ m^{-2}$)	Temperature (°C)	SOI	Solar activity (sfu)	Runoff ($m^3\ m^{-2}$)	Runoff $Precipitation^{-1}$	Rewetting	Drought start date	Dry period duration (days)	No. storm events
1999	NA	14.5	0.77	144	0.02	NA	25/9/1998	NA	NA	16
2000	568	13.1	0.71	180	0.03	0.05	15/9/1999	1/7/2000	81	17
2001	694	13.9	0.29	170	0.08	0.12	20/9/2000	14/6/2001	101	17
2002	912	13.3	–0.57	193	0.10	0.11	23/9/2001	NA	0	21
2003	758	14.4	–0.68	136	0.09	0.12	NA	1/7/2003	67	18
2006	694	13.4	–0.03	81	0.11	0.16	5/9/2005	9/6/2006	77	18
2007	567	14.4	–0.35	76	0.02	0.04	25/8/2006	12/6/2007	68	16
2008	612	13.3	0.84	70	0.05	0.08	19/8/2007	17/7/2008	103	12
2009	672	13.3	0.52	69	0.09	0.13	28/10/2008	5/7/2009	109	13
2010	714	13.2	0.14	78	0.08	0.12	22/10/2009	16/7/2010	64	15
2011	679	13.1	1.51	98	0.13	0.18	18/9/2010	10/8/2011	75	13
2012	714	13.9	0.24	126	0.16	0.23	24/10/2011	23/6/2012	121	10
2013	571	13.3	0.29	116	0.05	0.08	22/10/2012	25/7/2013	72	16
2014	682	13.8	–0.15	143	0.02	0.04	5/10/2013	19/7/2014	72	15
2015	508	14.4	−1.09	129	0.02	0.03	29/9/2014	23/6/2015	100	15
2016	NA	NA	NA	NA	NA	NA	1/10/2015	4/7/2016	100	NA

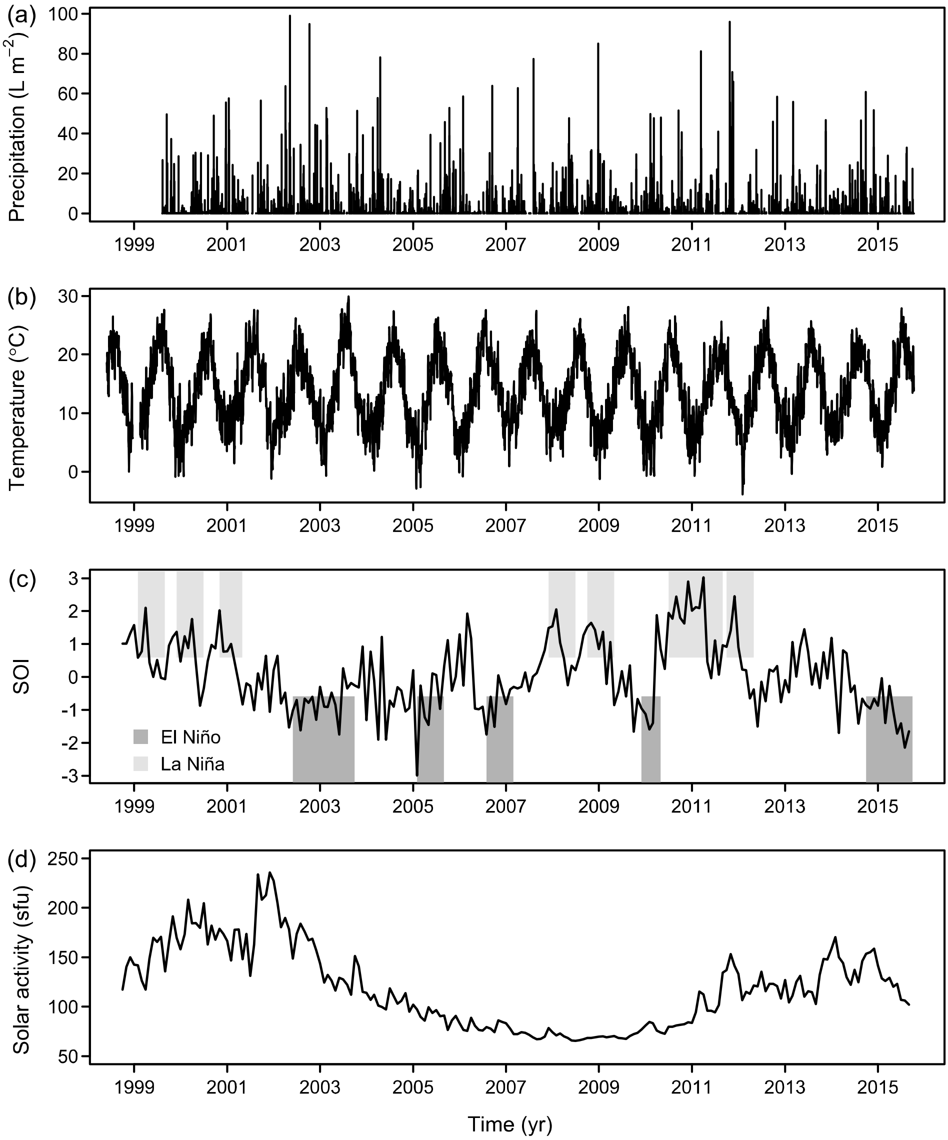

Fig. 1.1 Environmental parameters during the study period: daily cumulative precipitation (**a**); daily mean temperature (**b**); monthly SOI with El Niño (dark grey) and La Niña (light grey) phases (**c**); and monthly solar activity in solar flux units (**d**).

The SOI during the study period (Fig. 1.1c) showed five El Niño phases (2002–2003, 2005, 2006–2007, 2009–2010 and 2014–2015) and three La Niña phases (1999–2001, 2008–2009 and 2010–2012). Solar activity showed the well–known 11–year period cycle, with two maxima in 2000–2002 and 2013–2015 and a minimum in 2007–2009 (Fig. 1.1d). The two maxima were not identical, with the second clearly less active than the first.

Discharge temporal dynamics

The mean and median of daily discharge were 35.6 and 7.8 L s^{-1} respectively. Stream annual runoff ranged from 3% (2015) to 23% (2012) of the total annual precipitation (Table 1.2). Stream discharge showed the typical seasonal oscillations with a large dry period (no flow) in summer and permanent flow from autumn to early summer (Fig. 1.2). The smoothing using splines located maxima of discharge values in 2003 and 2011, while minima were found in 1999, 2007 and 2015. Thus, the monitoring detected two cycles of rising and decreasing discharges. The Mann–Kendall test found a significant decreasing trend in the daily discharge ($\tau = -0.11$, p-value $< 10^{-10}$). Therefore, Sen's slope for the whole period was -5.5×10^{-4} L s^{-1} d^{-1} wich represents an annual 0.6% decrease in mean discharge.

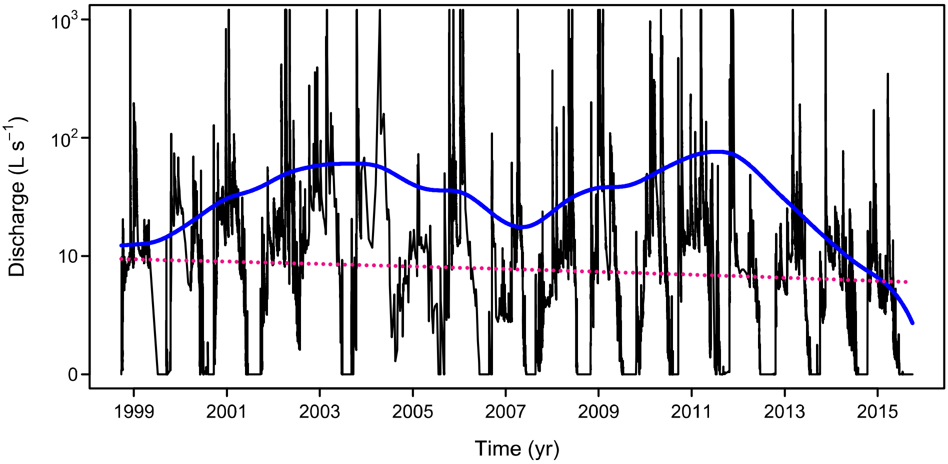

Fig. 1.2 Stream discharge during the study period. Included are the data smoothed with splines (blue line) and Sen's slope (pink line). Discharge values > 103 are not shown.

The probability distribution of mean daily discharge over the entire study period showed a clear bimodal pattern (Fig. 1.3a). The first and larger peak corresponds to the "no flow" condition (19% of observations). The second peak of the distribution was located at 8–10 L s^{-1} (8% of observations) and corresponds to the median discharge. In between the two peaks, the distribution showed a threshold at 2.5 L s^{-1}. Discharge from 0 to 2.5 L s^{-1} occurred in late spring/early summer, during the drying process, and represented 11% of total observations.

At the annual scale, the probability distribution of mean daily discharges can exhibit drastic inter-annual changes (Fig. 1.3a). For instance, a modal distributions appeared in three years (2007, 2008 and 2010). Furthermore, the mode of discharge (obtained by removing discharge values lower than 2.5 L s^{-1}) decreased significantly during the study period (Fig. 1.3b, $R^2 = 0.40$, p-value < 0.05). In more detail, the detection of mean daily discharges larger than 21 L s^{-1} gradually decreased from 2003 and was replaced by an increase of observed discharges between 2.5 L s^{-1} and 10 L s^{-1} (Fig. 1.3c). The annual runoff showed noticeable inter-annual oscillation (Table 2.1).

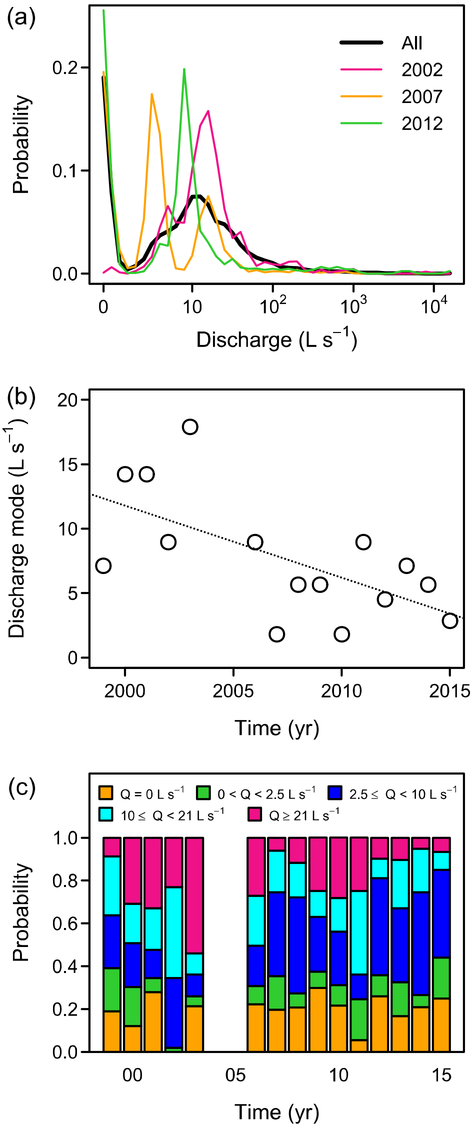

Fig. 1.3 Distribution of mean daily discharge. Probability distribution function of discharge values for the whole period (black line), 2002 (pink line), 2007 (orange line) and 2012 (green line) (**a**); annual mode of discharge excluding values lower than 2.5 L s^{-1} (**b**); and annual probability of dry period (orange), drying period (green), low discharge (cyan), mid discharge (blue) and high discharge (pink) (**c**).

However, it did not see a significant trend over the study period ($R^2 = 0.00$, p-value > 0.5). Therefore, the observed inter-annual changes of the probability distribution of mean daily discharge did not necessarily reflect quantitative changes in the annual water export. In fact, the annual runoff was related to peaks over a threshold of daily discharge ($R^2 = 0.61$, p-value < 10^{-3}), which did not show any consistent pattern.

Dry period

In June–July the stream flow ceased in Fuirosos. Only in 2002 was the water flow permanent. The duration of the dry period was 64–121 days (Table 1.2) and it was inversely related to the cumulative precipitation from July to October ($R^2 = 0.48$, p-value < 0.01). This relationship remained significant after removing the anomalous year without a drought ($R^2 = 0.37$, p-value < 0.05). The duration of the drought did not follow a significant trend over the period studied ($R^2 = 0.13$, p-value > 0.1) and was unrelated to annual solar activity ($R^2 = 0.13$, p-value > 0.1) or annual mean SOI ($R^2 = 0.09$, p-value > 0.1). However, the drought window was typically larger when the mean air temperature in September and August was higher ($R^2 = 0.30$, p-value < 0.05). The relationship remained significant after excluding the years with lowest (2002) and highest (2003) temperature ($R^2 = 0.34$, p-value < 0.05).

Meanwhile, the date of rewetting was significantly delayed after 2007 with respect to the earlier years (Fig. 1.4a, $t = -4.5147$, p-value < 10^{-3}). This change was rather abrupt: from 1999 to 2007 the rewetting occurred in August–September while from 2008 to 2016 it happened generally in October and the mean delay was of 34 days. The day of the year (DOY) of rewetting was highly sensitive to the cumulative precipitation in August and September (Fig. 1.4b, $R^2 = 0.67$, p-value < 10^{-3}). In contrast, air temperature did not show any relationship with the timing of the recovering of the stream flow. Thus, the rewetting delay responded to a precipitation shift from September to October.

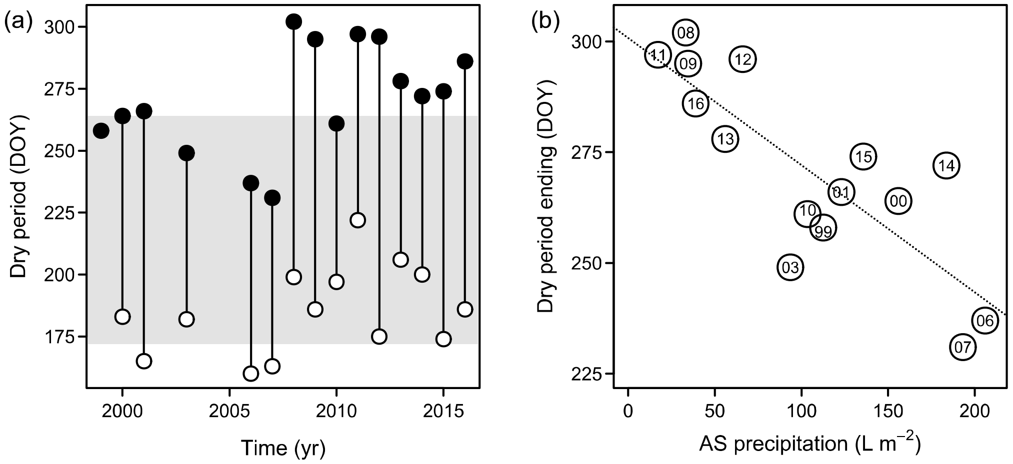

Fig. 1.4 Dry period in Fuirosos. Beginning (white dot), duration (segment) and ending (black dot) of dry episode in each year, with the grey area representing summer days (**a**). Relationship between the date of a dry period ending and the cumulative precipitation in August and September with the numbers in the circles indicating the hydrological year (**b**).

Storm events

The monitoring detected 232 high flow events. Their frequency ranged from 10 yr^{-1} to 21 yr^{-1} (Table 2) and the rate significantly decreased over the study period (Fig. 1.5a, $R^2 = 0.33$, p-value < 0.05). The frequency of storm events was positively related to the solar cycle and the best fit was detected at a lag of 2 years (Fig. 1.5b, $R^2 = 0.59$, p-value < 0.01). However, this relationships did not translate into a direct and significant link between annual cumulative flow and solar activity ($R^2 = 0.09$, p-value > 0.05). At the seasonal scale, the decrease in the frequency of storm episodes was especially severe during September, October and November (Fig. 1.5c), coinciding with the rewetting. From 1998 to 2006, an average of 6 events occurred during these months; while afterwards the average decreased to 3 events (t-test, t = 6.3, p-value $< 10^{-4}$).

The magnitude of the events reached up to 20000 L s^{-1} (16/1/2001, 8/5/2002 and 15/11/2011), but 75% of the events were below 76.5L s^{-1} , 50% below 17.7 L s^{-1} and 25% below 8.2 L s^{-1} . Regarding the number of events corresponding to each general quartile of magnitude, in the last years the proportion of high magnitude events ($\Delta Q > 77$ L s^{-1}) tended to decrease. However, POT of daily discharge did not show any consistent pattern.

The magnitude of the storm events was strongly related to the magnitude of the precipitation episode (Fig. 1.6a, $R^2 = 0.59$, p-value < 0.01). However, the slope of the relationship changed seasonally. Therefore, with the same rain magnitude, floods that occurred during drought and rewetting periods (summer–autumn) were typically lower than those that occurred in winter–spring. The magnitude of storm episodes was typically unrelated to air temperature and solar activity.

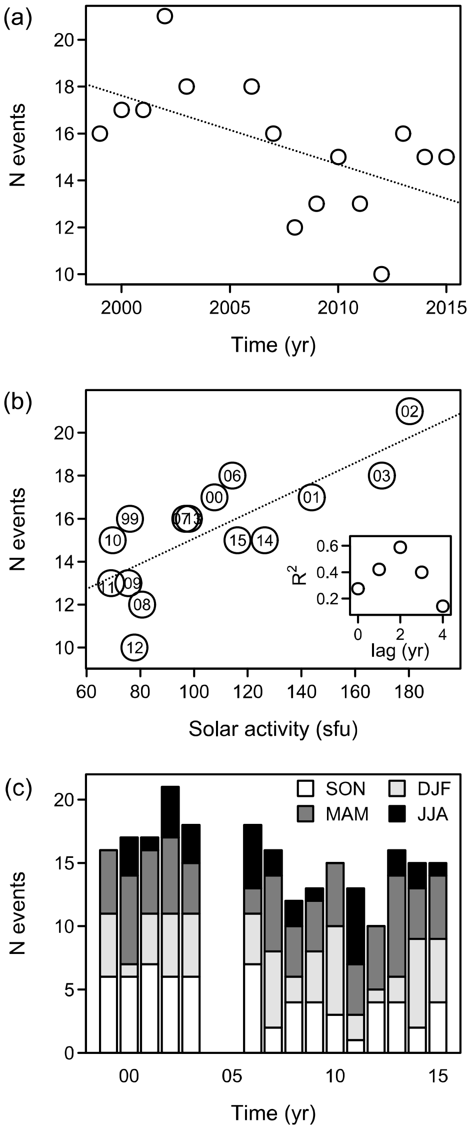

Fig. 1.5 Annual number of storm events during the study period (**a**); relationship between the annual frequency of storm events and the solar activity in solar flux units with a 2-year lag (1 sfu = 10^{-22} W m^{-2} Hz^{-1}) with the numbers in the circles indicating the hydrological year (**b**), the inset shows de fit of this relationship with different lags; annual number of storm events in September, October and November (white), December, January and February (light grey), March, April and June (dark grey) and June, July and August (black) (**c**).

However, the mean magnitude of storms that occurred during the autumnal months (October, November and December) was positively related to the mean SOI of those months (Fig. 1.6b, $R^2 = 0.36$, p-value=0.01). Thus, during El Niño phases, autumn high flows were typically less intense than during La Niña phases.

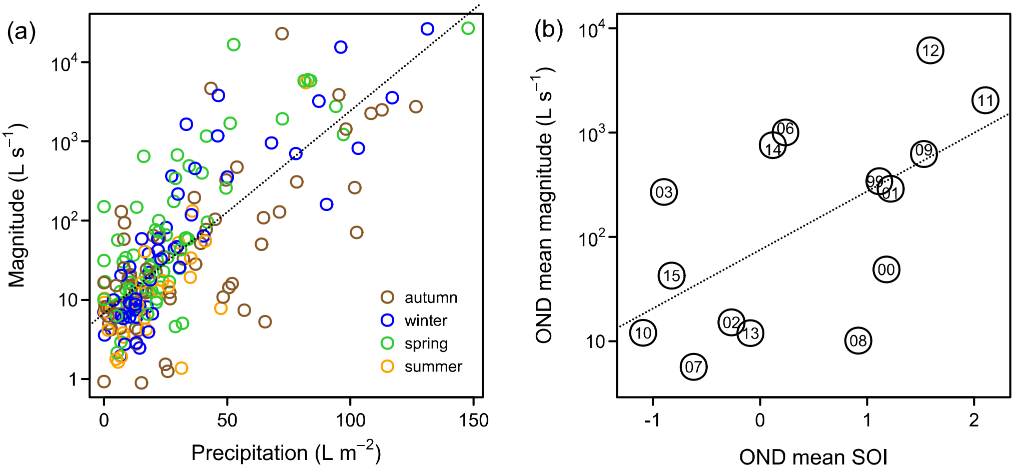

Fig. 1.**6** Magnitude of the storm events. Relationship between magnitude and cumulative precipitation during storm events in autumn (brown), winter (blue), spring (green) and summer (orange) (**a**). Relationship between the mean magnitude of storms that occurred in October, November and December and the mean SOI of those months with the numbers in the circles indicating the hydrological year (**b**).

Discussion

Flow patterns

The long-term monitoring in Fuirosos revealed some unexpected hydrological patterns. A decreasing trend was found in daily discharge, which implied that over 17 years, the flow reduced by 3.4 L s^{-1} on average. Given that the mean daily discharge of the stream was 35.6 L s^{-1}, this signified an annual reduction of 0.6%. Being conscious that a temporal window of 17 years is too short to extract definitive conclusions about long-term patterns, the decreasing trend detected in Fuirosos is in line with that detected in rivers in south–eastern Europe obtained with much longer time series (Stahl et al. 2010). More specifically, in the Iberian Peninsula the annual discharge reduction ranged from 0.25% to 1.68% and it was typically larger than 1% (Gallart et al. 2011, Martínez-Fernández et al. 2013, Buendia et al. 2016). Indeed, the annual reduction rate estimated in Fuirosos is in the lower quartile of the range of variations.

The hydrological time series from Fuirosos showed an increasing trend in the occurrence of mid–low discharge ($2.5 \leq Q < 10$ L s^{-1}) and a significant decrease of the median. Similar results have been reported in the central Pyrenees (López-Moreno et al. 2006), in near-natural catchments in Spain (Coch and Mediero 2016) and in the Mediterranean basin (Stahl et al. 2010). Remarkably, the lowest discharge interval ($0 \leq Q < 2.5$ L s^{-1}) did not suffer a clear temporal trend. At the other extreme of discharge distribution, the proportion of days with high flow, the frequency of storm events and the proportion of high magnitude storm events diminished throughout the study period. A decreasing temporal trend in the frequency of high discharge values was found in other fluvial systems in the Iberian Peninsula (López-Moreno et al. 2006, Mediero et al. 2014). However, the present study did not detect any significant change in the frequency of the highest daily mean flows measured as POT. This result is in line with that reported in a previous study wich did not find a clear trend in the frequency of extreme episodes in north-east Iberian Peninsula (Barrera-Escoda and Llasat 2015).

Meanwhile, solar activity with a 2-year delay emerged as a driver for the frequency of storm episodes. Nevertheless, this qualitative change did not translated into a change in the quantitative water fluxes. The impact of solar activity on climate is strongly debated and is an area of active on-going research (Lockwood 2012). Low solar irradiance might cause a greater ozone production in the stratosphere and the subsequent warming could be transmitted to the troposphere and alter the North Atlantic circulation (Gray et al. 2010, Wirth et al. 2013, Moffa-Sánchez et al. 2014). Hence, low solar activity would make the arrival of perturbations in Southern Europe more difficult, while it would favour perturbations in central and northern Europe. In this context some authors attribute high flood frequencies in Mediterranean rivers to periodos of high solar activity (Vaquero 2004, Barrera-Escoda and Llasat 2015). Our results confirm these observations, but it is essential to remark that the research by Barrera-Escoda and Llasat (2015) focuses on the frequency of extraordinary and catastrophic floods obtained from documentary sources and precipitation series registered over the last seven centuries. Consequently, that approach is totally different from ours. As far as we know, our study is the first to detect indications of a potential influence of solar activity on fluvial hydrology in the Iberian Peninsula using an in-situ hydrological data-set. It is interesting to remark that a 2-year lag between solar activity and flood frequency has been detected in rivers in central Europe (Czymzik et al. 2016) and the Alps (Peña et al. 2015). The relationship observed in these two rivers is the opposite to that observed in Fuirosos. Notwithstanding, this opposite response is coherent with the theoretical explanation provided above.

It is noticeable that the last period of high solar activity (2013–2015) saw clearly less activity than the previous one (2000–2002), which could be related to the reported decrease in the number of storm events. In fact, it was the lowest peak of solar activity measured in the last 100 years. Prudence is indispensable in connecting solar activity to hydrology. To reduce the uncertainty it is absolutely essential to extend hydrological monitoring to include at least another solar cycle. We could explore in more depth the link between solar activity and hydrology with the large hydrological time series obtained from gauging stations managed by water authorities in regulated rivers. Nevertheless, we would be unlikely to detect this causal relationship in regulated rivers.

