Antecedent conditions control carbon loss and downstream water quality from shallow, damaged peatlands

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Highlights:

- Event-based analysis of DOC, colour and E4/E6 in damaged shallow peatlands in SW UK
- Long-term dryness plays a critical role in controlling water quality
- DOC controlled by water table depth, discharge and temperature
- Predominance of humic acids in DOC, but relative temporal increase of fulvic acids

Keywords: DOC, drainage, water quality, colour, Exmoor, E4/E6, drought

Abstract

Losses of dissolved organic carbon (DOC) from drained peatlands are of concern, due to the effects this has on the delivery of ecosystem services, and especially on the long-term store of carbon and the provision of drinking water. Most studies have looked at the effect of drainage in deep peat; comparatively, little is known about the behaviour of shallow, climatically marginal peatlands. This study examines water quality (DOC, Abs^{400}, pH, E4/E6 and C/C) during rainfall events from such environments in the south west UK, in order to both quantify DOC losses, and understand their potential for restoration. Water samples were taken over a 19 month period from a range of drains within two different experimental catchments in Exmoor National Park; data were analysed on an event basis. DOC concentrations ranging between 4 and 21 mg L^{-1} are substantially lower than measurements in deep peat, but still remain problematic for the water treatment process. Dryness plays a critical role in controlling DOC concentrations and water quality, as observed through both spatial and seasonal differences. Long-term changes in depth to water table (30 days before the event) are likely to impact on DOC production, whereas discharge becomes the main control over DOC transport at the time scale of the rainfall/runoff event. The role of temperature during events is attributed to an increase in the solubility of DOC. Humification ratios (E4/E6) consistently below 5 indicate a predominance of complex humic acids, but increased decomposition during warmer summer months leads to a comparatively higher losses of fulvic acids. This work represents a significant contribution to the scientific understanding of the behaviour and functioning of shallow damaged peatlands in climatically marginal locations. The findings also provide a sound baseline knowledge, which can support research into the effects of landscape restoration in the future.

1. Introduction

Peatlands and carbon-rich soils have been shown to be an important contributor of Dissolved Organic Carbon (DOC) in watercourses (e.g. Aitkenhead et al., 1999; Hope et al., 2004). Over the past three decades, large scale increases in DOC loss from peaty catchments has been observed in northern Europe (e.g. Evans et al., 2005; Freeman et al., 2001a; Hejzlar et al., 2003; Skjelkvåle *et al.*, 2001) and North America (Driscoll *et al.*, 2003). This general trend suggests a systematic response to a combination of external drivers acting over large areas (Evans et al., 2005), such as a general increase in atmospheric CO_2 (Freeman *et al.*, 2004), a decrease in acidic deposition (Clark *et al.*, 2005; Evans et al., 2005), or the influence of climate change (Freeman et al., 2001a). However, fine-scale or local factors (i.e. land use) can have an additional effect on the general trend, and therefore may help to enhance or mitigate DOC export in the short-term (Worrall et al., 2007b). In the UK, DOC losses from peaty catchments have come under particular scrutiny in recent years, partly because of the heavy damage peatlands have sustained since the nineteenth century due to drainage for agricultural reclamation and peat cutting (Holden et al., 2006), or from erosion (Evans et al., 2006). By lowering the water table, management practices have changed the hydrological functioning of peatlands, further affecting the provision of several ecosystem services (ES), such as the support of specific habitats, the provision of water or the storage of carbon (C) (Hubacek et al., 2009). DOC is of particular interest, firstly because it represents an important pathway for C losses to the ocean from what is usually considered to be a long-term terrestrial C sink; in-stream processes leading to evasion of CO_2, however, mean that DOC will also have an impact on the radiative balance (Dinsmore et al., 2010). Secondly, DOC has been shown to have a strong effect on water quality and pollutant transport downstream (Thurman, 1985).

Water companies supplying drinking water from rivers or reservoirs that are fed by damaged upland catchments have to deal with the costly and complicated process of removing C from increasingly discoloured water supplies (Wallage et al., 2006), whilst ensuring that they meet environmental standards and regulations (e.g. EU Water Framework Directive 2000/60/EC). They also need to pre-empt the expected effects of upstream changes in land use, catchment characteristics and climate on both DOC concentrations and water quality, all of which are known to impact the treatability of water and the formation of carcinogen disinfection by-products (Ritson et al., 2014; Watts et al., 2001). As a result, water utilities in the UK (e.g. Severn Trent, United Utilities or South West Water) have been investing in long-term catchment management through the funding of peatland restoration projects, in order to avoid more costly, and relatively short-term, solutions downstream (Parry et al., 2014).

DOC losses from degraded peatlands have been widely investigated in order to estimate C budgets at the catchment scale (e.g. Dinsmore et al., 2010; Gibson et al., 2009; Worrall et al., 2009) or for modelling C losses at larger scales (e.g. Worrall et al., 2005). However, the processes controlling DOC losses in degraded peatlands, over both short- and long-terms, are still debated. A great body of work points towards the importance of dryness on DOC production in soils. DOC losses are significantly higher in drained, and therefore dry, peatlands compared to pristine sites (e.g. Glatzel et al. 2006; Holden et al., 2004; Holden, 2005a,b; Jones & Mulholland, 1998; Wallage et al., 2006; Worrall et al., 2006a; Worrall et al.,2007a,b). Water table drawdown and the consequent increased aeration of the peat soil, has been observed to stimulate soil respiration (Bubier et al., 2003).

Humification products are then released to pore water (Glatzel et al. 2006; Strack et al. 2008), or adsorbed and released during the subsequent rainfall event (Clark et al. 2009; Mitchell and McDonald 1992; Scott et al. 1998; Tipping et al. 1999; Watts et al. 2001). Air or stream temperature also seems to be a key factor in stimulating the biological productivity (Billett et al., 2006; Dinsmore et al., 2013), and in regulating the seasonal variations in DOC concentrations (Bonnett et al., 2006; Koehler et al., 2009), but also in controlling general long-term trends (Freeman et al., 2001a; Evans et al., 2005). In other cases, however, DOC concentrations have decreased in drought conditions (e.g. Clark et al. 2005; Fenner et al. 2005; Pastor et al. 2003; Scott et al. 1998). This has been explained by a higher consumption of DOC through heterotrophic respiration compared to production (Fenner et al., 2005, Pastor et al., 2003).

Other research points towards a control of DOC mobility by soil acidity that prevails over biotic factors, where drought induced acidity could inhibit DOC mobility, either through a sulphate increase affecting the ionic strength (Clark et al., 2005), or more generally, through a change in the acid neutralising capacity (Clark et al., 2012). Discharge was mostly shown not to have a significant control on DOC in peaty catchments (Billett et al., 2006; Hinton et al., 1997; Schiff et al., 1998), although fewer studies, have observed some influence of discharge part of the year, i.e. in the autumn (Clark et al., 2007; Koehler et al., 2009). Moreover, little is known about the importance of the condition of the peat, its depth, or the surrounding vegetation patterns (Lindsay, 2010) on DOC losses. Most research has focused on drainage occurring in deep peat in northern England (e.g. Armstrong et al., 2010; Clark et al., 2007; Turner et al., 2013), and the restoration of these peatlands appears to reduce DOC losses, at least in the long-term (Wallage et al., 2006), if not more rapidly (e.g. Wilson et al., 2011a).

The processes outlined above highlight several points: (1) management practices, such as drainage or burning, can affect DOC production at the catchment scale (Clutterbuck and Yallop, 2010; Yallop and Clutterbuck, 2009; Yallop et al., 2010); (2) external forcing mechanisms (i.e. acid deposition or temperature) might reverse or increase this trend, and; (3) both the decomposition process and movement of water through the peat are likely to control the export of previously produced DOC. The first aim of this study was therefore to understand both the quantity and quality of DOC losses from two heavily damaged and shallow peatlands in the south west of England using an event-based approach over a two year period, prior to restoration. A secondary aim was to go beyond the exclusive quantification of DOC losses and explore the influence of environmental factors controlling DOC loss, alongside other water quality parameters. This research was critical in order to establish a baseline understanding of the way in which such marginal peatlands function, and to support their proposed restoration. Our working hypotheses were as follows:

1. The heavily damaged upland peatlands of Exmoor National Park support poor water quality, which varies significantly between experimental catchments.
2. First order variables, including rainfall, air temperature and discharge, exert a strong control on DOC concentrations, which results in significant seasonal variability.
3. During rainfall events, DOC concentrations in catchment runoff are controlled by antecedent conditions (i.e. air temperature, total rainfall, depth to water table and total discharge) in the short-term, i.e. that of the duration of the rainfall/runoff event.

4. Quality of DOC, represented by the E4/E6 ratio, is directly related to DOC concentrations in runoff water, with higher DOC concentrations in the drains being characterised by a greater loss of fulvic acids (FAs).

2. Material and methods

2.1. Study sites

The study was conducted in two headwater catchments of the river Barle within Exmoor National Park, UK (51°9'N; 3°34'W), referred to here as 'Aclands' and 'Spooners' (1). These catchments are 4 km apart and are taken to be representative of the general peatland conditions found in the area. The altitude of the two catchments range between 380 to 450 m a.s.l., with an 30 year average daily temperature of 10-12°C and 4.5-5.5°C for summer and winter respectively, and an average annual precipitation between 1800 and 2600 mm yr^{-1} (Met Office, 2012). Peat depths on Exmoor are shallow, on average ca. 33 cm (Bowes, 2006), but surveys in these catchments have shown that peat depths frequently range between 50 cm and 1 m (Smith, 2010). The vegetation comprises numerous mire and wet heath communities, such as *Sphagnum* spp. and *Eriophorum* spp., but *Molinia caerulea* (Purple Moor Grass) is by far the most extensive (Drewit and Manley, 1997). The area is characterised by very little bare peat, but has been heavily damaged by intensive drainage for agricultural reclamation during the 19th and 20th century. This has left a very dense network of small ditches (about 0.5m wide by 0.5m deep) located approximately every 20 m, in a herringbone pattern (Figure 1). Peat cutting by hand has also been practiced on Exmoor since medieval times, and features indicate that large amounts of peat have been removed for domestic use (Riley, 2014).

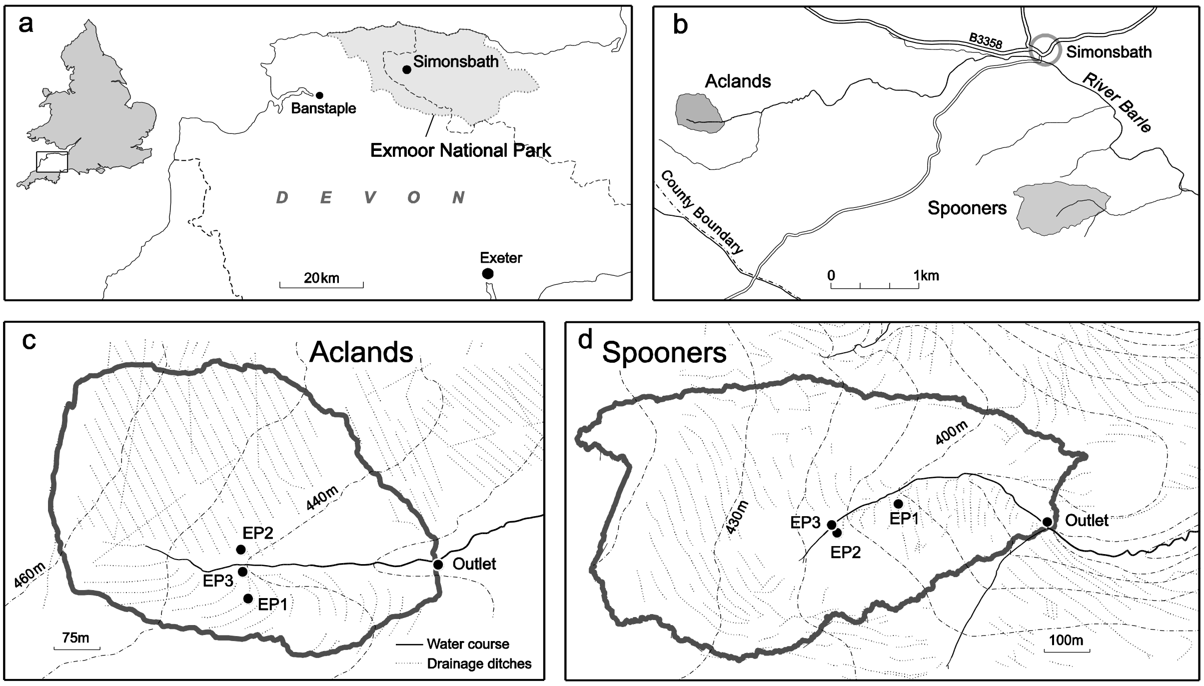

Figure 1. Map showing the location of the two catchments studied (a and b), and sampling locations with details of the drainage network for Aclands (c) and Spooners (d), covering an area of 19.5 ha and 46.5 ha respectively.

A monitoring experiment was set up to study three drainage ditches in each catchment, representative of a small, medium and large ditch (and referred to herein as Experimental Pools

(EP)), as well as the outlet of each catchment (Flume), giving a total number of sampling points of eight. The characteristics of each monitoring location are presented in Table 1. Data collection for water quality parameters started in October 2011 and is ongoing; results are however reported up to the period of restoration (April 2013).

Table 1. Details of each location monitored as part of this study, with ditch depth and width measured at the sampling location, and peat depth averaged along the entire ditch.

Site	EP	Drain class	Peat depth (m)	Ditch depth (m)	Ditch width (m)	Contributing area (m^2)
Aclands	1	Small	0.36	0.14	0.40	1,430
	2	Medium	0.35	0.34	1.30	11,220
	3	Large	0.33	0.55	1.80	53,160
	Flume	Outlet	0.40	1.30	2	195,030
Spooners	1	Small	0.50	0.31	0.30	1,770
	2	Medium	1	0.49	1	500
	3	Large	0.70	0.86	0.50	5,340
	Flume	Outlet	0.70	0.90	1	464,830

2.2. Water quality analysis

Storm-based, flow-integrated, water sampling was carried out across all sites using automatic pump samplers (Teledyne ISCO, USA) linked to pressure transducers located in the channel (Impress Sensors and Systems Ltd, UK), and a telemetry system (Adcon telemetry GmbH, Germany). Each pump sampler allowed the collection of up to 24 samples on a flow proportional basis. Samples were then collected as soon as practical, and subsequently stored at <4 °C in the dark prior to analysis within one week.