Dry period patterns

The duration of summer drought in Fuirosos slightly increased during the study period, although this trend was not significant. Very few time series have analysed drought patterns in intermittent streams. In a headwater stream in western France drought duration was monitored for 12 years and no trend was observed either (Humbert et al. 2015). Nevertheless, longer studies revealed that duration, frequency and severity of climatic drought are increasing in the Mediterranean basin (Spinoni et al. 2015) and in the Iberian Peninsula (Vicente-Serrano et al. 2014). Drought severity was found to be driven partly by a decrease in precipitation and increase in evaporative demand due to higher temperatures. In fact, drought duration during the study period was significantly related to the mean temperature in August and September, and to cumulative precipitation from July to October. Taking into account these observations, together with the scenarios of climate change, hydrological droughts in non-perennial streams are expected to be prolonged (Pumo et al. 2016).

In Fuirosos, the rewetting has been significantly delayed. Moreover, the day of the year of flow recovery was linked with cumulative precipitation during August and September. This pattern cannot be compared in other catchments due to the lack of summer drought monitoring data. However, in eastern Iberian Peninsula a delay was found in the occurrence of high storm events (Mediero et al. 2014), which often happened in autumn. In our case, in recent years the number of autumn storm events has decreased, which could explain the need for more time to recharge the aquifer and achieve permanent runoff. Finally, the mean magnitude of events occurring in autumn was related to the mean SOI in the same period. Thus, under low SOI the magnitude of storm events was lower and this might delay the rewetting. SOI during autumn has been linked to precipitation in the same catchment, specifically a lower mean SOI during July–November was correlated with higher annual precipitation (Sanpera-Calbet et al. 2016).

Implications

The Fuirosos stream drains a forested and near-undisturbed catchment. Moreover, water abstraction is negligible and land use changes are almost none. The catchment is not a remote site and its exceptionality resides in its geographical context, because it is a small semi-pristine island in the middle of a larger area altered by human activity and in the proximity of a high-density population zone (Barcelona metropolitan area is less than 30 km away).

The present study revealed that a relatively short (15-year) hydrological time series is long enough to estimate a decrease rate of annual mean discharge similar to those obtained from long-term monitorings (> 40 years) at sites that drain large catchments suffering severe and complex anthropogenic impacts. This finding shows that the study of the link of fluvial hydrology to climate might benefit enormously from long-term hydrological monitoring in small headwaters in semi-pristine catchments. It is not necessary to focus on remote and inaccessible sites. Therefore, the monitoring of these hydrological indicators is not necessarily more expensive than monitoring any other gauging station.

The estimated mean annual discharge decrease of 0.6% suggests that daily discharge will drop to 50% in 80 years. This is obviously a simplistic linear extrapolation that assumes that runoff processes (evapotranspiration, hillside runoff and groundwater recharge) will not change significantly. We know little of how these processes react, so it is premature to extract a definitive conclusion. The objective is to persist with hydrological monitoring and hope that the human impact remains at minimum levels. In the context of basic research, to preserve this latter condition is the essential step to advance in the individuation of climatic mechanisms that drive hydrological fluctuations in Mediterranean streams and rivers.

Chapter 2

Long-term temporal dynamics of dissolved organic carbon concentration in the Fuirosos stream.

Cartronada, Jordi Guarch Ribot 2015

Introduction

Dissolved organic matter (DOM) is an important source of carbon and energy for freshwater and marine aquatic microorganisms and it regulates many biogeochemical processes (Findlay and Sinsabaugh 2003). Therefore, changes in river DOM concentrations could notably affect the functioning of fluvial and coastal ecosystems and alter the global carbon cycle (Dai et al. 2012). DOM concentration, measured in terms of concentration of dissolved organic carbon (DOC), has been reported to have increased over the last few decades in many rivers and lakes of northern Europe and America (Andersson et al. 1991, Worrall et al. 2004, Evans et al. 2005, Erlandsson et al. 2008, Hruška et al. 2009, Couture et al. 2012). This pattern is not well understood. Analysis points to a combined effect of climate change, a reduction in acid precipitation and changes in sea-salt deposition (Evans et al. 2006), although changes in land-use and hydrological regimes cannot be excluded (Pagano et al. 2014, Huntington et al. 2016). In any case, an increase in DOC cannot be generalised worldwide because long-term biogeochemical monitoring programmes are not well established in other climate regions (Filella and Rodríguez-Murillo 2014). Additionally, where this information is available, in some cases the temporal trends do not show an increase (Rodríguez-Murillo et al. 2015).

At the intra-annual scale, DOC has shown some degree of seasonality in different catchments. Higher values of DOC were found in summer and autumn associated with leaf fall in a temperate forested stream (Singh et al. 2013). The same seasonal pattern was reported in catchments with peat soils (Dawson et al. 2008). Snowmelt also caused high DOC concentrations in mountain areas (Perdrial et al. 2014). Intermittent streams have two characteristic periods, the drying period and the subsequent rewetting, with remarkable influence on their biogeochemistry. More specifically, in an agricultural catchment DOC gradually decreased from the rewetting to the next summer drying (Humbert et al. 2015). High concentrations of DOC were found in a tropical rainforest river during the flushing periods after drought (Spencer et al. 2010). Mediterranean ephemeral (Catalán et al. 2013) or intermittent streams (Vázquez et al. 2015, von Schiller et al. 2015) have shown clear seasonality with high DOC concentrations during the rewetting and varying results under drying conditions. However, the periods studied rarely lasted more than one hydrological year.

More than seasonality, discharge (Q) has been signalled as the main driver of DOC in headwater streams (Butturini et al. 2008, Roig-Planasdemunt et al. 2017). Many studies have reported the relationship between discharge and DOC at different scales, some of them including long time series (Neal et al. 2005, Rodríguez-Murillo et al. 2015). However, few of those studies have analysed the inter-annual variability of that relationship (Humbert et al. 2015).

My purpose herein is to present an analysis of the temporal dynamics of DOC in a Mediterranean headwater stream at the decadal, annual and seasonal time scales. More specifically, my objectives are:

- To explore long-term trends of DOC at the decadal scale.

According to the gradual decrease of mean discharge detected (0.6%, see Chapter 1) and bearing in mind the pattern found in an arid stream (Jones et al. 1996), I expected a gradual increase of DOC concentration during the entire study period due to the reduction of water mass. Therefore, the long-term DOC trend will allow me to quantify the biogeochemical resilience of the catchment to the gradual increase in the hydrological stress reflected in the mean decadal discharge decrease.

- To analyse seasonal changes in DOC concentration at the intra-annual and inter-annual timescales.

I explored the impact of the severity of dry periods on temporal DOC seasonality during the successive hydrological year. A gradual DOC decrease from high DOC concentration during the rewetting to lower DOC concentration during the wet season was expected. The rate of this decrease may be related to the length of the antecedent drought. A more pronounced flushing is expected during large drought periods. As pointed out in the first chapter, drought phases last from 0 to 121 days. If a link between DOC flushing and drought duration exists it should emerge after 13 years of monitoring.

- To analyse the relationship between DOC and discharge during the drying, rewetting and wet hydrological seasons.

A previous study in Fuirosos showed that the strength of the DOC–Q relationship is much less during the rewetting and it becomes stronger during the wet period (Butturini et al. 2008). However, the short hydro-biogeochemical time series used in that preliminary research precluded studying the inter-annual variability of the DOC–Q relationship during the wet period in more depth. If the gradual discharge decrease determines a parallel long-term DOC increase, then I expect smaller DOC oscillation. In consequence, the slope of the DOC–Q relationship during the wet period should decrease.

In the present study nitrate (NO_3^-) is used as a reference solute. The two solutes, NO_3^- and DOC, are considered to be strongly related to terrigenous allochthonous hillsides inputs (Mulholland and Hill 1997). Therefore, similitudes and differences in their temporal dynamics and solute–discharge relationships help to weight the extent to which the observed DOC patterns and responses are solute specific, or rather respond to a broader catchment-scale biogeochemical property.

Methods

Weekly sampling was performed in Fuirosos from September 1998 to July 2013. Two years (2004 and 2005) were not included in the analysis because of the lower frequency of the sampling. Moreover, an automatic sampler (Sigma 900 max) took samples every 4–6 hours during storm events. Discharge was calculated from the water pressure level recorded hourly. Apart from DOC, we analysed NO_3^- concentration with ionic chromatography (Metrohm).

In accordance with previous studies of Fuirosos (Butturini et al. 2003, Vázquez et al. 2015) and results from the analysis of the long-term hydrological monitoring (Chapter 1), the hydrological year was split into 3 periods:

- Rewetting: from the recovering of the stream flow until discharge reached 5 L s^{-1}: it usually started in September or October.
- Wet: from the end of the rewetting phase to the beginning of the drying, generally from November to May
- Drying: starting when stream discharge is less than 2.5 L s^{-1}, usually lasting from June to July or August.

The long-term trends in DOC and NO_3^- were evaluated with the Mann–Kendall test (Mann 1945, Kendall 1975), and the magnitude of the trend was calculated as Sen's slope (Sen 1968). DOC and NO_3^- temporal intra-annual seasonality was studied from the rewetting to the drying period. The average seasonal trend was analysed with smoothed splines after assembling all the data in one hydrological year. Furthermore, we obtained DOC and NO_3^- mean for each hydrological period of the 13 years.

The rate at which the DOC decreased from the rewetting to the end of December (dDOC/dt) was calculated assuming an exponential model. It corresponds to the slope of the linear regression relating the logarithm of DOC to the time passed since the rewetting. dDOC/dt was estimated for each year and then related to the duration of the previous drought phase. In some years, it was not possible to obtain it because sampling was not sufficiently intensive (2003 and 2004) or because the drought length was not determined (1998, 1999 and 2005). I also calculated the slopes of the linear regressions relating DOC and NO_3^- to the logarithm of discharge (dDOC/dQ and dNO_3^-/dQ). This rate was estimated for each hydrological period every year.

Significance of differences between the distributions of DOC and NO_3^- data from different hydrological periods was tested with the Kruskall–Wallis test (Kruskal and Wallis 1952). This test does not assume the normal distribution of the residuals and does not require a balanced design. As a post-hoc test, to specify within wich groups the differences were located, I applied Dunn's test (Kruskal and Wallis 1952), which is appropriate for groups with unequal numbers of observations (Zas 2010). The significance level for the statistical tests was set at $p\text{-value} < 0.05$. All the analyses were performed with R version 3.3.0 (R Core Team, 2016), using the packages "birk" (Birk 2016), "zyp" (Bronaugh and Werner 2013), "dunn.test" (Dinno 2017) and "vioplot" (Adler 2005).

Results

Long-term trends

During the 13 years of monitoring the daily mean of DOC was 4.32 ± 2.37 mg $L^{-1}$and ranged from 1.58 mg L^{-1} in winter, base flow to more than 15 mg L^{-1} during some storm events (Fig. 2.1a). The DOC significantly decreased over the entire study period (Mann–Kendall test, $\tau = -0.05$, $p\text{-value} < 10^{-7}$) with a Sen's slope of -1.7×10^{-4} mg L^{-1} d^{-1}, which represented an annual 1.46% decrease of the mean DOC.

The daily NO_3^- concentration averaged 0.48 ± 0.63 mg N L^{-1} (Fig. 2.1b). In some samples the amount of NO_3^- was undetectable (< 10^{-3} mg N L^{-1}) while in others it was as much as 6.75 mg N L^{-1}. A significant temporal trend was also found (Mann–Kendall test, $\tau = -0.06$, $p\text{-value} < 10^{-9}$), but in this case it had a positive Sen's slope of 1.2×10^{-5} mg N L^{-1} d^{-1}, revealing an annual increase of 0.93% in mean NO_3^-.

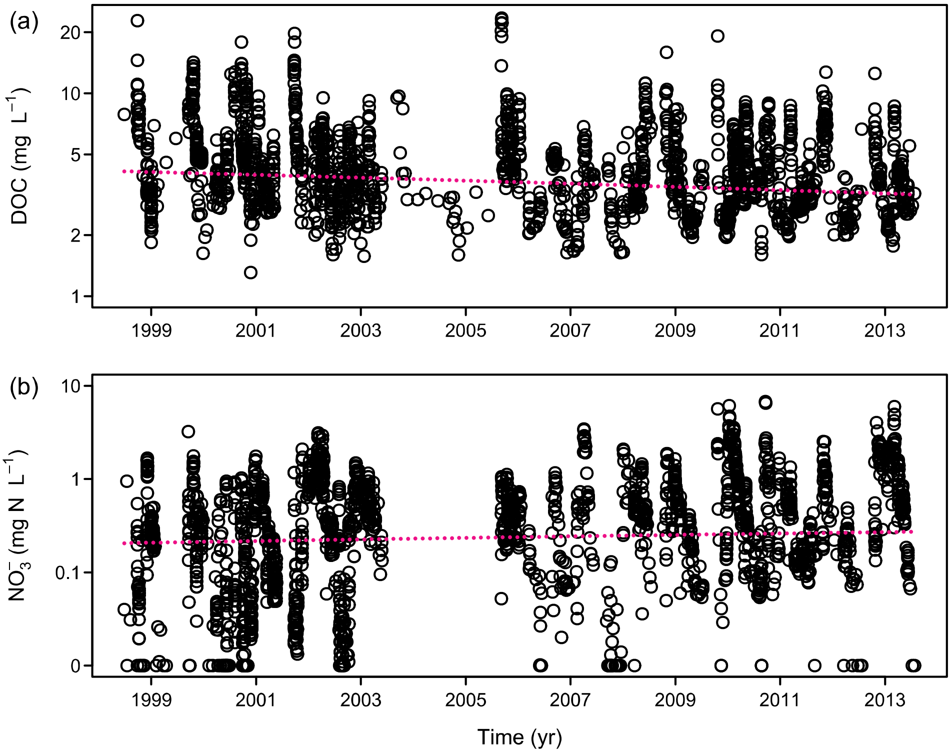

Fig. 2.1 Stream DOC (**a**) and NO_3^- (**b**) concentrations during the study period. The temporal trend is represented by Sen's slope (pink dotted line).

DOC and NO_3^- seasonality

DOC values showed a seasonal pattern consisting of the presence of high values at the beginning of the hydrological year (September–October), a gradual decrease until the end of December and a slight increase towards summer (Fig. 2.2a). The mean DOC concentration during rewetting, the wet period and drying was 7.9 ± 3.9 mg L^{-1}, 4.0 ± 1.7 mg L^{-1} and 4.4 ± 2.5 mg L^{-1} respectively. The distributions of the seasonal means of every year had significant differences (Kruskall–Wallis test, $\chi^2 = 17.648$, p-value $< 10^{-3}$). Specifically, mean DOC values during rewetting are those that presented a distinct distribution from both the wet period (Dunn's test, $Z = 3.78$, p-value $< 10^{-3}$) and drying (Dunn's test, $Z = 3.47$, p-value $< 10^{-3}$). Rewetting showed the highest dispersion among years and the median of the annual means was higher than that of the other periods (Fig. 2.2b).

The NO_3^- seasonal pattern was clearly different from that of DOC, with the largest concentration during late winter-beginning of spring and the lowest values during the summer drying. A NO_3^- flushing signal during the rewetting was missing (Fig. 2.2c). The mean NO_3^- concentration during rewetting, the wet period and drying was 0.5 ± 0.9 mg L^{-1}, 0.6 ± 0.7 mg L^{-1} and 0.2 ± 0.2 mg L^{-1} respectively. Distributions of NO_3^- values (Fig. 2.2d) were significantly different between the three hydrological periods (Kruskall–Wallis test, $\chi^2 = 14.6$, p-value $< 10^{-3}$) with drying being distinguishable from the wet period (Dunn's test, $Z = -3.71$, p-value $< 10^{-3}$) and rewetting (Dunn's test, $Z = -2.83$, p-value < 0.01).

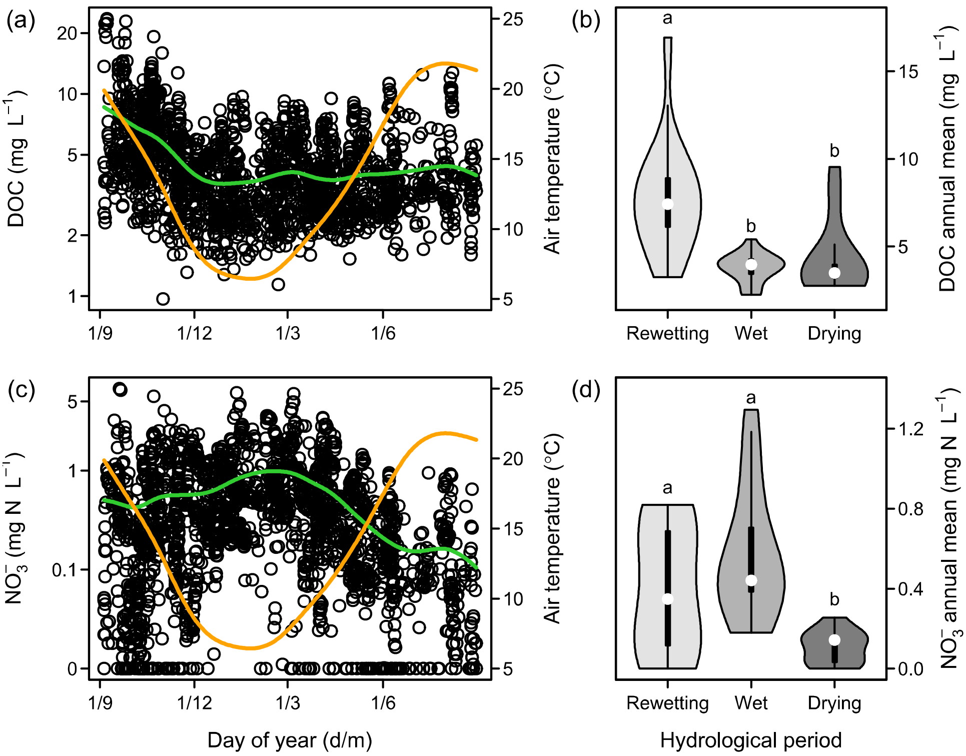

Fig. 2.2 Seasonality of DOC (**a**) and NO_3^- (**c**) concentration during the study period with smoothed splines of concentration (green line) and air temperature (orange line).The distributions of the annual mean DOC (**b**) and NO_3^- (**d**) concentrations are shown in violin plots for each hydrological period. The white dot marks the median and the black rectangle the interquartile range. Different letters indicate significant differences between distributions according to Dunn's test.

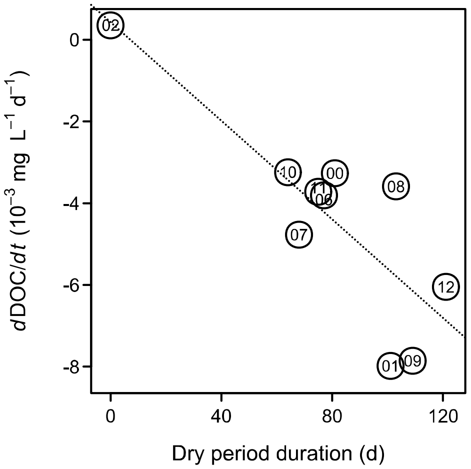

Fig. 2.3 Relationship between *d*DOC/*dt* and the duration of the previous dry period. Numbers in circles indicate the year. Dotted line indicates the significant linear relationship.

The rate at which DOC decreased from the rewetting to the end of December (*d*DOC/*dt*) changed interannually and ranged between 0 and − 0.008 mg L^{-1} d^{-1}. Its variability was significantly related to the duration of drought (Fig. 2.3, $R^2 = 0.69$, p-value < 0.01): after a long and severe drought, *d*DOC/*dt* was more pronounced. At the other extreme, the year when the stream did not dry up during summer (2002) the slope was slightly positive.

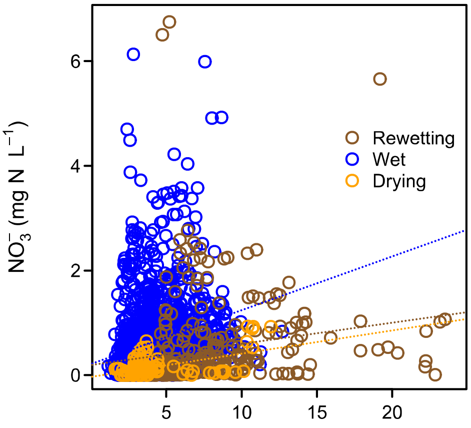

Fig. 2.4 Relationship between NO_3^- and DOC concentration. The slopes of the linear regressions for rewetting (brown), wet period (blue) and drying (orange) are shown as dotted lines.

Overall, the NO_3^- concentration was positively and significantly related to DOC. However, in statistical terms, the link was very weak ($R^2 = 0.03$, p-value $< 10^{-11}$). From analysing the relationship between the distinct hydrological periods, some differences emerged (Fig. 2.4). The weakest link was found during the rewetting ($R^2 = 0.04$, p-value < 0.01), while the strongest occurred under drying conditions ($R^2 = 0.24$, p-value $< 10^{-7}$). During the wet period, the strength of the NO_3^-–DOC relationship was in the middle ($R^2 = 0.06$, p-value $< 10^{-21}$), but the slope was larger. Thus, under identical DOC concentrations, the NO_3^-

concentration during the wet period was typically larger than in the other two hydrological periods.

*d*DOC/*d*Q and *d*NO_3^-/*d*Q

The DOC from the whole study period was significantly but slightly related to the logarithm of discharge (Fig. 2.5a, $R^2 = 0.01$, p-value $< 10^{-4}$). Nevertheless, if only the wet periods were considered, the relationship between DOC and discharge became much stronger ($R^2 = 0.52$, p-value $< 10^{-247}$). *d*DOC/*d*Q responses were estimated every year and for each hydrological period (Fig. 2.5b). During rewetting *d*DOC/*d*Q was higher and showed the largest inter-annual variability (0.5–12.1 mg s L^2). In contrast, the lowest values and inter-annual variability occurred under drying conditions. In addition, *d*DOC/*d*Q tended to be negative during that period (−0.9–0.1 mg s L^2). The distributions of *d*DOC/*d*Q values were significantly different for the different hydrological periods. (Kruskall–Wallis test, $\chi^2 = 25.259$, p-value $< 10^{-5}$), with drying showing lower values than rewetting (Dunn's test, $Z = -4.88$, p-value $< 10^{-5}$) and the wet period (Dunn's test, $Z = -3.77$, p-value $< 10^{-3}$).

Similarly, NO_3^- showed a weak relationship with the logarithm of discharge (Fig. 2.5c, $R^2 = 0.09$, p-value $< 10^{-45}$). In contrast to DOC, NO_3^- remained only slightly related to discharge even if only the samples from the wet period were considered ($R^2 = 0.10$, p-value $< 10^{-39}$). Still, that period had the highest *d*NO_3^-/*d*Q values (Fig. 2.5d). In contrast, during drying *d*NO_3^-/*d*Q was nearly null. The distributions of *d*NO_3^-/*d*Q values from each hydrological period showed significant differences (Kruskall–Wallis test, $\chi^2 = 17.367$, p-value $< 10^{-3}$) between the drying and wet periods (Dunn's test, $Z = -4.17$, p-value $< 10^{-4}$), between drying and rewetting (Dunn's test, $Z = -2.34$, p-value < 0.05) and between the wet period and rewetting (Dunn's test, $Z = 1.75$, p-value < 0.05).

The strongest DOC versus discharge relationship was observed during wet periods. Furthermore, the explanatory power of this relationship (expressed as R^2) increased over the years (Fig. 2.6, $R^2 = 0.49$, p-value < 0.01).

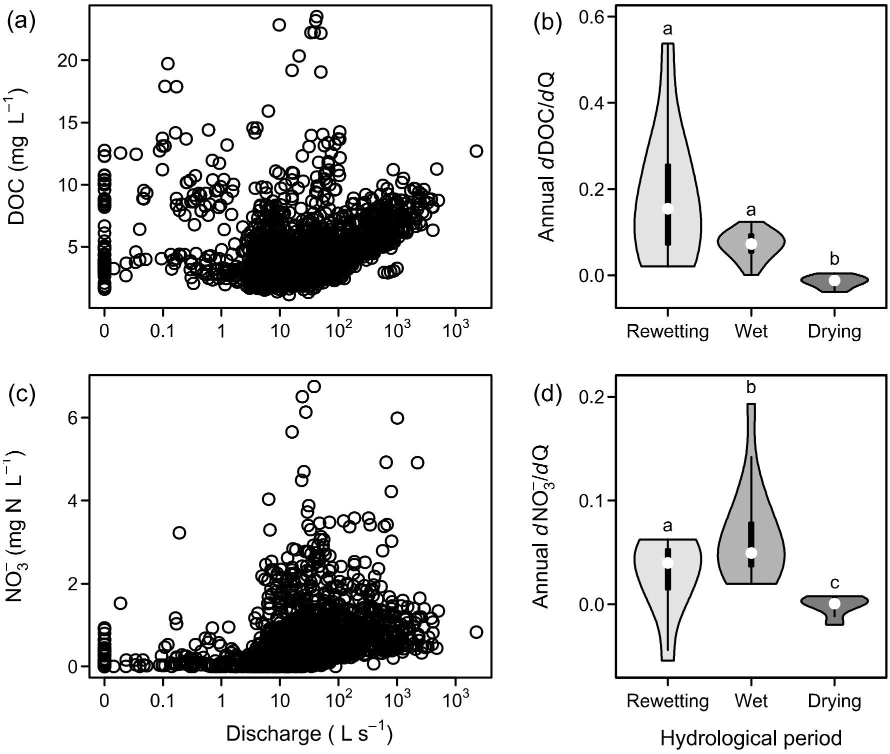

Fig. 2.5 DOC–discharge (**a**) and NO_3^-–discharge (**c**) scatter plots. The distributions of annual *d*DOC/*d*Q (**b**) and *d*NO_3^-/*d*Q (**d**) are shown in violin plots for each hydrological period. To be comparable, *d*DOC/*d*Q and *d*NO_3^-/*d*Q were estimated after rescaling DOC and NO_3^- concentration between 0 and 1.The white dot marks the median and the black rectangle the interquartile range. Different letters indicate significant differences between distributions according to Dunn's test.

The absolute value of the *d*DOC/*d*Q slopes tended to increase during the study period as well, although that pattern was not statistically significant ($R^2 = 0.20$, p-value = 0.12). Therefore, the link between DOC and discharge during the wet period strengthened over time and, additionally, DOC tended to be more sensitive to discharge changes. Meanwhile, the statistical significance of the

NO_3^- versus discharge relationship was typically lower than that estimated for DOC and did not show any long-term pattern ($R^2 < 0.03$, p-value > 0.6). Moreover, NO_3^- appeared less responsive to discharge oscillations ($d\mathrm{DOC}/dQ > dNO_3^-/dQ$).

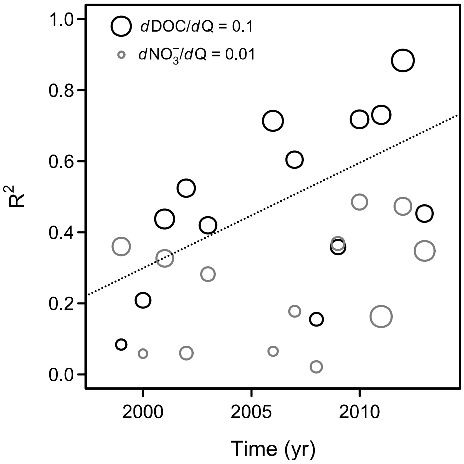

Fig. 2.6 Temporal dynamics of the explanatory power (expressed as R^2) of the linear regression relating DOC (black) and NO_3^- (grey) concentrations to discharge (log transformed) during the wet period. The area of the circles is proportional to $d\mathrm{DOC}/dQ$ (or dNO_3^-/dQ). The dotted line shows the linear model valid for DOC.

Discussion

DOC long-term trends

In Fuirosos, DOC significantly decreased over the study period. This contradicted our initial hypothesis, which stated that DOC concentration might increase in response to the decrease of discharge. Moreover, the observed pattern was the opposite of what has been reported for many rivers in the temperate and boreal regions of the northern hemisphere (Filella and Rodríguez-Murillo 2014). Some interesting exceptions are found (Bieroza et al. 2016). However, as far as I know, there are no DOC monitoring studies in the Mediterranean region that cover more than a decade. The DOC increase in boreal regions has been attributed to climate change, specifically the increasing temperature and atmospheric CO_2, and the diminution of atmospheric chemical deposition (Evans et al. 2006, Pagano et al. 2014).

Concerning climate change, higher CO_2 concentration would increase primary production and its organic exudates (Fenner et al. 2007b). Furthermore, warmer temperatures might enhance microorganism decomposition and the leaching of organic matter (Freeman et al. 2001, Fenner et al. 2007a). These factors are relevant at the global scale and therefore should affect Mediterranean regions too. Nevertheless, a DOC increase is totally absent from Fuirosos. Thus, the supposed increase of DOC exudates as a consequence of an increase of primary production seems to be non existent or irrelevant in our catchment. At the same time, it seems that warmer temperatures did not accelerate soil organic matter decomposition, during the study. However, it is important to remark that air temperature in Fuirosos did not show a substantial increase during the study period (Chapter 1, Fig. 1.1a).

As regards atmospheric chemical deposition, its reduction due to international air regulations has been correlated to increasing DOC concentrations (Monteith et al. 2007). Acid deposition, mostly in the form of sulphate (SO_4^{2-}), increases soil acidity. In consequence, DOM solubility decreases (Kalbitz et al. 2000), lowering the bulk of DOM that could reach streams. Therefore, the diminishing of SO_4^{2-} deposition (Fowler et al. 2005) has reversed this trend favouring the long-term DOC increase. The impact of acid deposition and its successive mitigation has been more significant in central and north Europe than in the Mediterranean region. Nevertheless , in a study area very close to Fuirosos, the rain pH increased from 4.7 to 6.5 over the period 1985–2000 (Ávila and Rodà 2002). Although more recent and detailed values are not available, global analysis corroborates that SO_4^{2-} wet deposition has reduced in Europe (Vet et al. 2014). Therefore, if acid deposition declined, it would result in an increase, rather than a decrease, of DOC concentration.

Meanwhile, the long-term DOC decrease might be related to the observed long-term discharge decrease. In an arid stream, an increase of the annual mean DOC concentration has been reported during years with low mean annual stream discharge (Jones et al. 1996). However, in forested catchments with an organic soil layer, this relationship might be the opposite because hillside surface runoff might reduce. Therefore, under low discharge conditions the hillside terrigenous DOC input is expected to decrease and its concentration in streams might decrease too. This reasoning has been adopted, for instance, to explain an increase of DOC concentration in rivers in temperate regions that experience long-term discharge increase (Huntington et al. 2016). Nevertheless, a reduction of the hillside runoff should diminish the mobilisation of NO_3^- : a highly soluble solute released by soils. However, in Fuirosos, NO_3^- increased slightly during the study period. Thus, its long-term trend is the opposite to that of DOC. Consequently, the hypothesis of a reduction in DOC concentration as a response of the decrease of hillside runoff seems inconsistent and would require further validation. However, NO_3^- concentration in precipitation increased significantly from 1983 to 2009 in a mountain area 20 km from Fuirosos (Izquierdo et al. 2012). Therefore, the long-term increase of NO_3^- atmospheric deposition might explain the observed slight long-term NO_3^- increase in stream water, rather than the discharge decrease.

Finally, a decrease of discharge implies larger water residence times in the stream channel. Therefore, DOC molecules have, a priori, more chances of being retained and processed by in-stream heterotrophic microbiota (Butturini et al. 2016). Thus, long residence times might contribute to reducing DOC concentration. Nevertheless, this hypothesis is not supported by the data from the present study. In fact, at low discharge under drying conditions, DOC tends to increase rather to decrease.

DOC and NO_3^- Seasonality

DOM and NO_3^- dynamics in Fuirosos showed clearly different temporal patterns. At the beginning of the hydrological year, during rewetting, DOC showed the highest concentrations. This result is in consonance with that reported in previous short-term studies performed in Fuirosos (Vázquez et al. 2007, von Schiller et al. 2015), in ephemeral Mediterranean washes (Catalán et al. 2013) and in agricultural catchments (Humbert et al. 2015). DOC flushing in Fuirosos has been related to the leaching of abundant leaf litter (up to 450 g dry mass m^{-2}, Sabater et al. 2001) accumulated on the stream bed and edges during summer dry period as a consequence of leaf input from the riparian vegetation (Sanpera-Calbet et al. 2016). During autumn, DOC concentration gradually recovered its base values. The rate at which this recovery occurred was a function of the length of the previous summer drought. As far as we know, no study has quantified the impact of drought severity on DOC temporal dynamics immediately after drought. However, our finding is in line with that reported by Humbert et al. (2015) that the length of the dry season regulates the mean annual DOC concentration in a small agricultural catchment in the north-west France.

*d*DOC/*d*Q showed the highest values during rewetting. Furthermore, these slopes strongly varied from year to year and this variability was unrelated to the characteristics of the previous drought. It is important to remark that the sampling of rewetting is a challenging matter because it is an abrupt and short phenomenon and its occurrence, magnitude and “flashiness” are unpredictable. In consequence, it is extremely complex to acquire a precise picture of the DOC–discharge relationship during this hydrological phase. Along these lines, the placing of in-situ DOM optical sensors might represent a fundamental step forward towards filling this methodological gap.

At the other extreme, *d*DOC/*d*Q, showed the lowest values during drying, at the beginning of summer: mainly negative or near zero. Therefore, DOC dynamics gradually disconnected from hydrology during low flow conditions. This disconnection coincided in time with the moment at which the stream became influent and recharged the surrounding riparian groundwater (Butturini et al. 2003). Allochthonous DOC inputs ceased and DOC in the stream water stabilised or increased slightly due to the increase in water residence time, water temperature (Vázquez et al. 2011) and particulate organic matter input from the riparian strip (Sanpera-Calbet et al. 2016).

Seasonal NO_3^- dynamics showed clear low concentrations during the growing season, from March to June. This NO_3^- pattern is similar to that observed in a small permanent Mediterranean headwater stream (Butturini and Sabater 2002) and in a temperate upland watershed with mixed land uses (Zhu et al. 2011). The reduction of NO_3^- during the growing season might respond to a reduction of terrestrial NO_3^- inputs and to an increase of in-stream N uptake by the photoautotrophic benthic community (Lupon et al. 2016).

The strong seasonality of NO_3^- dynamics coupled with the weak NO_3^-–discharge relationship detected under wet conditions provides evidence that nitrogen demand by terrestrial forest and in-stream communities strongly regulates the NO_3^- availability in Fuirosos. This does not necessarily mean that NO_3^- is insensitive to discharge oscillations. In fact, previous studies that analysed the NO_3^- dynamics in detail in Fuirosos over the first 3 years of the time series reported a significant relationship between NO_3^- and discharge during high flow events in late autumn–early spring (Butturini and Sabater 2002, Bernal et al. 2005). Nevertheless, the long-term monitoring relativised the importance of hydrology on NO_3^- when it is compared to DOC.

DOC and NO_3^- coupling

DOC and NO_3^- did not show a clear and robust relationship. Only during drying, when DOC was disconnected from discharge ,did a positive and more consistent relationship emerged. This positive relationship is the opposite to what has been reported in other terrestrial and aquatic environments (Taylor and Townsend 2010). In fact, some authors suggested that NO_3^- and DOC concentrations should be inversely related, arguing that under low DOC availability, microbial nitrogen immobilisation and denitrification should decrease and thus NO_3^- increase (Goodale et al. 2005). That DOC (quantity and/or quality) affects NO_3^- in headwater streams has been confirmed by some field experiments (Rodríguez-Cardona et al. 2016). However, denitrification in Fuirosos is not a relevant process at the catchment scale, because there are no wetlands and the nitrogen content in the soil is relatively low (Bernal et al. 2003). Therefore, the positive link between the two solutes reinforces the idea that denitrification is unimportant in Fuirosos and precluded DOC availability from modulating NO_3^- concentration.

*d*DOC/*d*Q inter-annual variability

During the wet period, the DOC concentration showed a strong relationship with discharge. However, drying and rewetting periods introduced a large dispersion in the DOC–Q scatter plot. Therefore, Fuirosos is a highly chemodynamic system. This result is in line with the hypothesis proposed by Creed et al. (2015) that headwaters should be chemodynamic while high-order rivers should be more chemostatic. In this framework, this study also revealed that in Fuirosos, discharge increased its relevance to DOC variability over the years. This is a noticeable and unexpected result that revealed that chemodynamic (or static) degree is not a fix property but can shift over time. In this context, it is essential to extend the long-term monitoring as much as possible to shed light on the hypothetical link between the shift of DOC chemodynamism and the long-term discharge decline (Chapter 1).

Chapter 3

Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis.

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La barraca de fang, Josep Ribot i Calpe 1939

Introduction

Dissolved organic matter plays a key role in freshwater ecosystems. Hydrology is a key driver of the DOM dynamic (Inamdar et al. 2011, von Schiller et al. 2015, Voss et al. 2015). DOM concentration typically increases during high flow conditions in forested streams (Hinton et al. 1997, Wiegner et al. 2009, Bass et al. 2011, Dhillon and Inamdar 2014). As a result, most organic carbon export occurs during high flows (Raymond and Saiers 2010). However, long-term studies in boreal streams reported that antecedent hydrological and climatic conditions are also important (Raymond and Saiers 2010, Ågren et al. 2010, Winterdahl et al. 2011). Consequently, to improve our understanding of the dynamic of DOM during storm events, it would be necessary to take into account the influence of pre-event hydrological conditions.

Most of the studies previously cited focused on the relationship between discharge (Q) and dissolved organic carbon (DOC) concentration. In contrast, little is known about the response of DOM qualitative properties. Spectroscopy techniques based on absorbance and fluorescence are a well-established tool to investigate DOM aromatic content (Fellman et al. 2013), composition (Cawley et al. 2014), origin and freshness (Kolic et al. 2014), degree of humification (He et al. 2013), anthropogenic inputs (Henderson et al. 2009) and potential bioavailability for micro biota (Guillemette and del Giorgio 2011). Some of these parameters are sensitive to hydrology. Thus, humic-like content, aromaticity, humification degree and DOM molecular weight generally tend to increase during storm episodes (Li et al. 2005, Hood et al. 2006, Duan et al. 2007, Vidon et al. 2008, Fellman et al. 2009, Nguyen et al. 2010, 2013, Inamdar et al. 2011, Pellerin et al. 2012), indicating a magnification of the terrigenous aromatic character of DOM, derived from shallow organic soils. Conversely, other parameters showed more unclear responses. For instance, the fluorescence index (FI, related to DOM sources) decreases (Vidon et al. 2008, Inamdar et al. 2011) or remains steady under high flows (Hood et al. 2006, Nguyen et al. 2010, 2013).

These studies originated from temperate and boreal streams and covered relatively short periods integrating a limited number of hydrological events (Hood et al. 2006, Vidon et al. 2008, Fellman et al. 2009, Nguyen et al. 2010, 2013, Spencer et al. 2010, Austnes et al. 2010, Inamdar et al. 2011). In contrast, research is still in the initial stage in intermittent streams that drain semi-arid or Mediterranean regions. Most of the on-going research specifically focus on the impact of drying-rewetting period on stream biogeochemistry (Fellman et al., 2011; Lake, 2011; Vázquez et al., 2011, 2007; von Schiller et al., 2015). However, intermittent streams are more complex than their well-known dry–wet cycle. Their hydrology shifts in a short time from unpredictable and intense storms to large, severe and predictable droughts. Consequently, it is possible to explore the plasticity of DOM quality under a large spectrum of hydrological conditions.

The specific aims of this study were:

- ❖ Describe the diversity of spectroscopic DOM properties under the widest range of hydrological conditions in an intermittent headwater stream and
- ❖ Investigate the potential legacy of antecedent hydrological, climatic and biogeochemical conditions on the variability of DOM–Q responses.

We hypothesised that discharge would modulate stream DOM properties and that this relationship would differ in contrasted hydrological periods. Moreover, we expected that the antecedent conditions of the storm events, such as the magnitude of the previous storm and the duration of the antecedent baseflow period, would affect the DOM–Q responses.

Here, we describe the results from an intensive, 2.5-year-long hydro-biogeochemical monitoring in a small, intermittent Mediterranean headwater stream. DOM was analysed in terms of carbon content (DOC) and spectroscopic properties (absorbance and fluorescence). The variability of responses of DOC and DOM qualitative descriptors with respect to discharge was explored at the hydrological seasonal scale and at the single storm event scale. Several hydrological, climatic and biogeochemical parameters were calculated for each storm event. The contribution of each significant driver that emerged in the most robust multiple linear regression model was assessed with a commonality analysis (Ray-Mukherjee et al. 2014).

Materials and Methods

Field monitoring strategy and water analysis

The hydrological year in Fuirosos can be split into four sub-hydrological seasons (Bernal et al. 2005):

- The rewetting period. Typically in early fall (September–October), it describes the beginning of the hydrological year, with an abrupt and short hydrological transition from the total summer drought to the re-establishing of the normal water flow.
- The wet period. From late fall to late winter (November–February) with base discharge typically higher than 5 L s^{-1}.
- The vegetative period. From early spring to early summer (March–June) with base flow of approximately 5 L s^{-1}.
- The drying period. In early summer (June–July), runoff disappears in the tributaries and decreases rapidly from the main channel. During the rest of summer, the runoff vanishes from the entire system with the exception of a few disconnected pools (Vázquez et al. 2011).

A sub-daily-frequency hydro-biogeochemical programme was performed from May 2009 to December 2011. A stage actuated water sampler collected a stream sample every 4–6 hours. Stream level was recorded every 30 minutes and discharge was estimated from these values. During the study, 47 hydrological high flow episodes occurred. The peak hydrographs were sampled in 72% of cases. The sampling captured the whole solute-discharge responses in 52% of the hydrological episodes. The wet and vegetative periods were the most represented, with 13 analysed storm events in each period. On the contrary, only 3 episodes from the drying period were captured.

Annual DOC export from the catchment was calculated by aggregating the daily fluxes obtained from the daily average values of discharge and DOC. Linear interpolation with time as the independent variable was performed on the days when data were not available. DOM characterization was carried out using spectroscopic techniques. DOM optical properties can be related to biochemical characteristics and compositional changes of DOM with a minimum sample manipulation, high instrument sensitivity and rapid execution (Fellman et al. 2010). Nine DOM descriptors were estimated in this study: DOC concentration; 4 chromophoric indices —specific ultraviolet absorbance at 254 nm (SUVA), two intensity ratio of absorbances (E_2:E_3 and E_4:E_6) and spectral slopes ratio (S_R); and 4 fluorophoric indices —humification index (HIX), fluorescence index (FI), biological index (BIX) and the intensity ratio of two humic-like fluorescence peaks (A_C:C). These optical indices and the related biogeochemical interpretation are described in Table 3.1.

Table 3.1 Optical indices analysed in this study, including the description of their calculation and their biogeochemical interpretation according to the referenced literature.

Index	Calculation	Interpretation
SUVA	The normalisation of UV absorbance at 254 nm by DOC concentration.	It indicates the DOM aromaticity (Weishaar et al. 2003).
E_2:E_3	The ratio of absorbances at 250 nm and 365 nm.	High values suggest a low average molecular size of DOM. (De Haan and De Boer 1987).
E_4:E_6	The ratio of absorbances at 465 nm to 665 nm.	It was first found to be inversely related to aromaticity, but was later found to be more related to humification (Chen et al. 1977).
S_R	The ratio of the log transformed absorbance spectra slope at 275–295 nm to that estimated in the range of 350–400 nm (Helms et al. 2008).	High values indicate a high proportion of the DOM molecular fraction with low molecular weight.
HIX	The sum of the fluorescence intensities between 300 and 345 nm divided by the sum of the intensities between 300 and 345 nm and between 435 and 480 nm, for an excitation wavelength of 254 nm (Ohno 2002).	Higher values indicate a greater degree of DOM humification. (Zsolnay et al. 1999).
FI	The ratio of emission intensities at 470 nm and 520 nm emitted at an excitation of 370 nm (Cory and McKnight 2005).	It provides information about DOM sources; high values (≈1.8) suggest the prevalence of autochthonous DOM, and low values (≈1.3) suggest the prevalence of allochthonous DOM. (McKnight et al. 2001).
BIX	The ratio of the fluorescence intensity emitted at 380 nm, corresponding to the maximum of intensity of the β fluorophore, and that emitted at 430 nm, which corresponds to the maximum of the humic fraction at an excitation of 310 nm (Huguet et al. 2009).	The β fluorophore is typical of autochthonous recent DOM release (Parlanti et al. 2000). Therefore, high BIX values (>1) suggest the presence of autochthonous and fresh DOM, whereas BIX values of 0.6–0.7 indicate a low or nil DOM autochthonous production.
A_C:C	The fluorescence intensity maxima in the area of 230−250 nm excitation and 420–460 nm emission wavelengths (peak AC) divided by that of the area of 330–370 nm excitation and 430–460 nm emission wavelengths (peak C) (Coble et al. 1990, 2014)	Peak AC is related to fulvic acids, more soluble and slighter in molecular size (McDonald et al. 2004), while peak C is associated with humic acids (Chen et al. 2003).

Description of DOM–Q responses

The relationship between DOM descriptors and discharge was explored for the entire data set, for each hydrological season and at storm events intervals. During the study period, discharge changed up to six orders of magnitude. As a consequence, the discharge was log transformed. The slopes of the DOM–Q relationships (*d*DOM/*d*Q, where DOM stands for DOC, SUVA, E_2:E_3, E_4:E_6, S_R, HIX, FI, BIX, and A_C:C) were considered significant at $p<0.05$.

The response of DOM during storm episodes was quantified by calculating the relative change of each DOM descriptor (ΔC), comparing the value during the storm peak with that one obtained during the pre-event base discharge conditions. ΔC ranged between −1 and 1. A negative ΔC value ($\Delta C < -0.1$) indicated a decrease of the DOM parameter, whereas a positive ΔC indicated an increase ($\Delta C > 0.1$). Chemostasis was assumed when $-0.1 < \Delta C < 0.1$ (Butturini et al. 2008). This descriptor was estimated for 34 storm episodes (72% of storms occurred during the study period).

In those cases when the entire storm episode was exhaustively sampled, the information regarding the nonlinearity of DOM–Q response and its rotational pattern (ΔR) was estimated. ΔR ranged between −1 and 1. If $\Delta R > 0.1$, the hysteresis showed a clockwise rotational pattern, meaning that the solute changes anticipated those of discharge. If $\Delta R < -0.1$, the hysteresis showed a counter-clockwise rotational pattern. In this case, the solute variations delayed those of discharge. If $-0.1 < \Delta R < 0.1$, this indicated that the DOM–Q loop showed an ambiguous or non-existent rotational pattern. In this study, this information was available for 25 storm episodes (52% of events occurred during the study period).

The methodological aspects of the calculation of ΔC and ΔR are described by Butturini et al. (2008). The ΔC and ΔR pairs were plotted in the ΔR versus ΔC unit plane. This plane synthesized the diversity continuum across the geometrical forms of DOM–Q responses (Butturini et al. 2008). The heterogeneity of the DOM–Q hysteresis of each DOM parameter (H) was defined as the proportion of area (%) of the convex envelope that contained all points with respect to the total area of the ΔR versus ΔC diagram (Fig. 3.1).

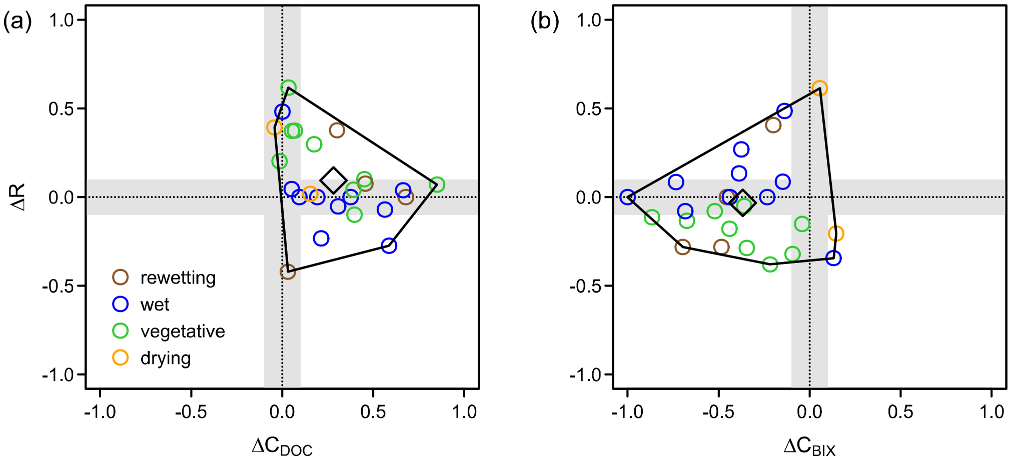


Fig. 3.1 ΔR versus ΔC diagram for DOC (**a**) and BIX (**b**), showing the construction of the convex envelope that contains all the storm events. The colour of the dots indicates the hydrological period of each storm event. The rhombus represents the mean value of all the storm events. The shaded area indicates chemostasis ($-0.1 < \Delta C < 0.1$) or no hysteresis loop ($-0.1 < \Delta R < 0.1$).

Data analysis and model selection

In this study, 18 environmental, hydrological, climatic and biogeochemical parameters were used as potential predictors of the variability of ΔC and ΔR descriptors during the storm events (Table 3.2, 3.3a and 3.3.b). These parameters attempt to capture the seasonal hydro-climatic variability and the short and long-term antecedent hydrological conditions.

Multiple linear regression and commonality analysis (CA) were used to explore the relationship between ΔC or ΔR (the dependent variables) and the potential drivers. The variables that did not satisfy normality according to the Saphiro–Wilk test (Shapiro and Wilk 1965) were log-transformed.

Table 3.2 Drivers included in the analysis of the variability of ΔC and ΔR descriptors. They are classified into three groups: storm event drivers (E), storm pre-event hydrological drivers (PEH) and storm pre-event biogeochemical drivers (PEB).

Driver	Description	Group
ΔQ	Magnitude of the event: the discharge difference between peak hydrograph and pre-event base discharge	E
L_{rs}	Length of the rising limb: the lag time (hrs) between peak flow and base discharge. It provides an idea of the flashiness of the storm episode	E
T_{min}	The minimal temperature of the day during the hydrological episode	E
Q_b	The pre-event base discharge	PEH
Q_m	The average discharge during the month prior to the storm event	PEH
Δt_{-1}	Inter-storm time interval: the lag time between the storm and the preceding one	PEH
ΔQ_{-1}	Magnitude of the previous storm event: calculated as ΔQ	PEH
Δt_0	The time elapsed from the starting of the rewetting period	PEH
DOM_b	DOC, SUVA, S_R, E_2:E_3, E_4:E_6, FI, BIX, HIX and A_C:C values during the pre-event base discharge	PEB
DOC_m	DOC concentration average during the month prior to the storm	PEB

All data were centred by subtracting the variable mean and scaled by dividing by the standard deviation.