For DOC and colour analyses, samples were filtered using syringe filters housing Whatman WCN 0.45 µm filter papers (Wallage and Holden, 2010) and transferred to 30 ml screw cap amber glass bottles. All equipment was acid washed in 10% HCl solution. Additionally, glass bottles were heated in the furnace at 450 °C for 4 h. Each analytical batch contained two blanks and one set of triplicates in order to check for potential contamination and check instrument variability.

DOC analyses were undertaken using UV spectrometry for chemical free substance analysis (TriOS ProPS analyser, TriOS GmbH, Germany), as this enabled rapid and cost effective analysis of a large number of samples (Glendell and Brazier, 2014; Sandford et al., 2010). The sensor was fitted with a deuterium lamp and measured absorption spectra in the range 190-360 nm. The path lengths used varied between 10 to 50 mm, depending on the colour of the samples. The spectra are used to distinguish various chemical species and their concentration in the natural sample, and further converted to DOC concentrations (mg L^{-1}) using a multivariate software algorithm based on principal component analysis.

Colour was measured by UV-Vis spectrometry (Unicam UV4-100 analyser, Thermo-Fisher scientific, UK) set at 254, 400, 465 and 665 nm, using a 40 mm cell. In order to take into account the variability in cell path lengths between spectrophotometric instruments and studies, the absorbance readings (au) were converted to standardised absorbance units per m (au m^{-1}) by multiplying the liquid cell width by the appropriate factor (Mitchell and McDonald, 1992).

For each sample, the colour per C unit (C/C ratio) was calculated by dividing the absorbance values at 400 nm (Abs^{400}) by the corresponding DOC concentrations (Wallage et al., 2006); the E4/E6 ratio was determined by dividing the absorbance at 465 nm (Abs^{465}) by that at 665 nm (Abs^{665}) for the individual samples (Thurman, 1985). pH was measured in the remaining unfiltered solution using an Accumet AB15/15+ pH meter calibrated (Fisher Scientific, UK) with buffer solutions at pH 4 and 7.

DOC composition is known to have an impact on spectral absorption properties (Dilling and Kaiser, 2002), and the correlation between colour and chemical methods for measuring DOC has been shown to vary between sites and seasons (Wallage and Holden, 2010). Therefore, a selected number of samples from each rainfall/runoff event were sent to the South West Water (SWW) analytical facilities, where samples were analysed for DOC by thermal oxidation (Hach Lange TOC Analyser, USA) and colour (Segmented Flow Analysis, Skalar, The Netherlands). Spearman's Rank (r_s) was used to investigate correlations between techniques. Coefficient correlations between DOC measured by spectrometry and thermal oxidation were 0.89 (P < 0.01, n = 149) and 0.83 (P < 0.01, n = 182) for Aclands and Spooners respectively; correlations between colour measurements (SWW and in-house UV-Vis spectrometry) varied between 0.98 (P < 0.01, n =149) for Aclands, and 0.99 (P < 0.01, n = 140) for Spooners, whilst coefficient correlations between in house absorbance and DOC concentrations (thermal oxidation method) ranged between 0.95 (Aclands, P < 0.01 and n = 863) and 0.98 (Spooners, P < 0.01, n = 780). A significant overestimation of DOC measured by spectroscopy over chemical method was observed (Wilcoxon test, P < 0.01, n = 376). To address this issue, spectroscopic concentrations were recalculated using linear calibration curves between the two methods established for each rain event. For some events, this calibration was not considered adequate (i.e. when r_s < 0.85); colour results, and the correlation between absorbance and DOC concentrations, were used instead. The linear correlation between recalculated DOC concentrations and results from thermal oxidation (SWW) showed an overall value of r_s = 0.94 and 0.98 for Aclands (P < 0.01, n = 149) and Spooners (P < 0.01, n = 182) respectively.

2.3. Other data collected

Details on the water quantity monitoring set up, rating curves and discharge calculations are found in Luscombe et al. (forthcoming, b). Briefly, flow in the channel was measured in each drain using an *in-situ* pressure transducer placed in a polypropylene stilling well. On each of the small, medium and large drains, depth to water table and overland flow along and also perpendicular to the drain were measured using a high density of 16 instrumented dip wells. All equipment was linked to an ADCON telemetry system, and data recorded on a 15 minute time step. The outlet of each catchment was instrumented by a trapezoidal and h-flume for Aclands and Spooners respectively, and equipped with an ISCO 2150 area-velocity meter (Teledyne ISCO, USA) to measure flow. Each catchment was equipped with a NOMAD Portable Weather station (Casella, USA), recording temperature and rainfall data at 15 minute intervals. Rainfall data were collected using a 0.2 mm tipping-bucket rain gauge in each catchment.

2.4. Data analysis

A wide range of rainfall/runoff events of magnitudes were sampled across all drains at both sites. To account for this temporal variability, data were summarized and analysed on an event basis. Event based data analysis has been widely undertaken at other peatland sites in the past (e.g. Austnes et al., 2010; Glendell et al., 2014; Worrall et al., 2008), however, no standard technique to define what constitutes a rainfall/runoff event has yet been developed for upland hydrology. Here, events were separated using the following criteria, based on Luscombe et al. (forthcoming, b) and Glendell et al. (2014). The start of a flow event was identified as the start of rainfall lasting over 15 minutes and with breaks of less than 60 minutes. In order to account for baseflow discharge and existing flow levels within each ditch, the instantaneous discharge at the start of the event was used as the baseflow level and subtracted from all discharges during the event. The event ended when the discharge returned to the initial, pre-event level. If the discharge did not return to its initial value, the event ended when flow reached its lowest value before the next increase in response to rainfall. Any rainfall break of over 3 hours marked the start of a new event.

For each flow event, the following hydrological parameters were calculated: total precipitation (P in mm), peak rainfall (Pp mm h^{-1}), total event discharge (Q in m^3), peak Q (m^3 s^{-1}), event duration (D in hours), and lag from peak rainfall to peak Q (Lp in min).

Sample collection did not always cover the whole duration of the event, and the number of samples and their spacing also varied between events and sites. In order to ensure a good representation of water quality during flow events, events with more than three samples collected, and covering over 75% of the total discharge of the event were selected; other events were discarded from the analysis. The total number of events ranged between 5 and 13, for Aclands, and 9 and 13 for Spooners (Table 2). To account for variations in flow and number of samples between events, flow weighted mean concentrations (FWMC) were calculated for DOC (expressed in mg L^{-1}) using equation (1) (Dinsmore et al., 2013), with *Ci* the instantaneous concentration, Qi the instantaneous discharge, and ti the time step between subsequent measurements.

$$FWMC = \frac{\sum(Ci \times ti \times Qi)}{\sum(ti \times Qi)} \quad (1)$$

Other parameters, i.e. Abs^{400}, pH, C/C and E5/E6 ratios, were averaged per event.