The data analysis consisted of the following 4 steps:

1. We started exploring if ΔC and ΔR were significantly and linearly related to the magnitude of the hydrological event (ΔQ). In forested catchments, DOC concentration is typically strongly related to discharge. Therefore, we expected to observe this relationship in some of the ΔC and ΔR descriptors. In those cases that the relationship was significant ($p<0.05$), the influence of ΔQ was removed by extracting the residuals and the dependent variables in the multiple regressions were these residuals ($\Delta C_{(r)}$ or $\Delta R_{(r)}$). If this relationship was not significant, the dependent variables were the ΔC (or ΔR) descriptors.

2. Multiple linear regression modelling was performed. We did an exhaustive search for the best subset (higher R^2) of each size (from 1 to 18 independent variables) among all of the combinations of potential drivers, using an efficient branch-and-bound algorithm (Lumley and Miller 2009).
3. The best model (that with an optimum number of drivers) was selected using the Bayesian information criteria (BIC), choosing the combination of potential drivers with the lowest BIC value (Schwarz 1978).
4. CA was performed to assess the contribution and relevance of each driver selected in the optimal model.

CA was recently proposed to assess the predictor contribution in multiple linear regressions on ecological and environmental data (Ray-Mukherjee et al. 2014). CA decomposes regression R^2 into its unique and common effects (Newton and Spurrell 1967, Mood 1969, 1971). Unique effects (U) indicate how much variance is uniquely accounted for by a single predictor, while common effects (C) indicate how much variance is common to a predictor set. Therefore, CA determines the variance contributed by each predictor by accounting for unique and common effects. A negative common effect, together with a large unique effect and a low R^2, may indicate that the variable is a suppressor (Zientek and Thompson 2006). Therefore, it removes irrelevant variance in another predictor and thus increases the predictive ability of that predictor (or set of predictors) and R^2 by its inclusion in a regression equation (Jobson 1991). We applied CA to the model selected by multiple linear regression for each DOM property in order to weight the importance and role of the predictors.

All of the data analyses were conducted with R version 3.1.1 (R Core Team 2014) using the "leaps" package (Lumley and Miller 2009) and the "yhat" package (Nimon et al. 2013).

Table 3.3a Values of the potential drivers for each studied storm event: base discharge (Q_b), magnitude (ΔQ), length of the rising limb (L_{rs}), minimal temperature of the day (T_{min}), number of days from the annual rewetting (Δt_0), time since the preceding storm event (Δt_{-1}), magnitude of the preceding storm event (ΔQ^{-1}) and mean discharge of the preceding month (Q_m).

Date	Q_b ($m^3 s^{-1}$)	ΔQ ($m^3 s^{-1}$)	L_{rs} (h)	T_{min} (ºC)	Δt_0 (d)	Δt_{-1} (d)	ΔQ_{-1} ($m^3 s^{-1}$)	Q_m ($L s^{-1}$)
23/10/2009	0	0.016	2	10.0	1	124	0.002	0
22/12/2009	0.005	0.008	10	9.3	62	61	0.016	3
05/01/2010	0.009	0.006	11	7.9	63	11	0.005	6
07/01/2010	0.009	0.038	12	0.8	77	3	0.006	7
15/01/2010	0.024	0.026	28	2.3	84	7	0.038	16
09/02/2010	0.011	0.952	18	0.4	104	4	0.005	20
17/02/2010	0.021	0.059	32	−1.7	115	8	0.952	42
20/02/2010	0.052	0.456	30	5.5	120	3	0.059	44
05/03/2010	0.016	0.060	58	6.5	132	14	0.456	76
09/03/2010	0.051	0.258	46	1.5	137	4	0.060	82
15/03/2010	0.148	0.149	62	0.7	143	5	0.258	89
04/05/2010	0.007	2.756	36	13.3	188	22	0.007	16
14/05/2010	0.075	0.646	39	9.3	203	10	2.756	116
18/09/2010	0	0.472	6	12.6	1	50	0.005	0
24/09/2010	0.014	0.025	5	14.7	5	6	0.472	58
12/10/2010	0.004	3.852	59	16.3	23	18	0.025	46
13/10/2010	0.825	3.242	7	12.2	27	1	3.852	144
23/12/2010	0.015	0.216	59	−1.5	91	23	0.011	15
17/02/2011	0.016	0.009	7	2.8	154	19	0.099	28
03/03/2011	0.011	0.034	20	3.1	167	14	0.009	23
12/03/2011	0.021	5.770	16	6.1	177	9	0.035	20
15/03/2011	0.532	16.511	24	7.1	179	3	5.770	199
28/04/2011	0.015	0.014	4	7.7	224	5	0.123	24
01/06/2011	0.003	0.034	23	11.5	243	17	0.014	9
02/06/2011	0.020	0.024	8	7.6	259	1	0.034	9
05/06/2011	0.012	0.017	15	9.6	260	3	0.024	10
10/06/2011	0.020	0.041	11	10.8	267	5	0.017	13
15/07/2011	0.001	0.009	28	14.5	301	34	0.041	1
17/07/2011	0	0.013	10	12.9	302	3	0.009	1
26/07/2011	0.003	0.055	4	14.9	313	9	0.013	2
24/10/2011	0	0.071	3	9.6	1	89	0.007	0
28/10/2011	0.005	0.308	26	9.6	1	4	0.071	5
06/11/2011	0.016	1.424	60	12.7	8	9	0.308	27
15/11/2011	0.026	22.789	15	8.8	22	2	0.013	56

Table 3.3b Values of the potential drivers for each studied storm event: mean DOC of the preceding month (DOC_m) and base values of DOM properties (DOC_b, $SUVA_b$, E_2:E_{3b}, E_4:E_{6b}, SR_b, HIX_b, FI_b, BIX_b and A_C:C_b).

Date	DOC_m (mg L^{-1})	DOC_b (mg L^{-1})	$SUVA_b$ (L mg C^{-1} m^{-1})	E_2:E_{3b}	E_4:E_{6b}	S_{Rb}	HIX_b	FI_b	BIX_b	A_C:C_b
23/10/2009	3.7	3.9	4.4	5.8	4.0	0.86	0.93	1.67	0.59	1.80
22/12/2009	2.2	2.0	6.1	5.2	0.6	0.88	0.87	1.66	0.60	1.79
05/01/2010	2.2	2.2	6.9	4.2	3.0	0.82	0.92	1.66	0.59	1.79
07/01/2010	2.2	2.0	7.5	5.1	6.0	0.88	0.91	1.63	0.61	1.87
15/01/2010	2.7	2.6	6.8	5.6	4.0	0.83	0.93	1.62	0.60	1.96
09/02/2010	2.8	2.6	5.7	5.9	4.0	0.85	0.89	1.60	0.61	1.94
17/02/2010	4.6	4.5	6.4	6.3	6.0	0.69	0.93	1.50	0.54	2.02
20/02/2010	4.9	4.3	6.4	5.6	2.5	0.77	0.93	1.49	0.54	1.97
05/03/2010	5.1	3.8	5.9	5.7	3.0	0.94	0.93	1.52	0.57	1.95
09/03/2010	5.1	3.6	6.9	5.1	2.3	0.93	0.94	1.50	0.55	1.91
15/03/2010	5.0	4.9	6.7	5.9	3.5	0.82	0.94	1.49	0.52	1.87
04/05/2010	3.0	2.8	5.5	5.9	4.0	0.88	0.86	1.54	0.57	1.98
14/05/2010	6.1	4.7	5.5	5.8	2.5	0.87	0.90	1.43	0.57	2.07
18/09/2010	4.0	3.7	7.3	6.4	3.2	0.77	0.92	1.78	0.61	1.76
24/09/2010	5.3	4.7	8.1	5.1	4.0	0.88	0.91	1.63	0.56	1.93
12/10/2010	5.9	3.7	7.4	6.0	8.0	0.81	0.91	1.68	0.58	1.80
13/10/2010	6.0	7.4	9.8	5.4	11.0	0.72	0.92	1.49	0.51	1.98
23/12/2010	2.6	2.4	5.8	6.3	4.0	0.77	0.88	1.61	0.61	1.93
17/02/2011	2.2	2.5	6.5	5.6	3.0	0.85	0.90	1.54	0.55	1.88
03/03/2011	2.4	2.0	6.8	5.6	2.0	0.85	0.91	1.53	0.59	2.02
12/03/2011	2.3	2.2	6.5	5.5	3.0	0.88	0.90	1.54	0.58	1.96
15/03/2011	3.8	5.3	7.7	5.6	6.0	0.81	0.93	1.45	0.51	1.93
28/04/2011	2.7	2.9	5.8	5.4	3.0	0.84	0.87	1.51	0.56	1.99
01/06/2011	2.7	2.6	5.5	6.0	6.0	0.79	0.90	1.57	0.57	1.96
02/06/2011	3.2	2.7	6.3	5.9	3.0	0.77	0.91	1.53	0.56	1.99
05/06/2011	3.1	2.7	6.2	5.8	2.0	0.90	0.87	1.58	0.59	2.07
10/06/2011	3.1	2.9	5.7	5.8	4.0	0.79	0.86	1.53	0.57	2.03
15/07/2011	3.3	3.2	6.6	5.1	4.0	0.98	0.92	1.69	0.58	1.80
17/07/2011	3.6	3.5	7.0	4.8	6.0	0.89	0.92	1.74	0.59	1.71
26/07/2011	3.5	3.2	5.9	6.5	4.0	0.89	0.90	1.59	0.58	1.96
24/10/2011	3.5	3.7	6.1	5.4	6.0	0.69	0.89	1.66	0.61	1.87
28/10/2011	7.7	6.6	6.8	4.8	8.0	0.72	0.90	1.92	0.57	1.35
06/11/2011	6.3	4.3	6.8	3.4	5.0	0.72	0.90	1.67	0.57	1.83
15/11/2011	6.8	5.4	6.6	5.5	6.0	0.77	0.92	1.59	0.56	1.84

Results

Hydrological variability and DOC fluxes

During the study period, Fuirosos surface flow stopped in June–July and recovered in September–October (Fig. 3.2). The base discharge typically increased to an average value of 18 L s^{-1} during the wet and vegetative periods. The magnitude of storm episodes (ΔQ) ranged widely from 5 L s^{-1} to 22789 L s^{-1}. The flashiness of the hydrographs also noticeably changed. The rising limb of the hydrograph (L_{rs}) was shorter than 12 h or 24 h in 51% and 72% of the events, respectively. The lag time between two consecutive rain episodes (Δt_{-1}) averaged 19 days. However, in summer, there were much longer periods without precipitation: 124 days in summer 2009, 77 days in summer 2010 and 89 days in summer 2011.

The annual DOC exports were 432 kg C km^{-2} yr^{-2} and 697 kg C km^{-2} yr^{-2} in 2009−2010 and 2010–2011, respectively. The vegetative period contributed up to 63–81% of the total annual flux, followed by the wet period (18–34%), the rewetting period (1–3%) and finally the drying period (0.2–0.3%). The 90–91% of the annual DOC export was flushed during storm events.

DOM-Q relationships

Seasonal variations

DOC and most of the DOM optical parameters were strongly related to discharge (Fig. 3.3 and 3.4; $10^{-66} < p < 10^{-11}$). The most discharge dependent parameters were DOC, BIX and FI ($0.326 < R^2 < 0.592$). SUVA, HIX and E4:E6 were also significantly related to discharge, although the explained variance decreased ($0.138 < R^2 < 0.18$). Finally, S_R, A_C:C and E_2:E_3 appeared nearly chemostatic with respect to discharge ($R^2 < 0.09$).

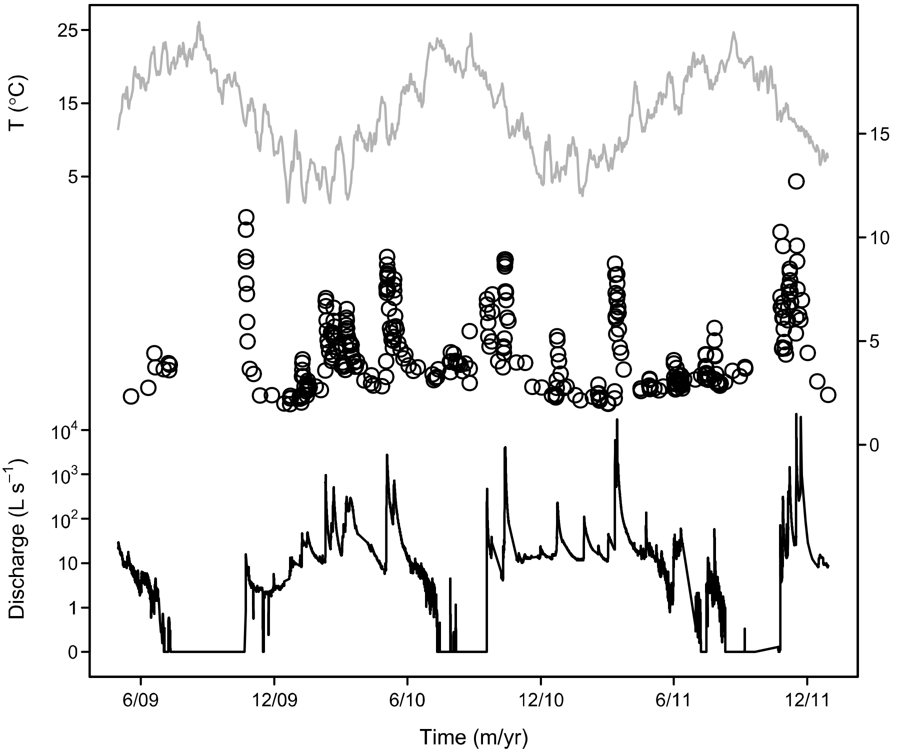


Fig. 3.2 Discharge (black line), DOC (dots) and water temperature (grey line) during the study period in Fuirosos stream.

The hydrological period greatly influenced the slope and strength of the relationships between DOM descriptors and discharge (Fig. 3.5). The *d*DOM/*d*Q values of SUVA, FI, BIX and A_C:C changed gradually from the rewetting to the drying period. The most notable shifts were those of *d*FI/*d*Q (which changed from a highly negative slope to a positive slope) and *d*A_C:C /*d*Q (which changed the opposite way). The S_R parameter also reversed the sign of its slope during the drying. During the drying period, most of the *d*DOM/*d*Q slopes were not significant ($p > 0.1$). The exception was the E_2:E_3 descriptor, with the strongest relationship with discharge ($p < 10^{-4}$) during this period.

Storm to storm responses

The ΔC versus ΔR unit plane synthesized the diversity of the DOM–Q loops at the storm event scale (Fig. 3.6 Table 3.4). The most homogenous DOM–Q loops were that of SUVA and DOC (H < 14%). Further, the convex envelopes of DOC, SUVA and E_4:E_6 nearly overlapped each other. Conversely, the most heterogeneous loops were that of E_2:E_3 and S_R.

Table 3.4 Distribution of DOM–Q loops types according the ΔC and ΔR descriptors for each DOM property, expressed in % of the studied cases. ΔC and ΔR were estimated for 34 and 25 storm episodes respectively. The last column describes the heterogeneity of DOM–Q loops responses (H).

DOM descriptor	**ΔC**			**ΔR**			**H (%)**
	Dilution $\Delta C < -0.1$	Chemostasis $-0.1<\Delta C<0.1$	Flushing $\Delta C > 0.1$	Counter-clockwise $\Delta R < -0.1$	No loop $-0.1<\Delta R<0.1$	Clockwise $\Delta R > 0.1$	
DOC	0	41	59	12	52	36	13.5
SUVA	0	29	71	8	24	68	12.5
E_2:E_3	59	29	12	60	28	12	20.8
E_4:E_6	9	24	68	32	40	28	17.3
S_R	65	15	21	48	32	20	26.8
FI	44	44	12	8	36	56	16.3
HIX	12	41	47	44	48	8	16.8
BIX	74	15	12	44	36	20	16.8
A_C:C	29	53	18	56	32	12	19.3

Flushing responses during storm events predominated for DOC, SUVA, HIX and E_4:E_6. Dilution prevailed for E_2:E_3, S_R and BIX. Chemostasis ($-0.1 < \Delta C < 0.1$) was the most frequent situation for A_C:C. Finally, both dilution and chemostasis were equally frequent for FI. DOM–Q rotational patterns, ΔR, were highly heterogeneous. For instance, comprising all DOM descriptors, clockwise,

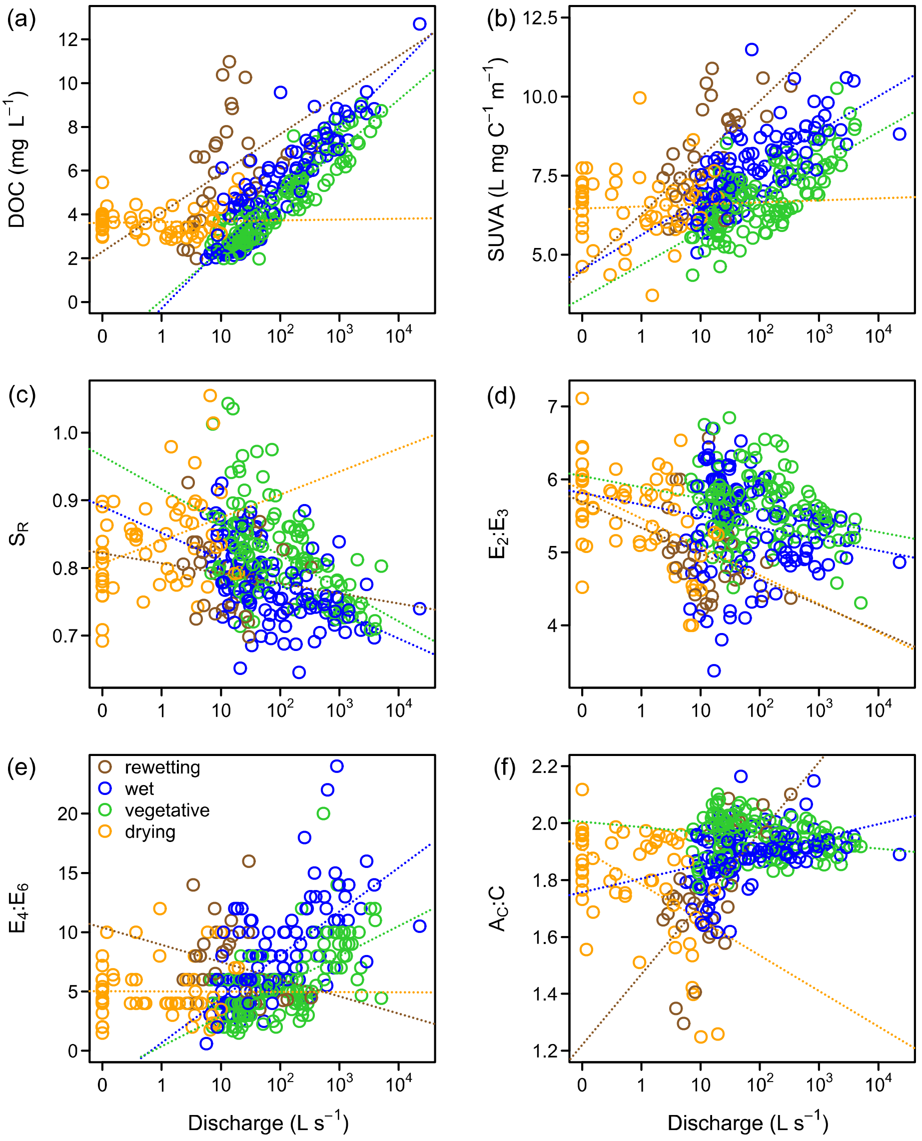


Fig. 3.3 Relationships between DOM descriptors —DOC (**a**), SUVA (**b**), S_R (**c**), E_2:E_3 (**d**), E_4:E_6 (**e**) and Ac:C (**f**)— and discharge during the study period. Dotted lines show the slope of the DOM descriptor versus discharge linear relationship for each hydrological period. Significance levels are described in Fig. 3.5.

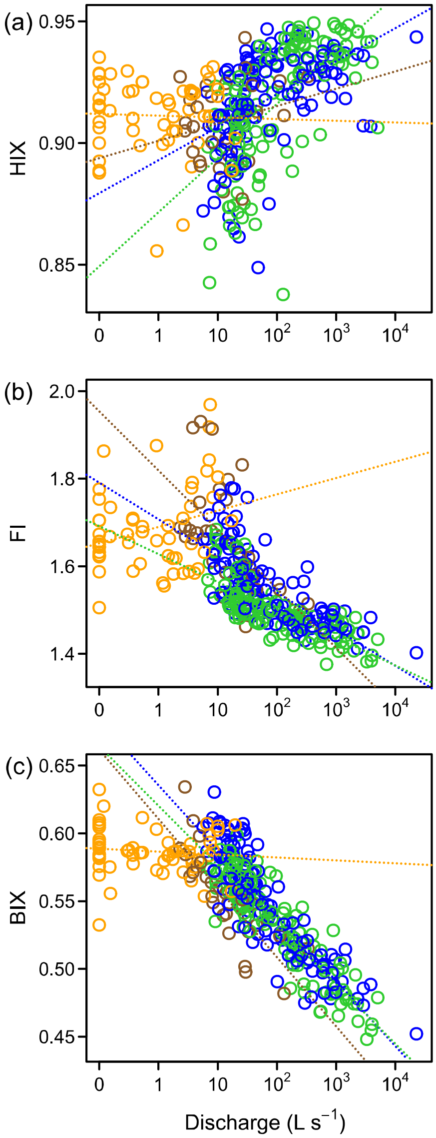


Fig. 3.4 Relationships between fluorescence indices —HIX (**a**), FI (**b**) and BIX (**c**)— and discharge during the study period. Dotted lines show the slope of the DOM descriptor versus discharge linear relationship for each hydrological period. Significance levels are described in Fig. 3.5.

no loop ($-0.1 < \Delta R < 0.1$) and counterclockwise hysteresis were the 29%, 36% and 35%, respectively. Clockwise loops predominated for SUVA and FI. Responses without a clear rotational pattern were more frequent for DOC and E_4:E_6. Counterclockwise loops emerged for E_2:E_3, S_R, BIX and A_C:C. Finally, for HIX the occurrence of ambiguous and counterclockwise responses was similar.

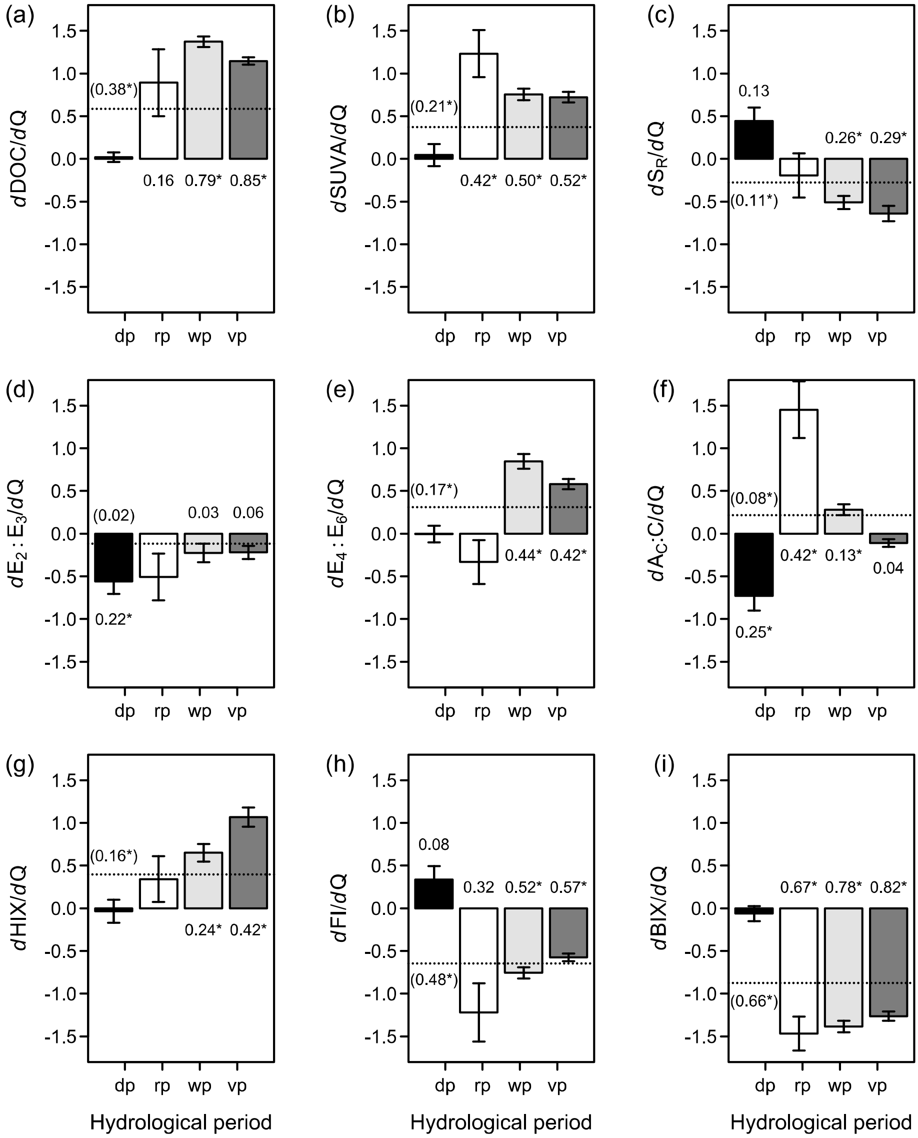


Fig. 3.5 Slopes of the linear regression relating the normalized DOM descriptors —DOC (**a**), SUVA (**b**), S_R (**c**), E_2:E_3 (**d**), E_4:E_6 (**e**), Ac:C (**f**), HIX (**g**), FI (**h**) and BIX (**i**)— with the logarithm of discharge in the different hydrological periods (dp=drying, rp=rewetting, wp=wet, vp=vegetative). Error bars indicate ± 1 standard error of the slopes. Dotted lines represent the slope of the entire data set. R^2 for each regression is shown when $p<0.05$ (in parenthesis accounting for the data altogether); * indicates that p-value < 0.001.

Clear differences in DOM–Q loops across hydrological periods were not observed. However, the most anomalous DOM–Q loops were typically monitored during rewetting (DOC, SUVA and E_2:E_3) and drying (S_R, FI and A_C:C) periods. BIX was the only DOM descriptor that showed a separation between hydrological periods, with rather clockwise loops in the wet period and counterclockwise loops in the vegetative period (Fig. 3.1).

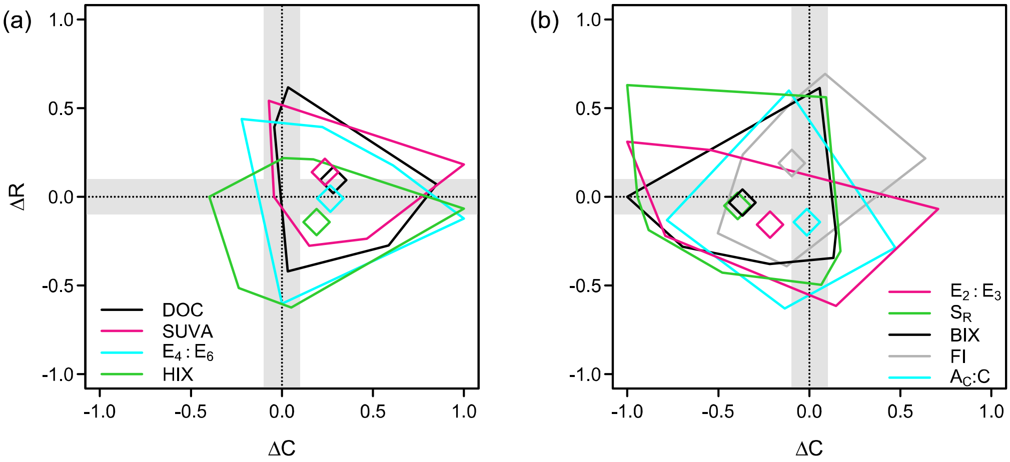


Fig. 3.6 Convex envelopes and mean (rhombus) for each DOM descriptor —DOC, SUVA, E_4:E_6 and HIX (**a**); E_2:E_3, S_R, BIX, FI and Ac:C (**b**)— in the ΔR versus ΔC unit plane.

Drivers of ΔC and ΔR descriptors

ΔC was significantly related ($p < 0.05$) to the magnitude of storm events (ΔQ) for most DOM descriptors, namely DOC ($R^2 = 0.500$), SUVA ($R^2 = 0.194$), E_4:E_6 ($R^2 = 0.153$), FI ($R^2 = 0.296$) and BIX ($R^2 = 0.459$). In those cases, we set the residuals ($\Delta C_{(r)}$) of the ΔC versus ΔQ regression as the dependent variables of the multiple regression. Table 3.5 summarizes the results of CA for each ΔC or $\Delta C_{(r)}$, after the selection of the optimal multiple regression model. 5 models explained more than 75% of the variance. The drivers more frequently selected were Δt_{-1} and Δt_0 (in 5 models) and Q_b (4 models). In most of the selected models, DOM biogeochemical status during the pre-event baseflow was a relevant driver, showing a negative relationship with ΔC.

Table 3.5 Total effects and unique effects (in parenthesis) obtained in the commonality analysis of each ΔC descriptor. The subindex (r) indicates that the residuals from the ΔC–ΔQ relationship are used as the dependent variable. A positive sign before a total effect value indicates a positive relationship between the driver and the ΔC; a negative sign indicates an inverse relationship. The higher value of each ΔC descriptor is in bold. The statistics of the multiple linear regressions are also shown. NS are non-significant relationship ($p > 0.05$).

Indep. variables	Dependent variables								
	$\Delta C_{DOC(r)}$	$\Delta C_{SUVA(r)}$	$\Delta C_{E4:E6(r)}$	$\Delta C_{FI(r)}$	$\Delta C_{BIX(r)}$	$\Delta C_{E2:E3}$	ΔC_{SR}	ΔC_{HIX}	$\Delta C_{A_C:C}$
ΔQ	removed	removed	removed	removed	removed	−0.008 (0.036)	−0.051 (0.159)		
L_{rs}				−0.045 (0.362)				+0.168 (0.228)	+0.077 (0.284)
T_{min}	+0.051 (0.074)					−0.030 (0.055)		−0.019 (0.031)	
Q_b		**−0.308** (0.075)		+0.055 (0.362)	+0.163 (0.063)				−0.002 (0.310)
Q_m								−0.069 (0.037)	
Δt_{-1}				+0.006 (0.308)	+0.128 (0.088)	−0.221 (0.037)		−0.018 (0.059)	−0.044 (0.434)
ΔQ_{-1}	**−0.394** (0.136)			−0.049 (0.072)					+0.001 (0.084)
Δt_0	−0.049 (0.118)	−0.067 (0.084)		**+0.179** **(0.432)**	+0.060 **(0.195)**				**−0.210** **(0.480)**
DOC_m						+0.034 (0.061)			
DOC_b				+0.022 (0.240)					−0.008 (0.172)
$SUVA_b$	−0.278 **(0.167)**	−0.251 **(0.160)**			+0.204 (0.028)				
$E_{2:}E_{3b}$			**−0.101**			**−0.467** **(0.486)**			
$E_{4:}E_{6b}$									
S_{Rb}					−0.016 (0.032)		**−0.256** **(0.364)**		
HIX_b				+0.023 (0.163)	+0.166 (0.079)			**−0.445** **(0.646)**	
FI_b					+0.070 (0.072)				−0.019 (0.156)
BIX_b				+0.085 (0.063)	**−0.481** (0.120)				
$A_C:C_b$						+0.006 (0.113)			−0.058 (0.127)
Statistics									
p-value	$<10^{-5}$	$<10^{-3}$	NS	$<10^{-5}$	$<10^{-5}$	$<10^{-7}$	$<10^{-3}$	$<10^{-8}$	$<10^{-5}$
R^2	0.652	0.491	0.100	0.779	0.803	0.809	0.414	0.818	0.798
BIC	80.7	90.2	102.4	79.4	79	67.4	91.4	62.1	79.8

The model for ΔC_{HIX} explained 81.8% of the variance with only 4 drivers, with HIX_b as the most important. Regarding $\Delta C_{E2:E3}$, the most relevant drivers were $E2:E3_b$ and Δt_{-1}. BIX_b explained 48.1% of the variance in $\Delta C_{BIX(r)}$, while 7 other drivers explained a little fraction each one. In this model Δt_0 showed relatively high unique effects and high negative common effects ($C = -0.136$), and, therefore, although it had low total effects, it acted as a suppressor driver. The model for ΔC_{SR} selected only 2 drivers, the most relevant was S_{Rb} explaining 41% of the variance. Finally, the model for $\Delta C_{E4:E6(r)}$ had a poor performance (10% of the variance explained), and $E_2:E_{3b}$ (negative relationship) was the single driver selected.

Δt_0 was the main driver for $\Delta C_{A_C:C}$ and $\Delta C_{FI(r)}$ and showed a positive relationship with them. The model for $\Delta C_{A_C:C}$ included 8 drivers, and Δt_{-1} acted as a suppressor ($C = -0.390$). The model selected for $\Delta C_{FI(r)}$ integrated also 8 drivers and Q_b ($C = -0.307$) and L_{rs} ($C = -0.317$) acted as suppressors.

Short time antecedent hydrological conditions were important drivers for some DOM descriptors. For $\Delta C_{DOC(r)}$ the selected model explained 65% of its variance and ΔQ_{-1} was the most relevant driver. With respect to $\Delta C_{SUVA(r)}$, the selected model included three drivers and explained 49% of the total variance. Q_b showed the higher total effects in this case. Both parameters were inversely related to the respective ΔC.

The models selected to explain the variability of ΔR_{DOM} descriptors (Table 3.6) were less robust than those selected for ΔC_{DOM}. The ΔR_{BIX} model was not significant ($p > 0.05$). The models with the highest explained variance were those selected for ΔR_{FI} and ΔR_{SUVA}. In the former, the most important predictor was ΔQ (52.3% of the variance explained), while in the latter it was S_{Rb} (15.8%). The drivers more frequently selected among the 9 models were Δt_0 and BIX_b (in 5 models) and DOC_b (4 models).

Table 3.6 Total effects and unique effects (in parenthesis) obtained in the commonality analysis of each ΔR descriptor. The higher value of each ΔR descriptor is in bold. A positive sign before a total effect value indicates a positive relationship between the driver and the ΔR; a negative sign indicates an inverse relationship. The statistics of the multiple linear regressions are also shown. NS indicates a non-significant relationship ($p > 0.05$).

Indep. variables	Dependent variables								
	ΔR_{DOC}	ΔR_{SUVA}	$\Delta R_{E2:E3}$	$\Delta R_{E4:E6}$	ΔR_{SR}	ΔR_{HIX}	ΔR_{FI}	ΔR_{BIX}	$\Delta R_{A_C:C}$
ΔQ	−0.099 (0.087)			−0.016 (0.071)			**−0.523** **(0.456)**		
L_{rs}			+0.014 (0.125)	+0.065 (0.225)					
T_{min}			+0.079 (0.177)	+0.007 (0.154)			+0.025 (0.041)		
Q_b		+0.014 (0.167)		+0.009 (0.313)					+0.010 (0.085)
Q_m		−0.009 (0.123)		−0.038 **(0.346)**					
Δt_{-1}		+0.017 (0.122)							
ΔQ_{-1}							−0.140 (0.056)		−0.009 (0.250)
Δt_0	**+0.273** **(0.444)**	+0.144 (0.056)	**−0.243** (0.242)				−0.022 (0.057)		−0.099 (0.069)
DOC_m		+0.022 (0.096)	−0.010 (0.276)		−0.026 (0.064)				
DOC_b		−0.025 (0.134)	+0.017 **(0.297)**		+0.024 (0.166)				+0.170 **(0.274)**
$SUVA_b$						**−0.168** **(0.287)**			
$E_{2:}E_{3b}$				+0.024 (0.073)				**−0.125**	
$E_{4:}E_{6b}$		+0.002 (0.224)							
S_{Rb}	−0.011 (0.243)	**+0.158** (0.113)			+0.155 (0.188)				
HIX_b					**+0.177** (0.117)				**+0.191** (0.089)
FI_b									
BIX_b			+0.086 (0.222)	**+0.094** (0.061)	+0.019 **(0.272)**	−0.047 (0.166)	+0.208 (0.038)		
$A_C{:}C_b$	−0.011 (0.066)	−0.035 **(0.228)**							+0.025 (0.236)
Statistics									
p-value	$<10^{-3}$	$<10^{-2}$	$<10^{-3}$	$<10^{-2}$	10^{-2}	<0.05	$<10^{-5}$	NS	10^{-2}
R^2	0.632	0.792	0.726	0.638	0.625	0.334	0.836	0.125	0.667
BIC	64	69	66	74	71	73	50	76	68

Discussion

DOM–Q relationships

This study revealed how a complex coupling of hydrological, climatic and biogeochemical factors modulated the variability of the DOM concentration and quality in a headwater intermittent stream. These factors interacted with each other and interfered with the DOM dynamic at annual, seasonal and storm event scales.

To date, hysteresis approach focuses on sediment transport (Ziegler et al. 2014), nutrients (Bowes et al. 2015, Darwiche-Criado et al. 2015) and DOC (Butturini et al. 2006, 2008). The present study is, as far as we know, the first attempt to describe shifts of DOM quality under a large spectrum of hydrological conditions in a Mediterranean headwater stream, and to relate these shifts to environmental drivers. A previous study performed in Fuirosos during four years did not identify any predictable pattern of DOC–Q responses (Butturini et al. 2008). Consequently, the analysis of predictability of DOM–Q hysteresis is a challenging task. Moreover, the hydro-climatic characteristics in the Mediterranean region are being altered (Vicente-Serrano et al. 2014, Barrera-Escoda and Llasat 2015). Therefore, it is crucial to assess how magnitude and frequency of storm events and severity of drought episodes influence on DOM quantity and quality in headwater streams.

Most of the DOM was flushed downstream under high flow conditions. This circumstance had enormous biogeochemical implications because over an entire year, a large proportion of DOM moved rapidly downstream with little chance to be processed by the system. However, these DOM pulses would be essential carbon and energy input sources for heterotrophic microbiota in downriver alluvial floodplains or even in the coastal system (McLaughlin and Kaplan 2013, Palmer et al. 2015).

DOM in Fuirosos is commonly terrigenous, aromatic, degraded, humic and with high molecular weight, but it strongly exacerbates these properties at high flows. These changes reflected modifications in flow paths during rain episodes (Hinton et al. 1998), with subsequent DOM mobilization from near surface organic rich soil, via overland flow or preferential flow through soil macropores (Vidon et al. 2008). Thus, DOM concentration and properties were greatly chemodynamic with respect to discharge. These results coincided with that reported in most of the forested headwaters located in boreal, temperate and alpine systems (Buffam et al. 2001; Li et al. 2005; Hood, Gooseff, and Johnson 2006; Vidon, Wagner, and Soyeux 2008; Fellman et al. 2009; Saraceno et al. 2009; Nguyen, Hur, and Shin 2010; Spencer et al. 2010; Inamdar et al. 2011; Nguyen et al. 2013; Fasching et al. 2015; Singh, Inamdar, and Mitchell 2015). These consistencies in the DOM–discharge relationship worldwide marked the bond between discharge and DOM concentration and quality.

Seasonal patterns: drying and rewetting

Sensitivity to discharge strongly varied across hydrological seasons. Thus, for most of the DOM descriptors, the connection with discharge vanished or reversed during the drying phase. In Fuirosos, this period implicated a rapid reduction of water flow, large water residence times and the fragmentation of the river continuum (Vázquez et al. 2011). The slight increase of FI and BIX might reflect a moderate increase of the contribution of autochthonous DOM during this phase. E_2:E_3 also increased as drying advanced, a pattern that revealed the decrease of the average DOM molecular weight. Von Schiller et al. (2015) attributed this trend to the decline in the proportion of large sized polysaccharides, probably due to their bioavailability as a source of DOM for microbial heterotrophs (Ylla et al. 2010).

The rewetting period represented a drastic change in the hydro-biogeochemical conditions. In few hours, the riparian groundwater was recharged by stream water, and the solute exchange across the stream–riparian interface was restored (Butturini et al. 2003, Vázquez et al. 2007). The abrupt hydrological reconnection between forest hillsides and stream channel, and the water–solute exchange across the stream–riparian interface, reactivated the DOM versus discharge relationship for most of the DOM descriptors and promoted the largest *d*DOM/*d*Q slope values for SUVA, A_C:C, BIX and FI. Therefore, high discharges during the rewetting period leaded to a disproportionate input of allochthonous, degraded and aromatic DOM. Among these parameters, the most remarkable response was that of the A_C:C. High values of A_C:C have been associated with photobleaching or microbial degradation of terrestrially derived DOM (Zhang et al. 2011, Hur and Cho 2012). The Fuirosos fluvial channel is mostly shadowed by a dense riparian strip. Consequently, the anomalous fulvic-like substances peak might reflect the accumulation of these substances in the stream bed during the drought period.

DOM–Q hysteresis heterogeneity

Although the analysis of hysteresis loops in fluvial hydro-biogeochemistry was proposed in the 1970s and 1980s (Walling and Foster 1975, Johnson and East 1982, Williams 1989), this approach is becoming a growing research topic after Evans and Davies (1998) and House and Warwick (1998) and is providing new advances into hydrological and biogeochemical functioning in rivers (Butturini et al. 2008, Fovet et al. 2015, Zuecco et al. 2015, Lloyd et al. 2016). Overall, DOM–Q hysteresis in Fuirosos were highly heterogeneous. However, within this high variability, some patterns emerged. Thus, the predominance of clockwise loops of SUVA and FI and the predominance of counterclockwise loops of E2:E3, S_R and A_C:C suggested a rapid mobilization of poorly degraded, large size and aromatic DOM pool from a near-stream source (Lloyd et al. 2016), such as a river bed, hyporheic or riparian zones (Butturini et al. 2006). Conversely, the input of more allochthonous and highly degraded DOM appeared more linked to a slower input from shallow soil and groundwater (Inamdar et al. 2013).

DOM–Q did not show a typical response in the ΔR versus ΔC plane . Their variability, with the exception of BIX variability, did not exhibit any seasonal pattern. Strohmeier et al. (2013) reported a clear counterclockwise response of DOC concentration in a forested catchment, with larger hysteresis in summer and fall. Our study covered 2.5 years, probably a temporal interval too short to discern consistent seasonal patterns. Storm events that occurred during the most short and abrupt periods (drying and rewetting periods) represent a relatively small fraction of the total sampled events (9% and 15%, respectively). Therefore, to have a more consistent opportunity to discern seasonality of DOM–Q loops, it is essential to incorporate more cases of these critical periods. This implicates to generate longer hydro-biogeochemical time series.

Drivers of ΔC and ΔR variability

Storm magnitude (ΔQ) emerged as an essential driver for ΔC variability. This is an expected result because the strong link between DOM and discharge is well known in headwater streams (Nguyen et al. 2013). However, ΔQ, with the exception of FI, did not emerge as a significant driver of DOM–Q hysteresis shape and rotational patterns (ΔR).

More interestingly, several pre-event drivers significantly influenced both the magnitude of DOM responses and the timing of the flushing/dilution responses. Thus, Δt_0 significantly explained the variability of ΔC and ΔR in many models. This result showed that the impact of a drought period on DOM properties variability could extend up to the successive drying phase. Base discharge (Q_b) significantly drove the variability of some models and resulted to be the most relevant driver for $\Delta C_{SUVA(r)}$, suggesting that Q_b shaped the flushing of DOM aromatic substances, with larger SUVA changes during storms preceded by low Q_b values. The magnitude of the antecedent storm episode (ΔQ_{-1}) was selected only in few models. However, it was the stronger driver for $\Delta C_{DOC(r)}$. Consequently, DOC flushing was amplified by the magnitude of the storm (ΔQ) but, at the same time, partially neutralized by the magnitude of the antecedent storm episode (ΔQ_{-1}). This flushing "memory" was similar to that reported in a boreal catchment, where the effect of a high export during the previous summer and autumn was still detectable during the following snowmelt (Ågren et al. 2010). However, the flushing memory reported in our study acted at storm-to-storm interval rather than at seasonal interval. The inter-storm time interval (Δt_{-1}) was selected in some models for ΔC. Larger Δt_{-1} intervals should promote a larger DOM flushing. However, this potential driver never emerged as the most relevant one, indicating that Δt_{-1} played a more subtle and diffuse role. Thus, a synergistic effect on DOC flushing between Δt_{-1} and ΔQ_{-1} did not appear, but it emerged between ΔQ_{-1} and Δt_0.

Pre-event base biogeochemical conditions were frequently selected in the models, and they were the most significant drivers in several of them. Consequently, the pre-storm biogeochemical status needs to be considered when studying the variability of ΔC and ΔR descriptors during storm episodes. On the contrary, more seasonal climatic related drivers, such as temperature during storms (Tmin) and average discharge during the month prior to the storm event (Qm), were selected sporadically, suggesting that climatic seasonality appeared unimportant.

It is necessary to note that most of the models that fitted ΔR variability were weaker than those selected for ΔC. As a consequence, some care is necessary in their interpretation. The estimation of ΔR is by far much more exigent than that of the ΔC because it depends on an exhaustive biogeochemical sampling during a whole storm episode. In this study, ΔR was estimated in only 52% of the observed storm episodes. Therefore, to advance in this direction, it is essential to minimise the gaps in the biogeochemical sampling programme and to increase the sampling frequency.

In the next future, the progressive improvement of large and high frequency DOM time series would stimulate the cross comparison of DOM time series worldwide. This step will be essential to have a full perspective of DOM quantitative and qualitative flushing responses and, at the same time, to capture the most relevant drivers for DOM dynamic under different climate types, flow regimes, groundwater contributions and land cover.

Chapter 4

Response of DOM dynamics in two headwater streams with contrasting hydrological regimes.

Jorn, Jordi Guarch Ribot 2016

Introduction

Headwater streams link terrestrial and aquatic ecosystems, thereby providing energy and nutrients to the ecosystem downstream (Battin et al. 2008, Kaplan et al. 2008). The flux of DOM greatly regulates ecosystem functioning (Aitkenhead-Peterson et al. 2003). The quantity and quality of the DOM delivered from the upper part of the catchment determines its ability to support heterotrophic metabolism (Guillemette and del Giorgio 2011, Kaartokallio et al. 2016).

The DOM concentration and properties in headwater streams are strongly influenced by hydrology as a consequence of changes in catchment flow paths (Boyer et al. 1997, Inamdar et al. 2011).. Therefore, storm events can influence streamwater DOM biogeochemistry through increase in DOM concentration and by imprinting a terrestrial signature on it (Hood et al. 2006, Nguyen et al. 2013, Guarch-Ribot and Butturini 2016). In consequence, most of the annual DOM export from forested catchments occurs during storm events (Raymond and Saiers 2010, Raymond et al. 2016). Thus, quantification and characterization of DOM during such events is crucial to understand its export patterns. This is particularly important to improve biogeochemical catchment models (Lauerwald et al. 2012). The predicted increase in frequency and intensity of extreme precipitation events and drought episodes (IPCC 2013) makes it even more relevant to understand event-driven DOM dynamics.

Besides the direct impact of storms and high flows on DOM, seasonal variability of baseflow also influences DOM concentration and hence its relationship with discharge. For instance, no flow during summer droughts and high baseflow during snowmelts are key hydrological phases in intermittent Mediterranean and alpine streams, respectively. Not surprisingly, several studies emphasized the importance of these hydrological conditions on DOM quantitative and qualitative properties (Vázquez et al. 2011, Fellman et al. 2011, Pellerin et al.

2012, von Schiller et al. 2015). Therefore, the analysis of DOM–discharge responses among streams with contrasting hydrological regimes is an essential step to further improve our knowledge on DOM export dynamics.

The aim of our study was to focus on identifying the singularities and similarities of DOM–discharge relationships between an intermittent Mediterranean (Fuirosos) and a perennial Alpine stream (Oberer Seebach, OSB). Both streams had clearly differing hydrological regimes (Butturini et al. 2008, Peter et al. 2014). We analysed the variability of DOM–discharge responses based on 3–year time series. The large temporal window and the high frequency sampling allowed exploring the DOM–discharge relationships at annual scale, at seasonal scale and at the scale of individual storm events.

DOM was described in terms of its fluorescence and absorbance properties and of dissolved organic carbon (DOC) concentration. We postulated that DOM properties in the Alpine stream should be more related to gradual seasonal discharge variability than to abrupt storms. In the Mediterranean stream, pronounced oscillations in discharge (with zero-day flows) should strengthen the relationship DOM–discharge.

Methods

The Oberer Seebach stream

OSB is a perennial headwater stream that drains a pristine catchment (25 km^2) in the eastern Alps (47° 51’ N, 15° 04’ E) with an elevation of 600−1900 m above sea level. Several studies have been carried out in this long-term monitoring site (Battin 1999, Peter et al. 2014, Fasching et al. 2016). Long-term annual air temperature averages 6.7°C and annual precipitation averages 1608 mm. The forested catchment is seasonally snow-covered (December–April), which results in a marked snowmelt in spring. The study reach is located in a glacial alluvial deposit underlain by a layer of fine, ancient lake sediments and calcareous rock. Catchment vegetation is dominated by *Fagus sylvatica*, *Picea abies*, *Fraxinus excelsior*, *Acer pseudoplatanus*, *Abies alba*, *Larix decidua* and *Salix caprea*.

Monitoring programme

We performed intensive hydrochemical monitoring during three years in each catchment. Stream discharge was inferred from the water level obtained every 30 min. We divided each catchment in 4 hydrological conditions. We considered as high discharge the values higher than 90% of the days based on a flow-duration curve of average daily discharge, excluding the days of no flow in the case of Fuirosos. Low discharge was defined as the values lower than 75% of the time. Therefore, intermediate discharge was set between these thresholds. In OSB snowmelt was delimited as the period of high day–night discharge oscillations, usually during March through May. In Fuirosos, rewetting was defined as the period from the first storm event after summer drought until when the stream flow regularly achieved 5 L s^{-1}.