Instantaneous loads were calculated by multiplying concentration of each sample (Ci) by discharge (Qi), and further averaged over the time period of the event. For each event, total loads over the time sampled were calculated using Equation 2 (Walling and Webb, 1985; Littlewood, 1992):

$$F = K \times Qr \times \left(\frac{\sum_{i=1}^{n} Ci \times Qi}{\sum_{i=1}^{n} Qi} \right) \quad (2)$$

with *F* the total DOC load carried over a time period, *K* the number of seconds in the time between samples, *Qr* the mean discharge from the continuous record throughout the event, *Qi* the instantaneous discharge, *Ci* the instantaneous concentration, and *n* the number of samples. Two events in October 2011 were removed from the load analysis at Spooners' flume, as discharge calculations were shown to be unreliable for this time period, further affecting load calculations.

Where data are grouped per season, the hydrological year was used, with winter covering the period from the 1st October to 31st March, and summer running from 1st April to 30th September (Gordon et al., 2004).

To investigate the influence of climatic parameters and hydrological changes on decomposition and DOC losses, and address hypothesis 3, antecedent conditions were calculated for the 1, 2, 5, 14 and 30 days prior to the sampling time. These time ranges were chosen to explore the effects of hydrological changes occurring immediately before the event (1 and 2 days), or at longer timescales (5 to 30 days prior). For each sample taken, total rainfall and mean temperature were calculated over these time periods. Depth to water table (DWT) was averaged across all 16 dip wells at each ditch for the various time periods considered up to the start of the event, and normalised by ditch depth. This variable will be referred to as normalised DWT.

2.5. Statistical analysis

Data processing and statistical analysis was performed using MS Excel 2010 and SPSS v.21. All variables included in the analysis were tested for normality (One-sample Kolmogorov-Smirnov test), and transformed using a natural logarithm or square root where appropriate. One way ANOVA tests were used to investigate differences of water quality between catchments and drains (Hypothesis 1). The non-parametric Kruskall-Wallis test was used to investigate the difference between ditches for non-normally distributed variables (i.e. E4/E6). The relationship between water quality parameters and transformed hydrological and climatic variable (Hypothesis 2) was examined using Pearson's correlation. Differences between winter and summer were tested with a generalised linear mixed model (GLMM) using 'R' (version 2.15.0), as this kind of model can cope with nested and repeated measurements, but also with uneven number of observations across the different treatments (Glendell et al., 2014). In order to eliminate co-linearity between climatic variables, Z scores were calculated. The control of antecedent conditions over DOC and colour (Hypothesis 3) was examined by building a stepwise multiple linear regression model considering pH, and all climatic variables prior and during the event. Both sites were considered simultaneously.

When boxplot diagrams are presented, the top box represents the third quartile and the bottom of the box represents the first quartile. Both boxes are separated by the median. The whiskers extend to the highest and lowest values within 1.5 interquartile ranges. Values outside the whiskers are the outliers in the distribution.

3. Results

3.1. Differences in hydrological response and water quality.

General climatic factors are likely to impact on water quality during the period sampled, and were therefore investigated for the sampling period (2012). Figure 2 represents monthly climatic variations during the year sampled, as well as the resulting depth to water table measured across all EPs. The total rainfall measured in 2012 was 2,462 mm. The sampling year was characterised by an unusually wet summer, with total monthly rainfall during the warmer summer months (June to August) ranging between 291 mm and 171 mm in June and August respectively. This largely impacted on water storage, with average depth to water table for all EPs being substantially higher during usually drier times of the year (Figure 2). However, water table levels during the wet but warm summers remained lower than during the winter months (i.e. November to January).

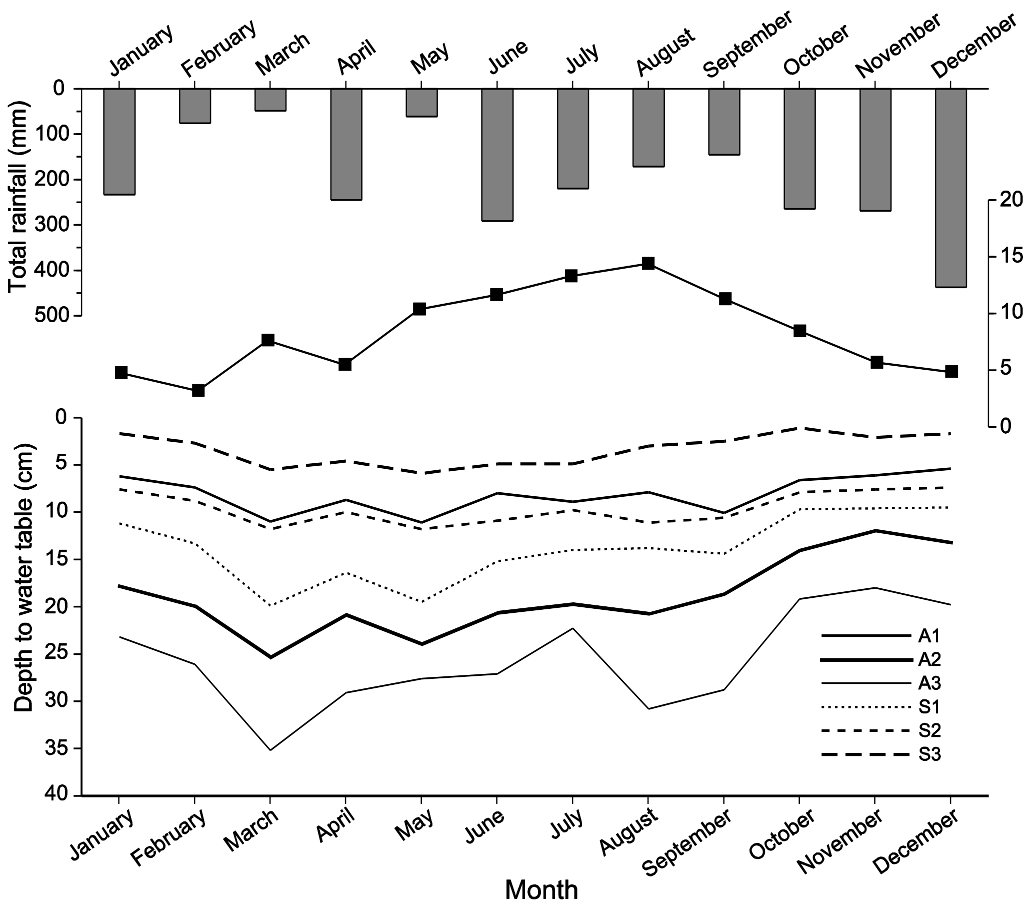

Figure 2. Monthly variations of total rainfall (mm), mean temperature (°C) and average depth to water table for each EP in 2012.

In this general climatic context, the hydrological response of each catchment to rainfall events was examined to understand if they were behaving in the same way (Hypothesis 1). The summary of the hydrological statistics of the events analysed for each of the eight sites is presented in Table 2. The number of events considered in the analysis was similar for all drains, apart from Aclands EP2 (medium size drain) where only 5 events were adequately sampled (i.e. with at least 3 samples taken over 75% of the total event discharge). For the events sampled, neither the range of triggering rainfall, nor the time variables (i.e. event duration and lag time between peak rainfall and peak Q) were significantly different for both catchments. However, the overall response of the two catchments was very different, with median total discharge values at Spooners being up to four times larger than Aclands ($P < 0.01$). Similarly, peak discharge at Spooners was significantly higher than Aclands ($P < 0.01$).