Autosamplers (ISCO in OSB, Sigma 900max in Fuirosos) took samples in prewashed bottles every 6 hours in OSB, and in Fuirosos every 6 hours too during storm events and weekly during baseflow. DOC concentration was estimated with a total organic carbon analyser (GE–Sievers 900 in OSB, Shimadzu in Fuirosos) coupled to an inorganic carbon removal unit. Absorbance spectra from 200 to 700 nm were measured with a UV-visible spectrophotometer (Shimadzu UV 17000) using deionised water (MilliQ) as a blank. Fluorescence spectra were measured with a fluorescence spectrophotometer (Hitachi F-7000 for OSB, Shimadzu RF-5301 PC for Fuirosos). Inner filter effects were corrected, the fluorescence intensity was normalized dividing by the area of Raman peak of deionised water and a blank of deionised water was subtracted.

Five optical indices were analysed in this study: the specific ultraviolet absorbance at 254 nm (SUVA), the spectral slopes ratio (S_R), the fluorescence index (FI), the biological index (BIX) and the humification index (HIX). Details of their calculation and interpretation can be found in General methods and in Table 3.1.

Data analysis

We performed linear regressions relating each DOM parameter to the logarithm of discharge for the two streams. We computed the regression slope (dDOM/dQ) for each hydrological condition and for each month. Previously, we normalised the values of each parameter (from 0 to 1 accounting for both streams) to be able to compare the dependence of discharge among parameters. The slopes were compared by including in the regressions the interaction of the location or hydrological condition (categorical factor) with discharge. The slopes were considered statistically different when the interaction was significant, since it meant that the effect of the continuous covariate (discharge) on DOM response depended on the level of the categorical factor (Townend 2002).

For each sampled storm event, we estimated the change of every DOM property during the rising limb of the hydrograph (ΔDOM) as the difference between the value during the storm peak and that one obtained during the pre-event base discharge conditions. We also analysed the recession limb of each storm event, which follows an exponential decay with time. Thus, we calculated the slope of the lineal regression linking the logarithm of normalised DOM properties to time (*d*DOM/*dt*). In this way we obtained an estimation of the rate of recuperation of base conditions. Moreover, we investigated whether there was a relationship between ΔDOM or *d*DOM/*dt* and the magnitude of the storm events (ΔQ), calculated as the difference between the discharge peak and the pre-event base value.

All analyses were performed with R version 3.2.1 (R Code Team 2015), using the packages "chron" (James and Hornik 2014) and "phia" (de Rosario-Martinez 2015). The significance level for the statistical tests was set at $p < 0.01$.

Results

Hydrology

Differences in the hydrological regimes were evident in the two streams during the study period (Fig. 4.1a). In OSB, discharge varied by three orders of magnitude, from 10^2 to 10^4 L s^{-1}, with highest values in April–May owing to snowmelt. The lowest values were observed in summer (typically < 600 L s^{-1}) and November–December (typically < 450 L s^{-1}). Thus, the lowest base discharge occurred during the periods of maximum and minimum air temperature, respectively. In contrast, in Fuirosos, discharge typically ranged between <10^{-1} to 10^3 L s^{-1} with two exceptional episodes larger than 10^4 L s^{-1}. Further, zero flow in Fuirosos occurred in summer and it recovered in autumn, after 77−124 days of drought. Largest base discharge values were typically observed in late winter (March). Overall, base discharge was significantly inversely related to air temperature ($r = -0.390$, $p < 0.001$)

The distributions of daily discharge values were significantly different between both streams (Fig. 4.1b), even after normalisation (that is, 0 to 1) to take into account the "shape" of these distributions (two samples Kolmogorov Smirnov test, $p < 0.001$). Mean daily discharge was higher in OSB, and the coefficient of variation suggests highest flow variability in Fuirosos (Table 4.1). High discharge was defined as > 2980 L s^{-1} in OSB and > 72 L s^{-1} in Fuirosos; intermediate discharge was defined as 315–2980 L s^{-1} in OSB and 7–72 L s^{-1} in Fuirosos ; and low discharge was defined as < 315 L s^{-1} in OSB and < 7 L s^{-1} in Fuirosos. In OSB, we identified on average 26 storm events per year with 12-d inter-event time; less such events were identified in Fuirosos, where inter-event time averaged 19 d (Table 4.1). The inter-event time in Fuirosos was more erratic ranging from less than 1 day to 124 days without rain episodes. The magnitude of the events was higher in OSB, but it was more variable in Fuirosos. Finally, storm hydrographs showed similar rising limb times. However, discharge recession limbs were typically longer in OSB than in Fuirosos.

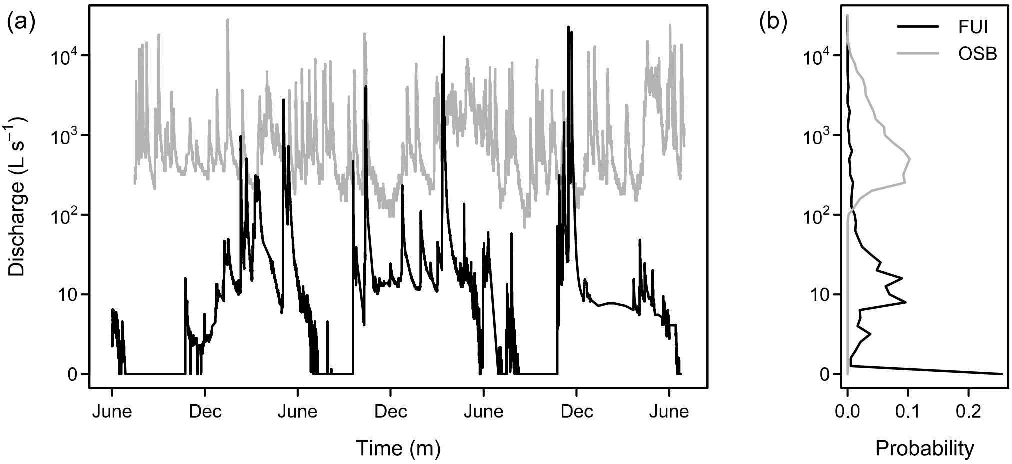


Fig. 4.1 Fuirosos (black line) and OSB (grey line) discharge during the study period (**a**) and distributions of daily discharge (**b**).

Table 4.1. Hydrological characteristics of the studied catchments. Significance of the t-test indicated for *p-values* * < 0.01, ** < 0.001, and *** < 0.0001 and not significant indicated as ns.

	Oberer Seebach	Fuirosos	
mean daily discharge ± SD (L s^{-1})	1181.4 ± 1739.5	61.6 ± 463.7	***
median daily discharge (L s^{-1})	553.3	8.2	
coefficient of variation	1.5	7.5	
baseflow < 75% time (L s^{-1})	314.8	6.6	
high flow > 90% time (L s^{-1})	2979.8	71.6	
number of storm events ($year^{-1}$)	26	21	
magnitude events ± SD (L s^{-1})	5930.1 ± 5587.8	1290.9 ± 4128.1	**
inter event time ± SD (days)	12.1 ± 9.9	18.6 ± 25.0	ns
duration rising limb ± SD (days)	0.77 ± 0.65	1.0 ± 1.2	ns
duration recession limb ± SD (days)	4.9 ± 4.1	2.9 ± 2.4	ns

DOM-Q relationship

Most of the DOM properties showed a clear relationship with discharge in Fuirosos and OSB (Fig. 4.2). Moreover, the sign of the global response was identical in both streams and statistically significant: DOC, SUVA and HIX were positively related to discharge (that is, flushing pattern), while S_R, FI and BIX were negatively related to discharge (that is, dilution pattern). However, all normalised slopes of the linear regressions relating DOM properties and discharge were statistically different between the two streams (interaction effect, $p < 0.001$).

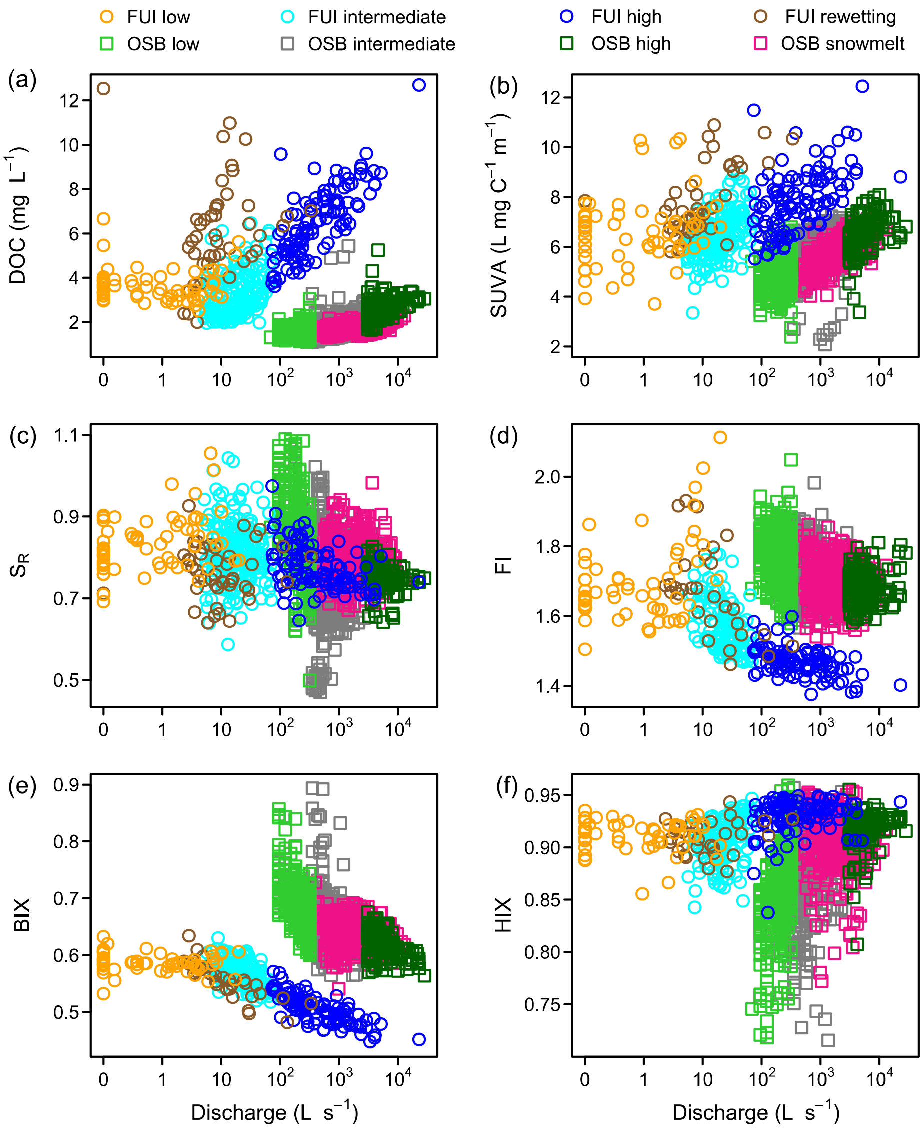


Fig. 4.2 Relationships between DOM properties and discharge in Fuirosos and OSB differentiating for hydrological conditions.

DOC was significantly higher in Fuirosos than in OSB (t-test, $p < 0.001$) and data dispersion in Fuirosos was also clearly larger than in OSB (Fig. 4.2a, 4.3). Discharge globally explained 39% and 29% of DOC variability in OSB and Fuirosos respectively, and dDOC/dQ was higher (interaction effect, $p < 0.001$)

in Fuirosos than in OSB (Table 4.2a and 4.2b). In both streams the lowest DOC values typically occurred at baseflow conditions and at lower flows DOC stabilized or increased. Focusing on the hydrological periods, the variability of DOC–Q response was smaller in OSB ($0.11 < dDOC/dQ < 0.42$) than in Fuirosos ($-0.03 < dDOC/dQ < 1.18$). The largest DOC flushing was observed during high flow in Fuirosos. In contrast, dDOC/dQ values under low flow and rewetting conditions in Fuirosos were statistically insignificant. In OSB, dDOC/dQ values under high and intermediate flow were similar to those estimated in Fuirosos during intermediate flow (interaction effect, $p > 0.05$). Finally, in OSB dDOC/dQ values during low flow and snowmelt were lower than during intermediate and high flows (interaction effect, $p < 0.01$).

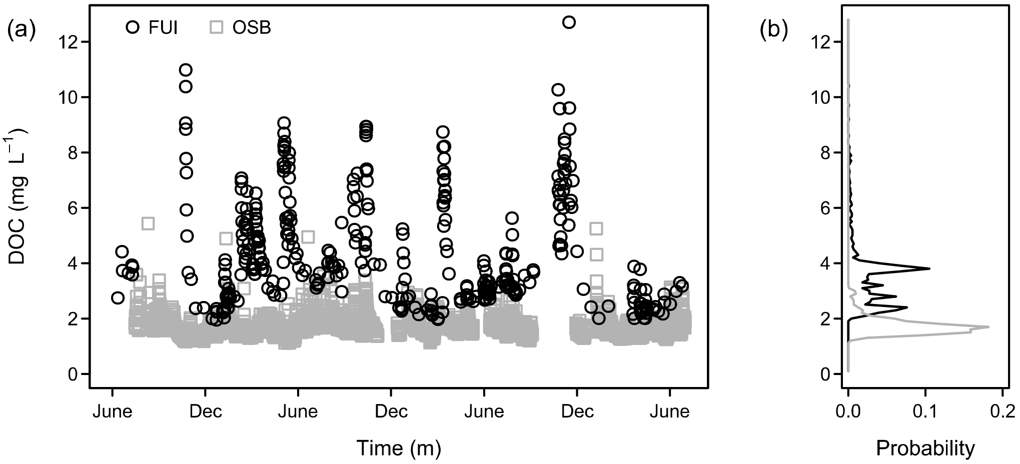


Fig. 4.3 DOC during the study period in Fuirosos (black) and OSB (grey) (**a**) and distributions of daily DOC (**b**).

SUVA was also higher (t-test, $p < 0.001$) and more dispersed in Fuirosos than in OSB (Fig. 4.2b). The variance explained by discharge was higher in OSB (45%) than in Fuirosos (21%) and the global flushing of aromatic substances (*d*SUVA/*d*Q) was larger in OSB too (interaction effect, $p < 0.001$). Analysing the distinct hydrological conditions, however, this difference occurred only under low flow in Fuirosos (interaction effect, $p < 0.002$), when SUVA was unrelated to discharge (Table 4.2a and 4.2b). In OSB there was no significant difference in *d*SUVA/*d*Q values between hydrological conditions (interaction effect, $p > 0.05$). S_R values were identical in both streams (t-test, $p = 0.05$) and discharge explained less than 12% of the variance (Fig. 4.2c).

Table 4.2a Linear regressions relating DOM parameters to the logarithm of Q for each stream and hydrological condition. Significance indicated for p-values * <0.01, ** <0.001, and *** <0.0001 and not significant indicated as ns.

parameter	system	*d*DOM/*d*Q ± SE	R^2	
DOC	**Fuirosos all**	0.50 ± 0.04	0.29	***
	F rewetting	0.10 ± 0.29	0.00	ns
	F low	−0.03 ± 0.06	0.00	ns
	F intermediate	0.51 ± 0.10	0.11	***
	F high	1.18 ± 0.09	0.62	***
	OSB all	0.24 ± 0.00	0.39	***
	OSB snowmelt	0.14 ± 0.01	0.24	***
	OSB low	0.11 ± 0.02	0.03	***
	OSB intermediate	0.37 ± 0.01	0.35	***
	OSB high	0.42 ± 0.07	0.18	***
SUVA	**Fuirosos all**	0.31 ± 0.03	0.21	***
	F rewetting	0.74 ± 0.16	0.34	***
	F low	0.19 ± 0.12	0.04	ns
	F intermediate	0.80 ± 0.10	0.24	***
	F high	0.70 ± 0.11	0.28	***
	OSB all	0.58 ± 0.01	0.45	***
	OSB snowmelt	0.66 ± 0.03	0.51	***
	OSB low	0.46 ± 0.08	0.04	***
	OSB intermediate	0.69 ± 0.04	0.21	***
	OSB high	0.78 ± 0.15	0.17	***
S_R	**Fuirosos all**	−0.14 ± 0.03	0.05	***
	F rewetting	0.09 ± 0.16	0.01	ns
	F low	0.27 ± 0.10	0.12	*
	F intermediate	−0.13 ± 0.16	0.00	ns
	F high	−0.43 ± 0.08	0.20	***
	OSB all	−0.49 ± 0.03	0.12	***
	OSB snowmelt	−0.14 ± 0.06	0.01	ns
	OSB low	−2.18 ± 0.15	0.21	***
	OSB intermediate	−0.21 ± 0.08	0.01	ns
	OSB high	−0.34 ± 0.11	0.07	*

Table 4.2b Linear regressions relating DOM parameters to the logarithm of Q for each stream and hydrological condition. Significance indicated for p-values * <0.01, ** <0.001, and *** <0.0001 and not significant indicated as ns.

parameter	system	*d*DOM/*d*Q ± SE	R^2	
FI	**Fuirosos all**	−0.54 ± 0.03	0.43	***
	F rewetting	−1.00 ± 0.28	0.32	*
	F low	0.48 ± 0.14	0.17	*
	F intermediate	−1.02 ± 0.16	0.24	***
	F high	−0.30 ± 0.05	0.27	***
	OSB all	−0.37 ± 0.02	0.15	***
	OSB snowmelt	−0.13 ± 0.05	0.01	ns
	OSB low	−0.93 ± 0.11	0.08	***
	OSB intermediate	−0.42 ± 0.05	0.06	***
	OSB high	0.12 ± 0.13	0.01	ns
BIX	**Fuirosos all**	−0.37 ± 0.02	0.66	***
	F rewetting	−0.62 ± 0.09	0.67	***
	F low	−0.03 ± 0.04	0.01	ns
	F intermediate	−0.59 ± 0.08	0.30	***
	F high	−0.49 ± 0.04	0.62	***
	OSB all	−0.59 ± 0.01	0.40	***
	OSB snowmelt	−0.28 ± 0.04	0.10	***
	OSB low	−1.43 ± 0.09	0.24	***
	OSB intermediate	−0.53 ± 0.04	0.11	***
	OSB high	−0.63 ± 0.09	0.24	***
HIX	**Fuirosos all**	0.19 ± 0.02	0.16	***
	F rewetting	0.16 ± 0.13	0.06	ns
	F low	−0.02 ± 0.06	0.00	ns
	F intermediate	0.71 ± 0.15	0.14	***
	F high	0.16 ± 0.07	0.05	ns
	OSB all	0.79 ± 0.03	0.26	***
	OSB snowmelt	−0.16 ± 0.08	0.01	ns
	OSB low	2.6 ± 0.16	0.25	***
	OSB intermedite	0.82 ± 0.08	0.09	***
	OSB high	0.43 ± 0.14	0.06	*

The most negative dS_R/dQ values occurred in OSB under low flow (Table 4.2a and 4.2b), showing significant differences with all other hydrological conditions (interaction effect, $p < 0.001$). In contrast, during low flow in Fuirosos an increase of S_R with discharge was detected.

FI was significantly higher (t-test, $p < 0.001$) in OSB than in Fuirosos (Fig. 4.2d). The variance explained by discharge was much higher in Fuirosos (43%) than in OSB (15%). Furthermore, *d*FI/*d*Q in Fuirosos ranged widely between −1 (rewetting and intermediate flow) and 0.48 (low flow). In OSB, *d*FI/*d*Q values were statistically significant during low an intermediate flow, but not during snowmelt and high flow (Table 4.2a and 4.2b).

BIX was also higher (t-test, $p < 0.001$) in OSB than in Fuirosos (Fig. 4.2e). Discharge explained up to 66% and 40% of its variance in Fuirosos and OSB respectively. In Fuirosos dBIX/dQ values were similar among hydrological conditions (Table 4.2a and 4.2b). However, during low flow BIX was unrelated to discharge (interaction effect, $p < 0.001$). Similarly, in OSB low flow showed a significantly distinct slope (interaction effect, $p < 0.001$), but in that case the slope was more negative and had a closer relationship with discharge. High and intermediate flow in both streams had similar slopes (interaction effect, $p > 0.05$).

HIX showed higher values in Fuirosos (t-test, $p < 0.001$), while its variability was higher in OSB (Fig. 4.2f). Discharge appeared more relevant in OSB (26% of explained variance) than in Fuirosos (16% of explained variance) and the global dHIX/dQ value was also higher in OSB (interaction effect, $p < 0.001$). In Fuirosos, HIX was related to discharge only under intermediate flow (Table 4.2a and 4.2b). In OSB, HIX was extremely sensitive to discharge during low flow conditions. Conversely, during snowmelt dHIX/dQ was not significant.

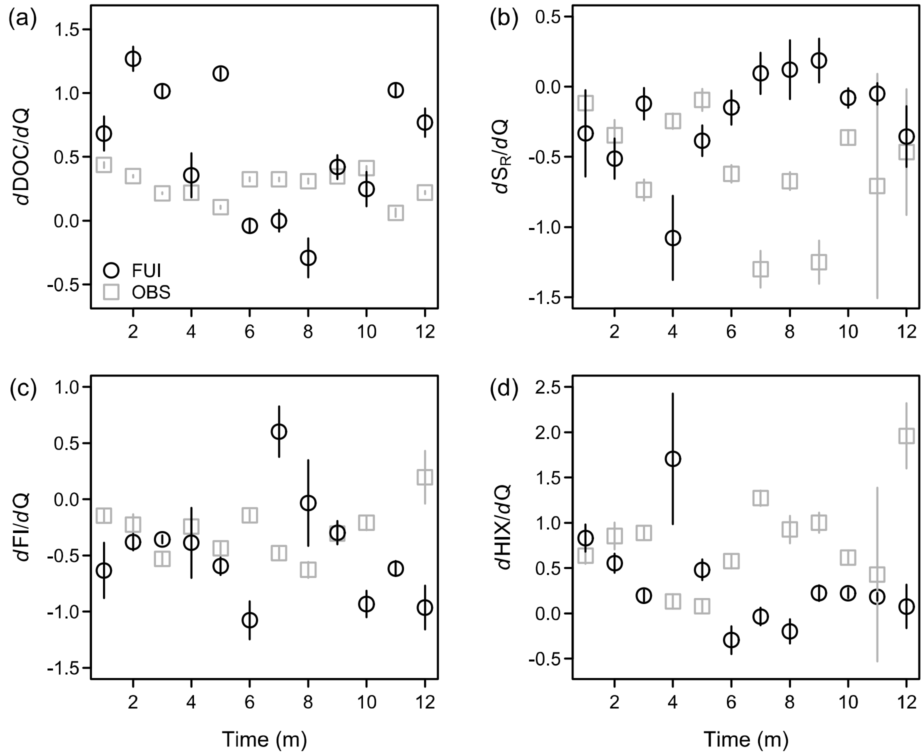


Fig. 4.4 Slopes of the linear regressions relating DOC (**a**), S_R (**b**), FI (**c**) and HIX (**d**) to the logarithm of Q for each month in Fuirosos (black) and OSB (grey). Error bars indicate ± 1 standard error of the slopes.

Some *d*DOM/*d*Q values showed a seasonal trend when samples were grouped at monthly intervals. However, the patterns differed among both streams. For instance, *d*DOC/*d*Q in Fuirosos decreased during summer months, while in OSB a seasonal dynamic did not emerged (Fig. 4.4a). dS_R/dQ values showed an opposite pattern in the two streams. Thus, in summer dS_R/dQ values were close to zero (positive) in Fuirosos and the lowest (negative) in OSB (Fig. 4.4b). A similar trend was observed in *d*BIX/*d*Q values. *d*FI/*d*Q was nearly steady in OSB with values close to zero during winter. Conversely, drought in Fuirosos caused a clear discontinuity in summer, with a gradual shift toward negative values from January to June and an abrupt positive *d*FI/*d*Q value in July (Fig. 4.4c). Finally, *d*HIX/*d*Q values were nearly steady throughout the year in

Fuirosos, with a peak in April (Fig. 4.4d). In contrast, in OSB slopes were lowest during snowmelt (April–May).

Storm events

DOM changes (ΔDOM) during the rising limb for each single sampled storm were related to the magnitude of the storm (Fig. 4.5). ΔQ significantly drove ΔDOC ($R^2 = 0.49$, $p < 0.001$), ΔFI ($R^2 = 0.23$, $p < 0.01$), ΔBIX ($R^2 = 0.46$, $p < 0.001$) and, partially, ΔSUVA ($R^2 = 0.16$, $p < 0.05$) in Fuirosos. This finding reinforces the notion that the flushing/dilution patterns observed in the scatter plots for DOC, FI, BIX and SUVA (Fig. 4.2) were essentially associated to the occurrence of storm episodes in Fuirosos.