Table 2. Summary statistics of hydrological events monitored for each drain on Aclands and Spooners between November 2011 and March 2013, with N the number of events, P the total precipitation, Pp the peak rainfall, Q the total event discharge, D the event duration, and Lp the lag from peak rainfall to peak Q.

Catchment	EP	N		P (mm)	Pp (mm h^{-1})	Q (m^3)	Peak Q (m^3 s^{-1})	D (h)	Lp (min)	Event sampled (%)
Aclands	1	13	Median	16.0	5.6	132.2	0.005	26.2	60.0	93
			Min	2.0	1.6	15.4	0.001	10.2	15.0	79
			Max	68.8	21.6	504.3	0.013	40.7	285.0	100
	2	5	Median	19.0	5.6	569.5	0.011	32.7	195.0	95
			Min	9.0	4.0	266.6	0.008	18.0	15.0	80
			Max	61.8	8.0	1553.9	0.036	33.0	1365.0	99
	3	13	Median	19.0	5.6	2270.1	0.031	41.0	135.0	87
			Min	8.6	3.2	445.4	0.010	12.5	30.0	77
			Max	68.8	21.6	8672.7	0.176	85.0	1095.0	99
	Flume	10	Median	22.3	4.8	1617.3	0.030	37.4	180.0	93
			Min	3.6	1.6	32.9	0.001	12.2	30.0	77
			Max	61.8	8.0	7266.0	0.238	60.0	1155.0	98
Spooners	1	9	Median	25.4	6.4	566.9	0.013	39.2	105.0	86
			Min	3.4	3.2	76.8	0.004	11.7	15.0	76
			Max	74.6	11.2	2772.5	0.038	74.0	735.0	99
	2	12	Median	25.1	6.4	1689.1	0.047	32.4	112.5	84
			Min	12.2	3.2	861.0	0.030	17.2	15.0	75
			Max	73.8	11.2	6162.1	0.097	72.5	615.0	99
	3	13	Median	24.6	6.4	1026.1	0.033	23.7	195.0	81
			Min	9.4	3.2	225.7	0.009	12.0	15.0	75
			Max	74.6	11.2	3148.7	0.051	46.7	1470.00	98
	Flume	10	Median	20.4	5.2	5698.4	0.164	23.5	97.5	89
			Min	8.0	3.2	734.7	0.032	17.2	30.0	81
			Max	67.8	11.2	24474.2	1.089	53.7	300.0	100

The DOC concentrations measured for all EPs (Figure 3) ranged between 5 and 20.5 mg L^{-1} for Aclands, and 4 and 21 mg L^{-1} for Spooners, with means of 13 mg L^{-1} (SD = 4.5, n = 41) and 9 mg L^{-1} (SD = 4.8, n = 44) respectively. The difference between the two sites was statistically significant ($P < 0.05$). A similar trend was observed for Abs^{400}, where concentrations were significantly higher at Aclands compared to Spooners ($P < 0.05$), with means of 8.15 au m^{-1} (SD = 3.13, n = 41) and 6.9 au m^{-1} (SD = 2.63, n = 44) respectively. pH measurements (Figure 3 e) were significantly higher at Spooners (mean = 4.9) compared to Aclands (mean = 4.7). The difference between both catchments was also highly significant for instantaneous loads (means of 0.3 g and 0.2 g per event for Spooners and Aclands respectively, $P < 0.01$), but not for total loads during the sampling period (means of 14.9 kg for Aclands, 15.3 kg for Spooners, F = 1.905, $P = 0.171$).

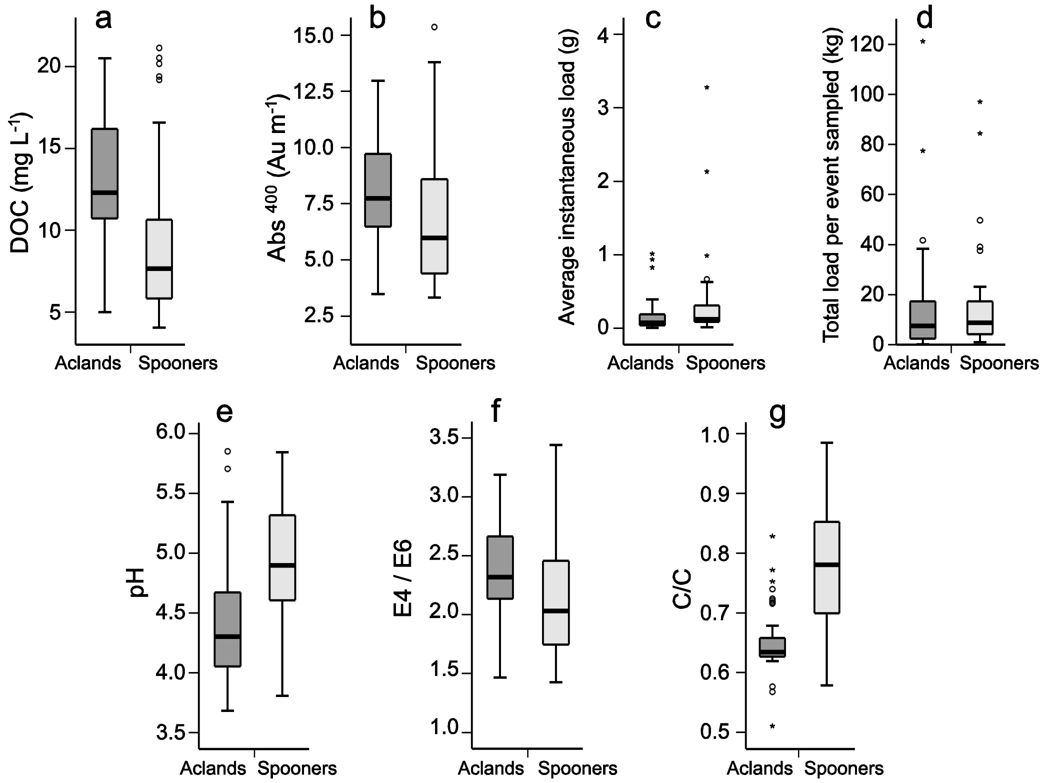

Figure 3. Boxplot diagrams of DOC - FWMC (a), Abs^{400} (b), average instantaneous load per event (c), total load per event sampled (d), pH (e), E4/E6 ratios (f) and, C/C ratio (g), for all events considered on Aclands (n = 41) and Spooners (n= 42).

The characteristics of the DOC lost during events were also significantly different between the two catchments: although both sites have E4/E6 ratios < 5, which indicates a predominance of humic acid (HAs) in DOC, significantly higher ratios at Aclands show that this site is losing DOC containing comparatively more FAs compared to Spooners. The mean E4/E6 ratios across all events were measured at 2.35 (SD = 0.46) for Aclands and 2.14 (SD = 0.51) for Spooners. However, although Aclands is losing more DOC and has higher colour concentrations (Abs^{400}), the C/C ratios showed that the DOC lost at Spooners was significantly more discoloured ($P < 0.001$, Figure 3 c).

Differences in water quality were also noticeable within catchments, as presented in Figure 4. Both sites showed a scaling effect with drain size, with DOC, Abs^{400} and E4/E6 decreasing with increasing drain size. At Aclands, the highest concentrations were measured in the smallest drain (EP1), and lowest concentrations occurred in the main channel (e.g. DOC ranging between 17.3 and 8 mg L^{-1}; mean Abs^{400} decreasing between 10.5 and 5.4 au m^{-1}). The difference between sites was statistically significant for DOC ($F = 16.38$, df = 3, $P < 0.01$), Abs^{400} ($F = 13.42$, df = 3, $P < 0.01$), and E4/E6 (Kruskall Wallis test, $P < 0.01$). A similar trend was also observed at Spooners, although the lowest concentrations for all variables studied occurred on the main channel (EP3). Differences between sites were statistically different for DOC ($F = 4.96$, df = 3, $P < 0.01$), Abs^{400} ($F = 5.48$, df = 3, $P < 0.05$) and E4/E6 ratio (Kruskall Wallis, $P < 0.01$). Despite higher concentrations, the small drains on both catchments experienced lowest DOC loads due to lower discharge (Figure 4 c and d), whilst most export of DOC was measured at the outlet of the catchment. Loads for the events sampled were especially high at Spooners' outlet (mean of 37 kg and maximum 97 kg). The difference at the EP scale was statistically significant for both Aclands ($F = 8.1$, $P < 0.01$) and Spooners ($F = 21.7$, $P < 0.01$) for instantaneous loads, and total loads during the time period sampled ($F = 9.2$, $P < 0.01$ and $F = 7.1$, $P < 0.01$ for Aclands and Spooners respectively).

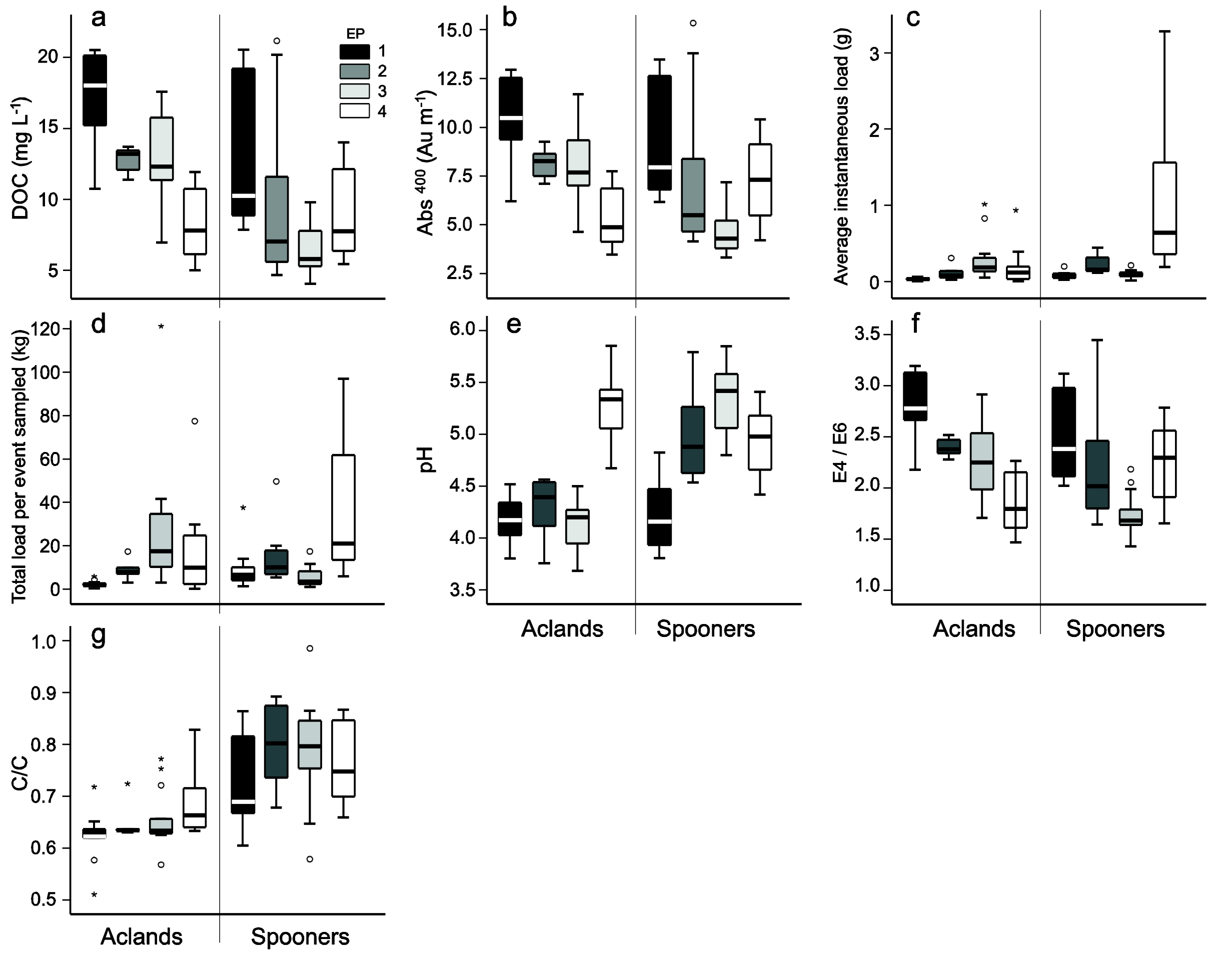

Figure 4. Boxplots summarizing water quality measurements on Exmoor for each drain sampled within the two studied catchments (Aclands and Spooners): DOC concentrations (FWMC) (a), Abs^{400} (b), average instantaneous load (c), total loads per event during sampling times (d), pH (e), E4/E6 index (f) and C/C (g).

Differences between pH levels at the catchment and EP scale were also evident, with Aclands showing low pH on small to large drains (mean pH between 4.1 and 4.3 for drain 2 and 3 respectively), whereas pH at the outlet of the catchment ranged between 4.6 and 5.8. For Spooners, the lowest pH was measured on EP1 (3.7 to 4.8), whereas values from all three other sampling locations ranged between 4.5 and 5.7. Clear differences between catchments in terms of C/C were consistent at the EP level, with more coloured DOC lost consistently at Spooners (C/C between 0.6 and 0.9) compared to all EPs at Aclands (mean of 0.65 across EP1, 2 and 3), whereas greater variability was measured at the outlet of the catchment.

3.2. First order control of water quality variables

To address Hypothesis 2, Table 3 describes the relationships between water quality parameters and first order controls. There was a strong positive correlation between Ln DOC and temperature (r = 0.53, $P < 0.01$), and a strong negative correlation between Ln DOC and Ln Total Q per event (r = -0.33, $P < 0.01$), but no relationship between DOC and Ln total rainfall during the event. Because of close inter-correlation between DOC, Abs^{400} and C/C, similar relationships were found between first order control parameters and colour and C/C. This analysis also showed that the type of DOC correlated strongly with all three water quantity variables, as indicated by the E4/E6 ratio. Finally, there was a good correlation between pH and other water quality parameters (i.e. r = -0.58 for DOC, r = -0.53 for E4/E6, and r = 0.4 for C/C, with $P < 0.01$), and with rainfall (r = -0.25, $P < 0.05$) but not with temperature or discharge.