In contrast, and unexpectedly, in OSB ΔQ significantly explained only ΔDOC ($R^2 = 0.58$, $p < 0.001$). All DOM qualitative properties were unrelated to ΔQ ($R^2 < 0.1$; $p > 0.05$). Storms in OSB were behind the DOC oscillations, but did not explain the magnitude of oscillations of DOM quality. This was especially surprising for SUVA, BIX and HIX, which were related to discharge ($R^2 > 0.25$, Fig. 4.2). Therefore, the observed pattern of ΔDOM versus ΔQ suggests that, in OSB, seasonal changes of base discharges were equally or more important for DOM qualitative changes than storms. Thus, when storm events were removed from the data set, the relationship between discharge and qualitative parameters kept their significance in OSB ($p < 0.001$). In contrast, in Fuirosos *d*SUVA/*d*Q, dS_R/dQ and *d*HIX/*d*Q were not significant when the storm event samples were removed ($p > 0.1$) and slopes remained significant for DOC, BIX and FI ($p < 0.001$). Moreover, *d*DOC/*d*Q followed a dilution pattern thus reversing its sign.

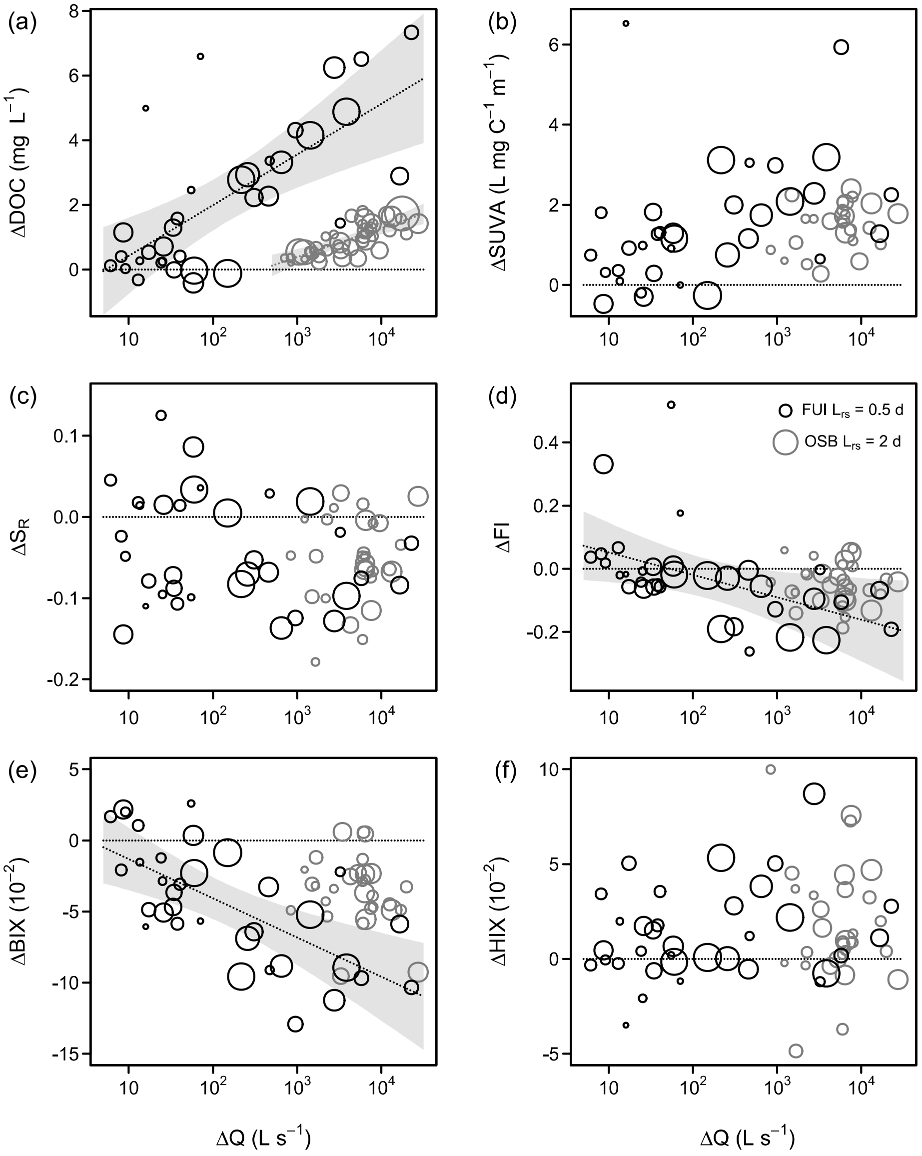


Fig. 4.5 Relationships between DOM changes during the rising limb of each storm event —ΔDOC (**a**), ΔSUVA (**b**), ΔS_R (**c**), ΔFI (**d**), ΔBIX (**e**) and ΔHIX (**f**)— and its magnitude in Fuirosos (black) and OSB (grey). The area of the circles is proportional to the length of the rising limb (L_{rs}). Dashed lines show the significant slopes and the grey areas represent the 0.99 confidence interval of those linear regressions.

The flashness of the storms, estimated by the duration of the rising limb, did not appear as a relevant driver for ΔDOM values. However, some abrupt and small storm event during rewetting in Fuirosos caused extreme ΔDOC, ΔSUVA and ΔFI values. These outliers were especially relevant for the ΔDOC *versus* ΔQ relationship, which was, as mentioned before, statistically significant (ΔDOM/ΔQ=1.57). Fig. 4.5a visualises two outliers located outside the 95% of prediction range. These two events coincided with two rewetting periods after prolonged droughts. Removing the two outliers, the ΔDOC *versus* ΔQ relationship improved ($R^2 = 0.70$, $p < 0.001$) and the slope (ΔDOM/ΔQ = 1.74) was larger than that estimated for OSB (ΔDOM/ΔQ = 0.89; interaction effect, $p < 0.02$). Therefore, although in both streams the ΔDOC *versus* ΔQ relationship fit significantly a linear model, DOC sensitivity to storms was larger in Fuirosos than in OSB.

During the recession limb of the storm events, DOM properties tended to recover the values measured during the pre-storm baseflow. Therefore, the sign of the slope of the regression relating DOM properties to time was opposite to that of the change in the rising limb: negative slope in the case of DOC, SUVA and HIX, and positive in S_R, FI and BIX. DOC concentration typically recovered faster than the other DOM parameters in both streams (Fig. 4.6). The most inertial parameter was HIX, with slope values around 0. The slopes of DOM properties were not significantly related to the magnitude of the storm event. The exception was observed in OSB, where larger storm events prompted faster DOC recovery to its pre-storm concentration ($p < 0.05$).

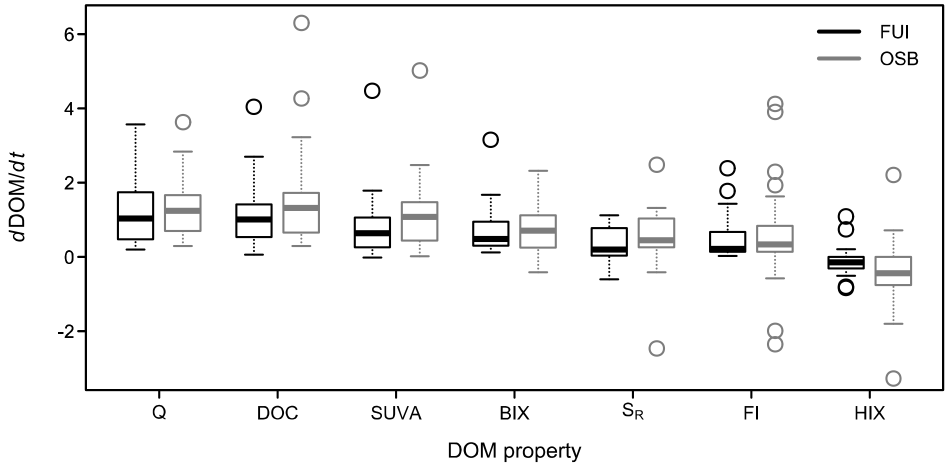


Fig. 4.6 Boxplots of the slopes of the recession limbs of storm events in Fuirosos (black) and OSB (grey). The slopes come from the linear regressions relating the logarithm of normalised DOM properties to time. *d*Q/*dt*, *d*DOC/*dt* and *d*SUVA/*dt*, which had originally mainly negative slopes, were multiplied by −1 to allow for the comparison of values.

Discussion

Numerous studies have shown the influence of variation in discharge on DOM quantity and quality in headwater forested streams (Buffam et al. 2001, Inamdar et al. 2011, Wilson et al. 2016). Fewer studies have highlighted how the hydrological regime over longer time may shape the response of DOM to discharge. Our study reveals that hydrology can modulate DOC concentration and DOM composition because of abrupt shifts from low to high flow and by modulating the intensity and timing of base discharge.

DOM-discharge response variability

DOC concentrations in the Mediterranean Fuirosos stream were significantly higher than in the Alpine OSB stream. Both streams drain forested catchments of comparable size, and the mass of DOM entering the streams was therefore expected to be similar. However, climate caused higher discharge in OSB than in Fuirosos and the hillside groundwater reservoir in OSB might contribute to dilute DOC concentration (Battin 1999). DOM also differed between both streams. DOM in Fuirosos was more terrigenous (lower FI), more degraded (lower BIX), more aromatic (higher SUVA) and more strongly humified (higher HIX) than in OSB.

Generally, our analyses also revealed that DOM variability in OSB was to a larger extent controlled by discharge than in Fuirosos. For instance, low flow, including zero-flow, and rewetting in Fuirosos induced large scattering in these plots at the low discharge interval and debilitated the explanatory power of discharge. This result suggests that in Fuirosos a) factors other than discharge affect DOM variability and/or b) DOM sensitivity to discharge greatly varied across hydrological conditions. The high DOM variability across values of low discharge is a relevant property of intermittent and ephemeral streams, and of small tropical streams (Bass et al. 2011). However, it is missing in permanent Mediterranean (Butturini et al. 2005), continental (Wilson et al. 2013) and alpine (Fasching et al. 2016) headwater streams.

Drying and rewetting in Fuirosos did not alter DOM characteristics in the same direction. During drying, for most of DOM parameters the relationship with discharge disappeared or even reversed. Remarkably, under low flow conditions in OSB, the inverse pattern emerged with DOM optical properties being significantly related to discharge. Summer drying in Fuirosos is a seasonal and well predictable period that reflects the vanishing of the stream-catchment connectivity with water constrained in few isolated, small and disconnected pools (Vázquez et al. 2011). Typically, this period lasts over one to three months and can be easily monitored, which facilitates the study of biogeochemistry and hydrology in these ecosystems (Vázquez et al. 2007, Fellman et al. 2011, von Schiller et al. 2015). In line with our findings, most of these studies evidenced the enhancement of in-stream DOM production that may explain the rupture of DOM–discharge relationship.

In contrast, DOM responses during rewetting were usually in the same direction to that observed under intermediate and high flows. However, these responses were highly variable and strongly depended on the exact timing and magnitude of the first flushing episode after the drought period. The clearest example was that of DOC concentration. During two rewetting episodes, the first flushing determined a disproportionate ΔDOC. Thereafter, ΔDOC strongly decreased during the immediate subsequent storms. Hydro-biogeochemical modelling adapted to intermittent streams (Butturini et al. 2005), demonstrated that the instantaneous and abrupt DOC peak concentration can be attributed to the leaching of abundant particulate organic matter accumulated during the drought in the stream channel or its adjacent riparian strip (typically larger than 0.45 kg dry mass m^{-2} in Fuirosos according to Sabater et al. 2001). This result shows the importance of rewetting for triggering a biogeochemical change in intermittent streams. In contrast to what occurred with the drying period, it is key to remark that a biogeochemical characterization of the rewetting period is challenging because of its unpredictable nature and short duration. Therefore, a full picture of DOM response during rewetting is largely missing. Inexorably, high-resolution biogeochemical sampling using automated sensor networks are required to fill this gap (Kirchner et al. 2004).

Snowmelt usually initiates DOC flushing in alpine streams (Hornberger et al. 1994, Boyer et al. 1997, Burns et al. 2016). However, we could not observe this typical response in OSB and it fitted better the pattern reported by Pellerin et al. (2012). Thus snowmelt did not add a clear noise to the DOM–discharge scatter plot and did not enhance the input of a different DOM quality with respect to high flows in summer, fall or winter. On the contrary, during snowmelt the sensitivity to discharge decreased for DOC concentration and BIX, for instance, or disappeared for S_R, FI and HIX. This finding is similar to that reported by Burns et al. (2016) for FI, HIX and BIX and by Pellerin et al. (2012) for SUVA. It suggests a partial biogeochemical disconnection between stream flow and hillsides during this period, suggesting that water from snowmelt flows rapidly downslopes with small interaction with soil.

Similarities and differences between Mediterranean and Alpine streams

When rewetting restarted and normal flow conditions resumed, DOM–discharge relationships in Fuirosos become stronger and converged to those observed in OSB and other catchments (Spencer et al. 2010, Wilson et al. 2016). These similarities in DOM–discharge plots suggest that analogous large-catchment-scale hydrological-hillsides processes modulate DOM flushing independently of the hydrological regime. Thus, under normal hydrological conditions, DOM transport from hillsides to stream channel is not limited. However, these similarities were apparent. The analysis of DOM–discharge relationships at storm-event scale showed a subtle but relevant divergence among the two streams: abrupt floods impacted severely DOM in Fuirosos, whereas base flow oscillations were more significant in OSB. These results are in line with our initial hypothesis that the larger hydrological oscillations in Fuirosos magnify DOM changes and make more likely to fix the strength of the DOM–discharge relationships.

Moreover, an unexpected and important dichotomy emerged in OSB. While DOM quality change was more coupled to base flow conditions, DOC flushing was significantly related to storm magnitude. This linear relationship illustrates an important similarity between the two streams. However, DOC responses were significantly less sensitive to storm magnitude in OSB than Fuirosos. This result points out that the hillside-stream connection is stronger in Fuirosos than in OSB and that DOM quantity and quality in Fuirosos is strictly bound to allochthonous terrigenous inputs. In-stream processes are unimportant for most of the time, except during the low flow period. The observed dichotomy between DOC and DOM quality in OSB evidenced that terrestrial DOM deliveries during storms are a fundamental source to the DOM pool but that in-stream processes gain relevance under base flow. Previous studies point out that benthic primary producers and hyporheic heterotrophic community imprint more autochthons DOM properties under base flow in OSB (Fasching et al. 2016). Such in-stream processes at base flow amplify the qualitative differences on DOM between the two streams, attenuating the DOM terrigenous signature in OSB by reducing its aromaticity and humification degree concomitantly increasing the signature from fresh autochthonous DOM (Fasching et al. 2014).

The present study is a first attempt to compare pluri-annual time series of DOM concentration and DOM characteristics with an appropriate sampling design to capture hydrological extremes. It highlights the importance of comparative studies among ecosystems with contrasting climate and hydrological regimes to advance our understanding of DOM biogeochemistry in headwater streams.


Ribot

General discussion

Paisatge des de la Teuleria, Josep Ribot i Calpe 1943

This thesis explores the influence of hydrology on DOM quantity and quality in an intermittent headwater stream. Its hydrological regime is described in Chapter 1. Analysis of long-term DOC dynamics appears in Chapter 2; while Chapter 3 describes a further step detailing the relationships between DOM quality and hydro-biogeochemical drivers. Finally, the DOM–discharge relationships detected in the Mediterranean stream are compared with those in an Alpine stream (Chapter 4). In the present section results from this thesis are discussed in a wider hydro-biogeochemical context.

Discharge patterns

The long-term hydrological monitoring revealed a decreasing trend of daily discharge in the Mediterranean stream that is subject of this thesis (Chapter 1). Lower flows might have some ecological impacts: reduction of the density and diversity of biota; mediation of the diversity and distribution of biota by species-specific patterns in water quality tolerances; and decreases in the rate of energy transport within food webs, resulting in limited ecosystem production (Rolls et al. 2012).

The annual reduction of 0.6% in daily discharge is similar to reports of other rivers of the Iberian Peninsula (Table D.1). Those studies based their conclusions on long-term hydrological series from gauging stations managed by water authorities. Obviously, the monitoring stations are located in rivers that drain large catchments (typically more than 100 km^2) with heterogeneous land uses and significant human pressure. In most of the studies the observed hydrological alteration was attributed to an increment of evapotranspiration due to higher temperatures or an increase of forest cover as a consequence of the abandonment of agriculture (García-Ruiz and Lana-Renault 2011). Some other studies also detected climatic divers such as a decrease of precipitation or shorter snowmelt.

Table D.1 Hydrological time series in the Iberian Peninsula.

Study area	Monitoring period	Catchment area (km2)	Annual decrease (%)	Explanation	Reference
Ter (Roda de Ter)	1950–1996	1386	0.25	Forest cover increase	Gallart et al. 2011
Cardener (Olius)	1954–1996	256	0.82		
Llobregat (La Baells)	1976–1999	504	1.1		
187 large sub-basins	1945–2000	Large basins	Not quantified	Water management strategies (dams)	Lorenzo-Lacruz et al. 2012
Duero (56 gauging stations)	1961–2006	35–45	Not quantified	Decrease in winter precipitation and reduction of snowmelt	Morán-Tejeda et al. 2011
287 gauging stations	1961–2009	Large basins	Not quantified	Higher evapotranspiration and decrease in precipitation	Vicente-Serrano et al. 2014
Duero (17 sub-basins)	1966–2005	14–2384	1.11	Forest cover increase and higher temperature	Martínez-Fernández et al. 2013
Tajo (4 sub-basins)			1.49		
Júcar (5 sub-basins)			1.68		
Ebro (35 sub-basins)			1.41		
Noguera Pallaresa (Ebro sub-basin)	1965–2009	2807	0.5–1.3	Higher temperature and potential evapotranspiration and forest cover increase	Buendia et al. 2016
Turia (Júcar sub-basin)	1973–2008	3936	Not quantified	Higher temperature (forest cover decrease)	Salmoral et al. 2015

Meanwhile, water management as a cause or driver is mentioned only timidly in one study. This is rather surprising because the monitored periods covered a time lapse characterised by a dramatic increment in the population of Spain (from 26 million in 1940 to 47 million in 2010) that prompted an increase in water demand for irrigation, industry and domestic uses (Wada et al. 2013). Thus, all large Iberian rivers suffered severe hydrological alterations due to the building of dams and water abstraction. For example, in Spain, the total annual gross surface and groundwater abstraction increased from 25×10^{12} m^3 in 1970 to 45×10^{12} m^3 in 2000 (http://appsso.eurostat.ec.europa.eu).

In any case, the combination of a growing population, increased water abstraction, land use changes and the intrinsic large inter-annual climate variability in Mediterranean areas, make it extremely difficult to identify hydrological trends that can be attributed to climate change. In this complex framework, divergences in the interpretation of data are of no surprise (Table D.1). For instance, in the Duero catchment some authors attributed the decadal discharge decrease to climate (Morán-Tejeda et al. 2011) while others also pointed to land use changes (Martínez-Fernández et al. 2013). In this framework, it is evident that long-term and high frequency hydrological monitoring in small semi-natural headwater catchments may be the solution to explore the link between hydrology and climate without the interference of additional overlapping factors. Unfortunately, there is not tradition of establishing large hydrological monitoring programmes in small Mediterranean headwater stream. Pioneering exceptions are those of Vallcebre, a Mediterranean mountain catchment monitored since 1991 (Gallart et al. 2005, Latron et al. 2010) and the Torrent de la Mina stream in Montseny, studied since 1977 (Hereter and Sanchez 1999). Headwaters streams are not of interested to water management, and even less so intermittent ones, and water authorities do not establish long-term monitoring programmes. Thus, if monitoring of some has been established, it started much later.

The duration of the summer dry period in Fuirosos did not show a significant trend during the study period (Chapter 1). However, the frequency and severity of climatic droughts are increasing in the Mediterranean basin (Vicente-Serrano et al. 2014, Spinoni et al. 2015) and hydrological droughts in non-perennial streams are expected to be prolonged (Pumo et al. 2016). Therefore, it is probable that drought duration will increase in the near future. A longer dry period would cause changes in the quality of the DOC in remaining pools (Vázquez et al. 2011); decrease the release of inorganic N during rewetting (Gómez et al. 2012); increase vertical riparian inputs (Sanpera-Calbet et al. 2016); decrease leaf litter breakdown (Datry et al. 2011); and decrease the abundance and richness of some taxa of macroinvertebrates as well as those of seedbank (Storey 2016, Stubbington et al. 2016).

The frequency of storm events decreased in Fuirosos and revealed an intriguing link with the 11–year solar activity cycle. Especially if the number of the most severe storm events is reduced, this might imply lower sediment transport, a decrease of nutrient export from the hillsides, a decrease in woody debris input and a reduction of floodplain inundation (Poff et al. 1997).

DOC patterns

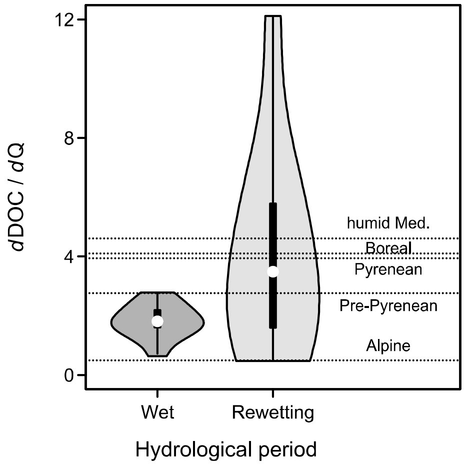
The analysis of the temporal pattern of DOC concentration in Fuirosos showed a slight decreasing trend over the study period (Chapter 2). This trend is opposite to the increase detected in boreal regions (Filella and Rodríguez-Murillo 2014), which has been attributed to climate change, specifically to the increase of air temperature and atmospheric CO_2 pressure, and to the diminution of atmospheric chemical deposition (Evans et al. 2006, Pagano et al. 2014). Therefore, these factors cannot explain the DOC decline in Fuirosos. However, this might be related to the observed decreasing discharge trend (Chapter 1): a flow decrease could imply a reduction of terrigenous DOC inputs and thus lower in-stream DOC concentrations. Notably, nitrate showed a subtle long-term increase. In forested catchments, NO_3^- availability is typically related to catchment hillside inputs. Consequently, the long-term NO_3^- dynamics does not support the hypothesis of a reduction of allochthonous DOC input. However, an increase of atmospheric NO_3^- deposition has been reported in the study area over the last years (Izquierdo et al. 2012). Therefore, the observed NO_3^- increase in Fuirosos might be related to atmospheric deposition and not to the hillside stream hydrological connection. Consequently, the possibility of a causal relationship between lower DOC and lower flows cannot be excluded.

The DOC concentration showed notable seasonality in Fuirosos (Chapter 2, 3 and 4). The highest values were observed during rewetting, due to the leaching of leaf litter that had accumulated on the streambed during the summer drought. Moreover, the slopes of the relationship with discharge (*d*DOC/*d*Q) were also the highest in this period. Meanwhile, the drying period saw a disconnection of DOC concentration from discharge.

During wet periods, *d*DOC/*d*Q averaged 1.8 ± 0.6 mg s L^{-2} (range: 0.6 − 2.8 mg s L^{-2}). These values are in the lower range of the flushing values reported in other pristine/semi-pristine streams (Fig. D.1). All the streams included in the Figure D.1 drain relatively small catchments (< 16 km^2) and are permanent, except Fuirosos. Under normal hydrological conditions such as the wet period, DOC flushing in Fuirosos was typically half as high as that estimated in boreal, Pyrenean and humid Mediterranean streams and it was between that from Alpine and pre-Pyrenean streams. In contrast, during rewetting the picture changed totally and the DOC flushing rate increased up to 12 mg s L^{-2}. This range of oscillation of *d*DOC/*d*Q is much higher than that reported in the literature. Unfortunately, Figure D.1 includes a reduced set of streams evidencing the lack of information. The study of DOC in freshwater ecosystems has greatly expanded during the last two decades. Nevertheless, few studies analyse time series and only a small subset of these studies focus on DOC–

discharge relationships. Being conscious of this gap, the present research reports one of the highest DOC flushing systems studied to date and it emphasises that little is still known about the DOC–discharge relationship in headwaters around the world.

Fig. D.1 *d*DOC/*d*Q of different headwater streams. The violin plot shows the distribution of the values for Fuirosos; the white dot marks the median and the black rectangle the interquartile range. Dashed lines show *d*DOC/*d*Q of Riera Major in orange (Butturini et al. 2006), Västrabäcken in black (Ågren et al. 2010), Contraix in pink (unpublished data from Lluís Camarero), Can Vila in green (Roig-Planasdemunt et al. 2017) and Oberer Seebach in blue (Fasching et al. 2016). All models were converted to linear-log models.



DOM quality patterns

Beside DOC concentration, DOM quality has also been studied in many fluvial systems and the influence of hydrology on DOM properties has been reported in depth in several studies (Table D.2). Storms are the hydrological episodes that have been analysed most worldwide. High flows imply rises in aromaticity, the degree of humification, molecular weight and the allochthonous character in Fuirosos (Chapter 3) and also in an Alpine stream (Chapter 4). In most of climates, storm events increase the terrigenous character of DOM. This is the case in temperate, Mediterranean and subtropical catchments.