Broad seasonal trends of DOC and Abs^{400} were observed on both sites (Figure 5). Generally, DOC and Abs^{400} values on each catchment increased between April and August, coinciding with higher temperature and lower water tables (Figure 2). However, a drop in concentrations occurred at Spooners in July, a substantially wetter month. The evolution of E4/E6 throughout the year (Figure 5 d) showed that the humification index follows DOC and Abs^{400} very closely. Both sites tended to release comparatively more FAs during the summer months. Finally, the marked difference in C/C between both catchments was also visible throughout the year, with DOC being more discoloured at Spooners compared to Aclands, but also more variable during the summer. Seasonal DOC loads variations showed relatively high values in the autumn, but also the impact of a particularly wet June 2012 (mean total DOC load during the sampling period of 33.9 kg for Aclands and 29.7 kg for Spooners) in contrast with drier periods in the rest of the summer.

Table 3. Pearson's correlation between water quality parameters and first order climatic variables based on events for both sites (n between 77 and 85).

		Ln DOC	Abs^{400}	E4/E6	C/C	pH	Ln tot Q event	Temp Start	Ln Rain event
Ln DOC	Pearson Correlation	1							
	n	85							
Abs^{400}	Pearson Correlation	0.936[b]	1						
	n	83	83						
E4/E6	Pearson Correlation	0.938[b]	0.987[b]	1					
	n	83	83	83					
C/C	Pearson Correlation	-0.726[b]	-0.509[b]	-0.516[b]	1				
	n	83	83	83	83				
pH	Pearson Correlation	-0.578[b]	-0.506[b]	-0.529[b]	0.400[b]	1			
	n	77	76	76	76	77			
Ln tot Q event	Pearson Correlation	-0.327[b]	-0.305[b]	-0.301[b]	0.269[a]	0.068	1		
	n	85	83	83	83	77	85		
Temp Start	Pearson Correlation	0.530[b]	0.558[b]	0.562[b]	-0.297[b]	-0.147	-0.158	1	
	n	85	83	83	83	77	85	85	
Ln Rain event	Pearson Correlation	-0.176	-0.238[a]	-0.220[a]	0.142	-0.249[a]	0.679[b]	-0.135	1
	n	85	83	83	83	77	85	85	85

[a] $P < 0.05$

[b] $P < 0.01$

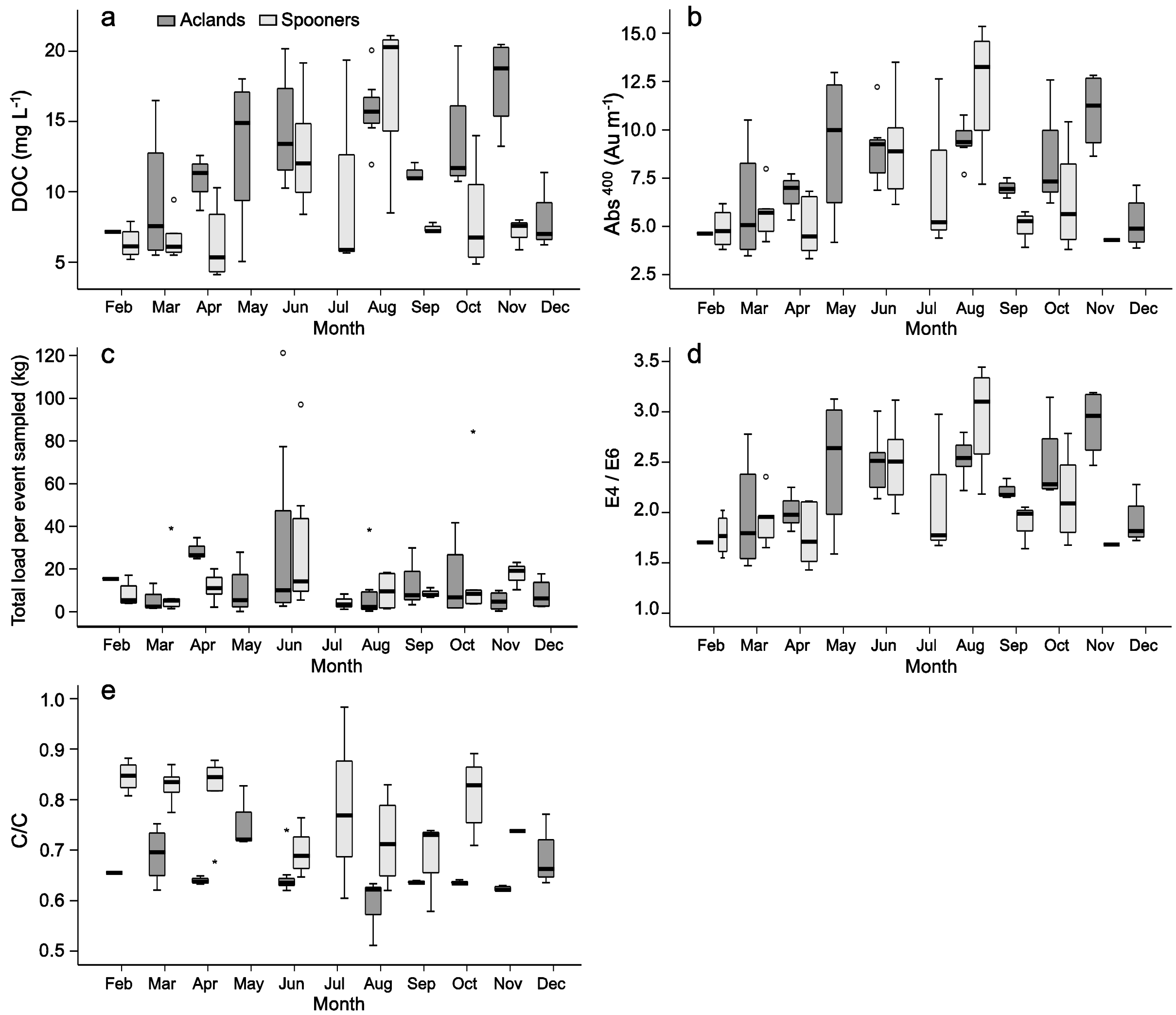

Figure 5. Temporal variations of DOC FWMC (a), Abs^{400} (b), total loads per event sampled (c), E4/E5 (d) and C/C (e), for Aclands (n = 41) and Spooners (n= 44).

The direct comparison between hydrological winter and summer across all sites (Figure 6) further confirmed these general trends. Overall, DOC concentrations, Abs^{400} and E4/E6 were significantly higher in the summer months (GLMM, $P < 0.01$), whereas the C/C was significantly lower in the summer, showing increased losses of less complex and less coloured DOC in the generally drier and warmer months. Mean loads during the events sampled for all sites ranged between 17.6 kg in the summer, and 11.6 kg in the winter. This difference was statistically significant (GLMM, $P < 0.05$).