Table D.2. Patterns of DOM quality under hydrological episodes worldwide

Catchment	Hydrological episode	Aromaticity	Humification	Molecular weight	Humic/Proteic components	Allochthonous Source	Potential bioavailability	References
Temperate	Storm	↑	↑	↑	↑	↑≈	↑	(Buffam et al. 2001, Li et al. 2005, Hood et al. 2006, Vidon et al. 2008, Nguyen et al. 2010, 2013, Inamdar et al. 2011, Wilson et al. 2016)
Mediterranean	Storm	↑	↑	↑	NA	↑	NA	(Saraceno et al. 2009, Guarch-Ribot and Butturini 2016)
Subtropical	Storm	↑	NA	↑	↑	↑	NA	(Johnson et al. 2011, Yang et al. 2013)
Wetland/ Peatland	Storm	↓	NA	↓	↓	NA	↑	(Fellman et al. 2009, Austnes et al. 2010)
Mediterranean, subtropical, tropical, boreal	Drying	↓	≈	↓	↓	↓	↑	(Wu et al. 2007, Spencer et al. 2010, Vázquez et al. 2011, 2015, Hong et al. 2012, von Schiller et al. 2015)
Mediterranean, tropical	Rewetting	↑	↑	↑	↑	↑	↑	(Vázquez et al. 2007, 2015, Spencer et al. 2010, von Schiller et al. 2015)
Boreal	Snowmelt	↑	NA	↑	NA	↑	NA	(Walker et al. 2013, Voss et al. 2015)
Temperate	Snowmelt	↓	↑	NA	↑↓	⇅	NA	(Pellerin et al. 2012, Perdrial et al. 2014, Burns et al. 2016)

The relationship between DOM quality and storms has especially been reported for forested headwater forested streams, but the same pattern was also found in large rivers and agricultural areas (Vidon et al. 2008, Nguyen et al. 2010, Yang et al. 2013). The exceptions were wetlands (Fellman et al. 2009) and peatlands (Austnes et al. 2010), where high flows reduce DOM aromaticity and molecular weight while increasing protein-like fluorescence. During storm events, runoff follows surface flowpaths, flushing DOM with a highly allochthonous character (Inamdar et al. 2013, Yang et al. 2015). Nevertheless, in peatlands, stream DOM is highly degraded when the water table is low (Fraser et al. 2001) and thus more aromatic than the allochthonous input, which in fact dilutes its humic character.

The DOM response to flow recession is similar in different biogeographical regions and opposite to that during most storm events. DOM aromaticity and molecular weight decrease, while the protein fraction and its autochthonous character increase. All this agrees with the increase of in-stream production enhanced by the higher water residence time (Battin et al. 2008). Rewetting implies a sudden input of allochthonous DOM that has accumulated during the drought on the streambed and further on surrounding hillsides. Therefore, the pattern is reversed and the DOM character becomes terrigenous again. It should be highlighted that all these hydrological episodes —storm events, the drying period and rewetting— have been reported to increase the bioavailability of DOM (Romaní et al. 2006, Vázquez et al. 2011, Wilson et al. 2016).

A more ambiguous case is that of snowmelt. It seems that this has a distinct impact on DOM depending on the location. In boreal catchments the spring freshet implies an increase of DOM aromaticity, molecular weight and allochthonous sources. Those fresh inputs are microbially processed later, so under base flow conditions the DOM terrigenous character decreases. In mountain watersheds in temperate regions, the DOM response is more diverse. DOM aromaticity is lower during snowmelt, which has been related to microbial processing under the snow-pack (Brooks et al. 2011). At the same time, humification increases and the protein-like fraction and allochthonous character show different patterns. Therefore, a local characterisation of the DOM response to snowmelt is crucial. These controversial results point to the need to remember that not all the DOM pool is fluorescent (Fellman et al. 2010). Thus, it is important to consider analysis that is not based only on fluorescence properties.

Drivers of DOM

In this thesis, I have revealed the role of hydrological and biogeochemical antecedent conditions as drivers of DOM. In contrast with other studies, climatic parameters such as temperature did not have a significant influence. Previous drought duration in Fuirosos increased the rate at which DOC decreased from the rewetting to the beginning of the wet period (Chapter 2). However, the flushing/dilution patterns (ΔC) during storm events had some memory effects as well (Chapter 3). The DOM biogeochemical status during the pre-event base flow influences the change in humification, molecular weight and freshness; the magnitude of the antecedent storm event was inversely related to ΔDOC; and a high base discharge before the storm event prevented a major increase in aromaticity.

In other catchments, the antecedent conditions were also found to be important for DOM dynamics. In the short term, the discharge of the previous 3 days regulated stream DOC concentration during storm events in small forested catchments. In the longer term, DOC was influenced by discharge conditions over the previous 5 months in boreal streams. Furthermore, the inter-annual variability of DOC concentration during snowmelt was related to the duration of the preceding winter and to the export of DOC during summer and autumn. The depth of the water table during the 30 days prior to the storm event also modulated DOC concentration in peatlands. In an intermittent stream, mean annual DOC was linked to the length and severity of the drought. All these studies focused on DOC concentration. Conversely, my study expanded on this knowledge since for the first time, qualitative DOM properties were connected to the antecedent hydro-climatic descriptors.

These findings outline the importance of the memory effect on DOM. Therefore, under the threat of a change in frequency and magnitude of storm and drought episodes in Mediterranean catchments (Vicente-Serrano et al. 2014, Barrera-Escoda and Llasat 2015), it will be necessary to generate larger pluri-annual high-frequency DOM time series to determine the possibility of an impact of an accumulative effect of concatenation of severe drought episodes on long-term DOM flux and fate.

Comparison of a Mediterranean and an Alpine stream

The biogeochemical analysis of two hydrologically different headwater streams that experience relatively reduced human activity (Chapter 4) motivates me to speculate on the impact of hydrological regime alteration forced by atmospheric drivers (Botter et al. 2013, Hall et al. 2014) on DOM quantity and properties.

Fuirosos and Oberer Seebach are located in geographical areas that are experiencing severe changes in their hydrological cycles (Chapter 1, Martínez-Fernández et al. 2013, Bocchiola 2014). The trend in the flood frequency in north-east Iberian Peninsula is unclear and largely debated (Mediero et al. 2014, Barrera-Escoda and Llasat 2015). However, little uncertainty exists about the evidence that drought severity is increasing in response to lower annual precipitations and higher evaporative demand (Vicente-Serrano et al. 2014, Spinoni et al. 2015). Thus, a scenario in which drying phases start prematurely and last longer is plausible with a hydrological shift from an intermittent regime to an ephemeral one. Therefore, the relevance of the drying and rewetting phases should increase, and the importance of base flow conditions should decrease.

Similarly, severe changes in the fluvial hydrological regime are expected in Alpine areas as a consequence of a warmer climate. The frequency of floods and severity of drought are expected to increase and snow cover is expected to decrease (Gobiet et al. 2014). Furthermore, evapotranspiration driven by temperature should increase (Bocchiola 2014). All together, these alterations are expected to provoke a notable decrease of discharge in spring and summer.

These hydrological scenarios might be combined with results from my study to produce two biogeochemical scenarios that describe how DOM concentration and quality are expected to shift under: 1) a rise of ephemerality in Mediterranean streams: and 2) a rise of intermittency in Alpine headwaters (Fig. D.2).

Under the perspective of more frequent droughts in Mediterranean areas, the highest DOC concentrations should coincide during storm episodes and the drying phase. Nevertheless, the DOM signal should clearly differ between the two hydrological extremes: an allochthonous character during floods and of autochthonous origin during drying (Fig. D.2.l). In the context of the DOM–discharge relationship, the scattering of data should greatly increase (Fig. D.2.i) as a consequence of: a) higher variability in the ΔDOM responses related to more frequent rewetting episodes; and b) DOM changes modulated by in-stream processes and unrelated to discharge during longer drying periods.

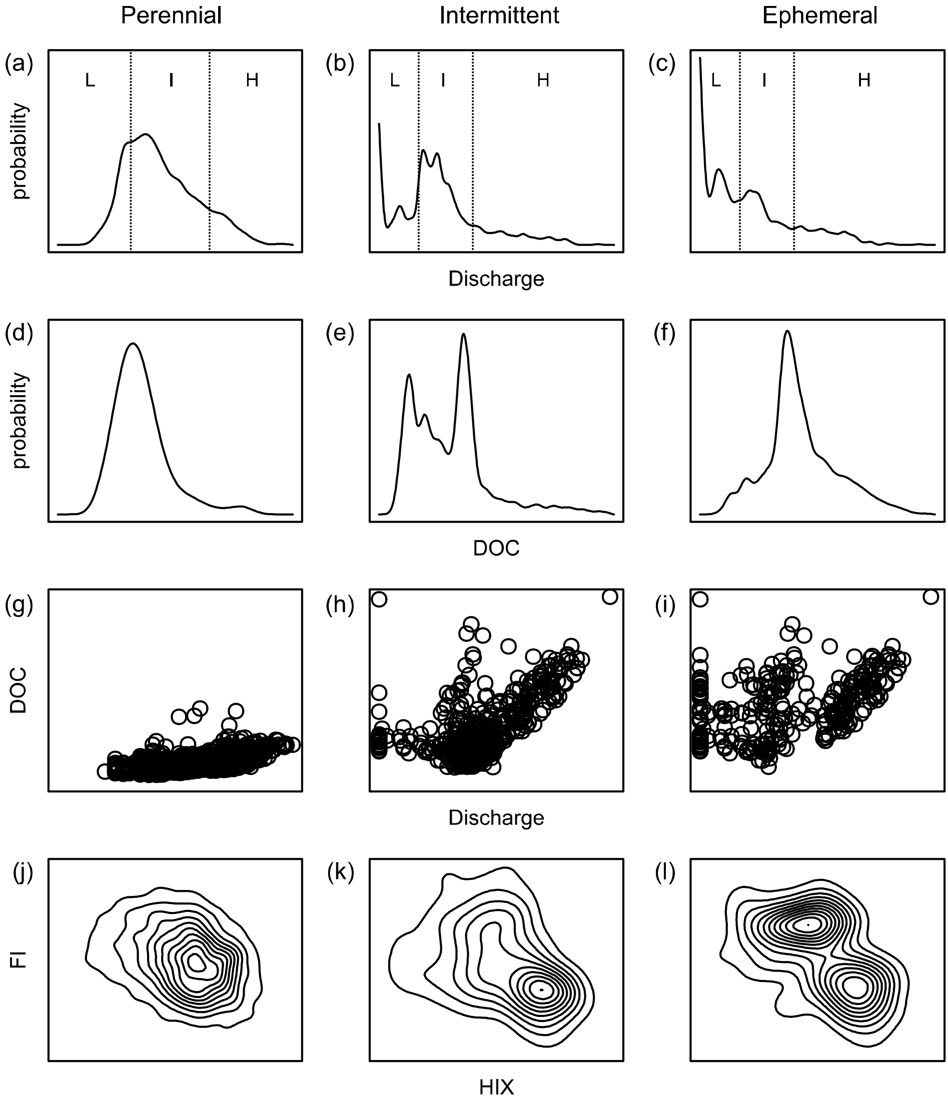


Fig. D.2 Probability distribution of daily mean discharge (**a**–**c**), probability distribution of daily mean DOC (**d**–**f**), DOC–discharge scatter plot (**g**–**i**) and HIX–FI Kernel density plot (**j**–**l**) for a perennial stream (**a**, **d**, **g**, **j**), an intermittent stream (**b**, **e**, **h**, **k**) and an ephemeral stream (**c**, **f**, **i**, **l**). Low flow, intermediate flow and high flow conditions are marked in **a**–**c**. The figures for the perennial and intermittent streams were obtained with Oberer Seebach and Fuirosos data, respectively. The figures for the ephemeral stream are hypothetical, considering larger periods of low flow than currently in Fuirosos.

Meanwhile, the hydrological adjustment in Alpine areas might involve modifications in the hillside flowpaths and flushing of terrigenous DOM. Assuming, for sake of simplicity, no changes in the terrestrial environment, apparently less relevant snowmelt and more frequent storms should strengthen the DOM–discharge relationship. So, the ΔDOM/ΔQ ratio should increase during moderate–high flows and approach similar values to those observed in Fuirosos. At the same time, more severe droughts together with higher summer temperatures might reinforce the in-stream metabolism and the related autochthonous DOM production. Therefore, the significant link between DOM parameters and discharge detected at low flow at Oberer Seebach could vanish in the near future.

It is interesting to consider that, in Oberer Seebach and Fuirosos, the lowest DOC concentrations did not coincided with the lowest discharge values (Fig. 4.2a). In both streams, the DOC tended to be higher at the lowest discharge values. DOC increase is outstanding in Fuirosos and much more subtle in Oberer Seebach. Is this similitude between the two streams in their DOC patterns at low discharges a clue that DOC concentration could increase more markedly at low flow in Oberer Seebach under a scenario of more severe summer droughts? Then, does the DOC–discharge scatter plot reported for Fuirosos (Fig. D.2.h) shed light on the DOC–discharge plot expected for Oberer Seebach under a warmer climate scenario?

In this thesis I examine the relationship between DOM and hydrology in a Mediterranean stream. The thesis is structured along three main axes: an undisturbed headwater stream, hydrological intermittency, and long-term and high-frequency biogeochemical monitoring. To further advance in these fields it is necessary: i) to promote comparison of DOM responses between sites across the world and between the largest possible spectrum of hydrological regimes; and ii) to establish long-term and high-frequency sampling hydro-biogeochemical programmes that take advantage of expanding use of in-situ

DOM optical sensors (Lee et al. 2015). In Fuirosos, we are working in this direction (Fig. D.3), with preliminary results showing detailed patterns of the DOM response to hydrological episodes.

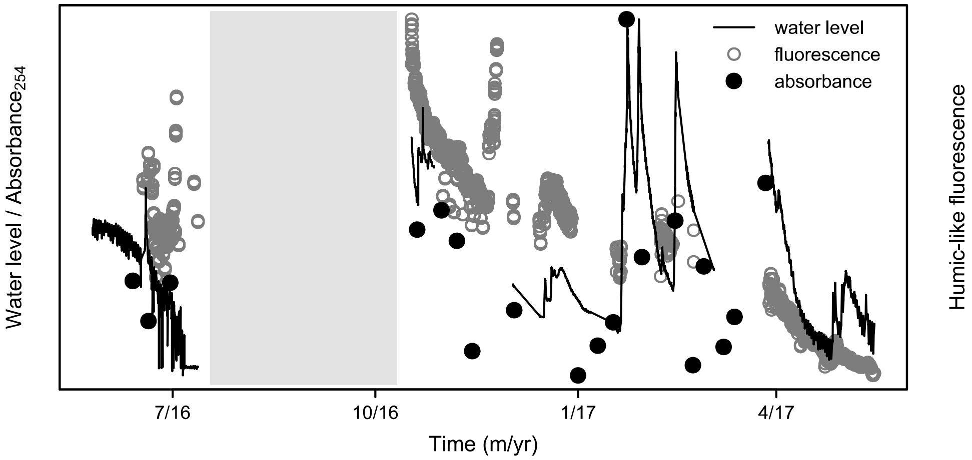
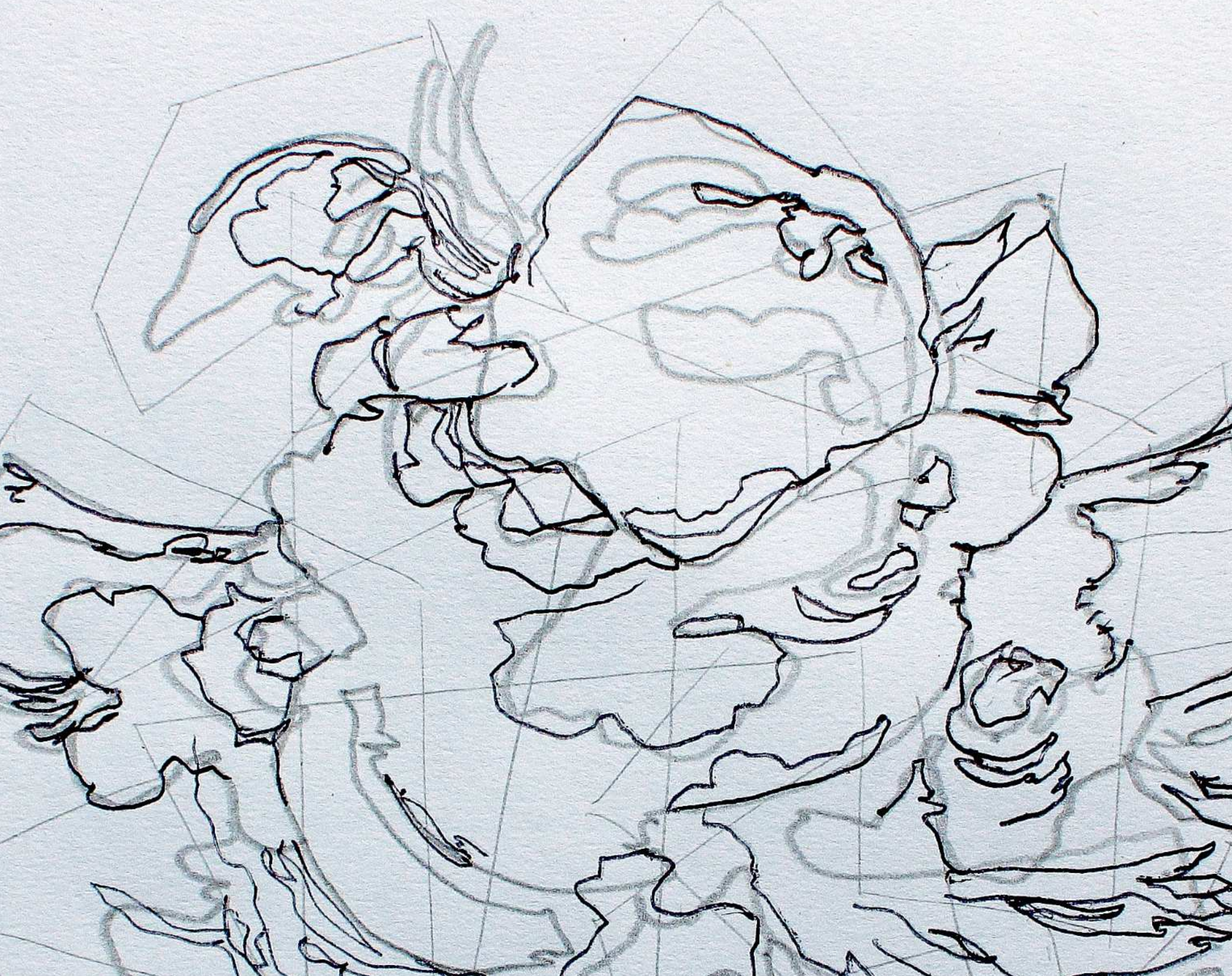


Fig. D.3 Preliminary results from the submergible humic-like fluorescence sensor Cyclop 7 Turner (grey dots) installed in the Fuirosos stream, together with discharge (black lines) and absorbance at 254 nm measured in the laboratory from manually obtained water samples (black dots). The grey area indicates the dry period (Butturini, unpublished data).



Conclusions

Composició 8, Jordi Guarch Ribot 2015

Chapter 1: Hydrology of an intermittent headwater stream: results of a decade of high-frequency monitoring

- Long-term monitoring in the Fuirosos stream revealed a decrease in discharge from 1998 to 2015, although the trends in temperature and precipitation were not significant. A decadal discharge decrease has been detected in many Mediterranean rivers, especially in response to increasing temperatures. Despite the high inter-annual variability, the mode of discharge has clearly decreased in Fuirosos.
- Dry period duration was highly variable and it did not show a significant trend during the study period.. However, rewetting has been significantly delayed, moving from September to October. The mean magnitude of autumnal storm events was lower in the years with El Niño phases.
- The frequency of storm events decreased during the study period, showing a significant positive relationship with solar activity with a 2–year lag.

Chapter 2: Long-term temporal dynamics of dissolved organic carbon concentration in the Fuirosos stream

- The DOC concentration experienced a slight decrease over the interval 1998–2013 in Fuirosos. This decrease is the opposite to that expected, in accordance with the observed long-term decrease of discharge and to that observed in boreal systems.
- This reduction cannot be predicted by the reported long-term decrease of acid precipitation. In fact, the decrease of acid deposition should drive an increase of DOC rather than a decrease. The causes of this decrease are, to date, unclear. However, this pattern might respond to a reduction of terrigenous DOC input from forest hillside as a response to a reduction of flushing episodes.

- DOC concentration and dynamics in Fuirosos is strongly related to discharge and to the length of dry episodes. Firstly, drought duration regulates DOC temporal dynamics (expressed as $d\mathrm{DOC}/dt$) during rewetting and the beginning of wet periods (October–December). Secondly, discharge oscillations explain up to 50% of total DOC variability during the wet period. Noticeably, the weight of discharge increased significantly over the years.
- Finally, very few small streams are the subject of long-term and high-frequency biogeochemical monitoring. Therefore, little is known about the DOC–discharge response in small streams. However, the DOC flushing rate (expressed as $d\mathrm{DOC}/d\mathrm{Q}$) in Fuirosos is one of the highest recorded in small semi-pristine streams worldwide.

Chapter 3: Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis.

- Most DOM properties were strongly related to discharge, revealing the input of allochthonous, degraded, aromatic, humic and large-molecular DOM under high flow conditions. However, these relationships disappeared or were reversed during drying and had extreme values in rewetting periods.
- At the storm event scale, DOM–Q hysteresis was highly heterogeneous, especially in their rotational pattern, but storm magnitude appeared to be an important driver for ΔC, coupled to antecedent hydrological and biogeochemical conditions.
- For a short time, DOC flushing was partially inhibited by the magnitude of the previous storm episode, and aromatic DOM flushing was more marked under low pre-event base flow conditions.

- With regards to a longer time interval, the time elapsed since the previous summer drought modulated the origin of the DOM flushed during storms, from an accentuated allochthonous source during rewetting to slightly more autochthonous sources during the successive drying.
- DOM–Q responses during storm events did not show a clear seasonal pattern. Longer and higher-frequency temporal monitoring is needed to capture sufficient events from each hydrological period.

Chapter 4: Response of DOM dynamics in two headwater streams with contrasting hydrological regimes

- The DOM in the intermittent Mediterranean stream studied here (Fuirosos) was significantly more concentrated than in the perennial Alpine stream (Oberer Seebach), and also more terrigenous (lower FI), more degraded (lower BIX), more aromatic (higher SUVA) and more humified (higher HIX).
- Most of the DOM properties showed a clear relationship with discharge and the sign of the global response was identical in both streams. However, discharge was a more robust predictor of DOM variability in Oberer Seebach than in Fuirosos. In fact, low flow and rewetting periods in Fuirosos introduced considerable dispersion into the relationship. During snowmelt in Oberer Seebach, the sensitivity to discharge also decreased or disappeared.
- The magnitude of the storm events (ΔQ) in Fuirosos significantly drove the changes in DOC, FI, BIX and SUVA. This suggests that DOM patterns were essentially associated with the occurrence of storm episodes in Fuirosos. In contrast, in Oberer Seebach, all the qualitative DOM properties were unrelated to ΔQ which only significantly explained the change in DOC. While storms were

behind the DOC oscillations, DOM quality change in Oberer Seebach was more closely coupled to base flow conditions.

- Finally, the biogeochemical analysis of two hydrologically different headwater streams motivated me to speculate concerning the impact of hydrological regime alteration forced by atmospheric drivers on DOM quantity and properties. A higher frequency of floods would reinforce the link between DOM quality and discharge in the Alpine stream. In contrast, DOM in the Mediterranean stream would have a bimodal flood–drought character, due to the diminution of base conditions.

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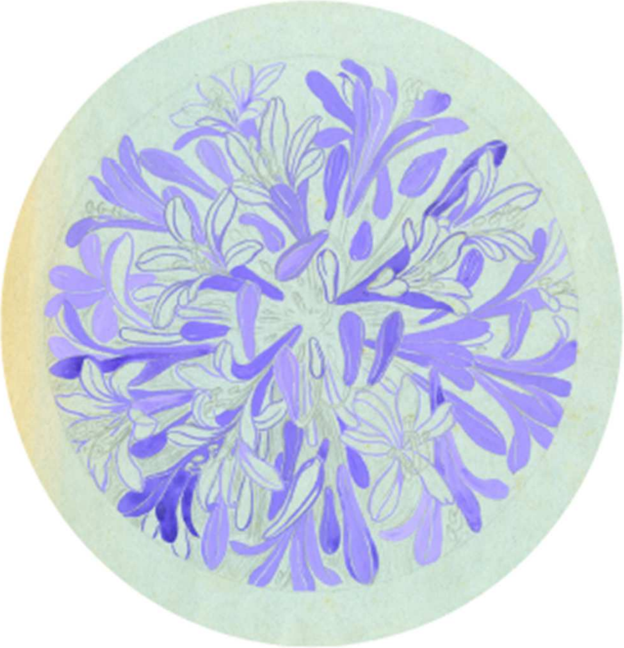

Dissolved organic matter (DOM) is an important source of carbon for aquatic microorganisms and it regulates many biogeochemical processes. This thesis focuses on the temporal dynamics of DOM quantity and quality in Fuirosos, an intermittent Mediterranean headwater stream. Temporal DOM variability has been related to stream hydrology. The link between DOM and discharge is assessed, with special emphasis placed on the annual, seasonal and storm event temporal scales. Environmental drivers that modulate the DOM–discharge relationship are studied in depth and results are compared with a similar data set from an Alpine stream. This study attests to the importance of generating and analysing long-term and high-frequency biogeochemical series, which allow relationships between DOM and hydrology to be explored in streams that are subjected to extreme hydrological regimes.