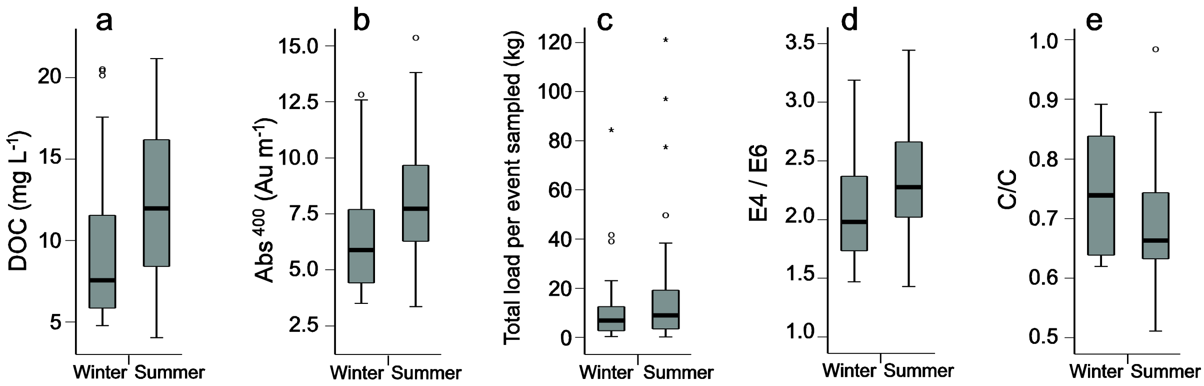

Figure 6. Comparison of winter and summer DOC FWMC (a), Abs^{400} (b), total loads per sampling periods (c), E4/E6 (d) and C/C (e) during rainfall/runoff events across both catchments (n= 37 for winter, n =48 for summer).

3.3. Importance of antecedent conditions in the control of DOC concentrations in runoff

The results of the stepwise regression conducted to address Hypothesis 3 and gain a better understanding of the importance of antecedent conditions controlling DOC, are presented in Figure 7. Overall, amongst all variables considered in the model (temperature, rainfall, Q and depth to water table during the event and at various time scales before the event), 68% of the variance of DOC was explained by a range of factors ($F = 33.2$, $P < 0.01$): total Q during event, the temperature at the start of each event, and the depth to water table during the 30 days prior to the event.

Amongst the three variables included, depth to water table presented the best partial correlation ($r = 0.73$, $P < 0.01$), followed by total Q during the event ($r = -0.52$, $P < 0.01$), and current air temperature ($r = 0.46$, $P < 0.01$). It is worth noticing that neither pH nor any of the rainfall parameters were included in the model. Residuals were normally distributed ($P = 0.20$), and using Z scores for all variables successfully dealt with co-linearity (VIF between 1 and 1.08).

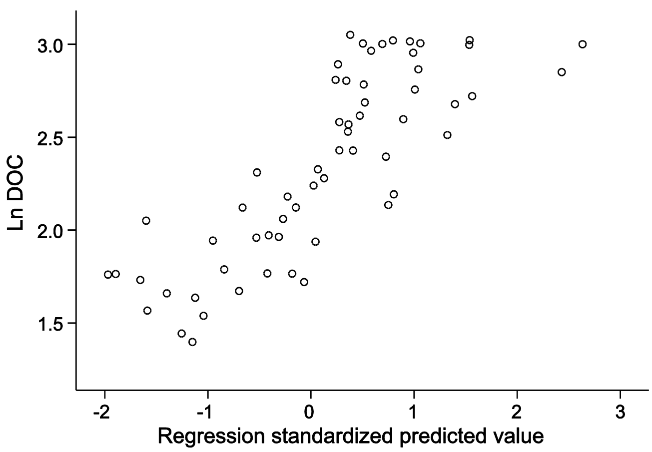

Figure 7. Ln DOC determined by multiple regressions, including Ln total Q per event, temperature at the start, and Ln depth to water table during the 30 days prior to the event as predicting factors (r^2=0.68).

3.4. Variations of fulvic to humic acid ratio with DOC concentrations

The relationship between DOC and the E4/E6 ratio was considered to understand the connection between DOC lost during rainfall/runoff events and its characteristics (Hypothesis 4). Figure 8 shows a close relationship between DOC concentrations and E4/E6 ratios (r = 0.92 for both Aclands and Spooners), indicating that increased DOC concentrations led to more FAs being lost (higher E4/E6). Nonetheless, these values remained below 5, which means that overall, most of the DOC being lost was composed of HAs.

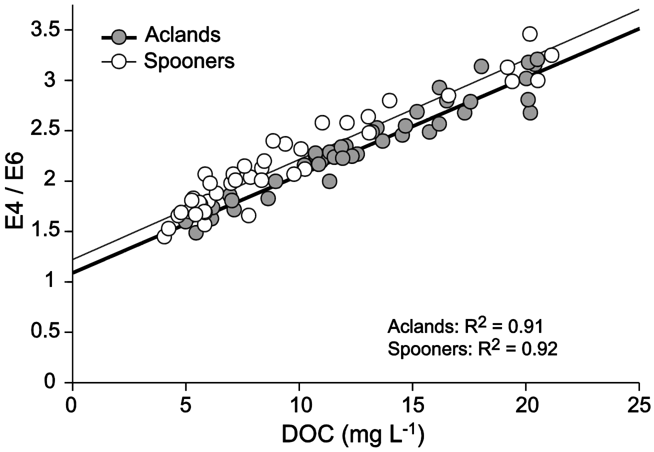

Figure 8. Fulvic to humic ratio (E4/E6) variations with DOC concentrations (FWMC); n = 41 and n = 44 for Aclands and Spooners respectively.

4. Discussion

4.1. Impact of local spatial differences on DOC losses.

Runoff from damaged deep peat in the north of the UK has been observed to cause low water quality downstream (e.g. Armstrong et al., 2010), but little is known about the impact of such damage on shallow peatlands. In this study, two experimental sites were monitored to understand the spatial and temporal variability of water quality sourced from damaged marginal and shallow peatlands in Exmoor National Park in the south west of the UK. The work presented here is distinct from other studies because it takes an event-based analysis approach to understand the influence of several environmental factors and their interaction on water quality, rather than solely quantify C fluxes at the single catchment scale.

The first hypothesis tested in this work addressed the effect of spatial variability between catchments on water quality. Average DOC concentrations during events ranging between 4 mg L^{-1} and 21 mg L^{-1} across both catchments were slightly under the national average of 31 mg L^{-1} measured by Armstrong et al. (2010), and substantially lower than concentrations measured in deep peat further north, i.e. between 20 and 62 mg L^{-1} (Wallage et al., 2006), or even reaching 80 mg L^{-1} (Upper Teesdale; Turner et al., 2013). Similarly, colour values reported for the two Exmoor sites were significantly lower than measurements elsewhere, e.g. Abs^{400} reaching 30 Au m^{-1} (Grayson and Holden, 2012), but remained over 10 times the EC maximum colour standard for treated water

(Abs^{400} of 1.5 Au m^{-1}) (DWI, 2010). Differences between catchments were statistically significant, Aclands experiencing higher DOC concentrations and colour, more acidic waters and lower C/C. The two catchments also showed very different hydrological behaviour: for equivalent rainfall events (i.e. amount of triggering rainfall), although the response time of the two catchments was similar (i.e. lag and event duration), the total discharge was significantly lower at Aclands. This indicates that less water is moving in a much shallower peat system (Table 2). These results are also confirmed by the analysis of Luscombe et al. (Forthcoming, a), who show that, with poorly maintained baseflow and a significantly flashier hydrological regime, Aclands is generally drier than Spooners. Drier conditions could subsequently lead to increased decomposition in the peat surface at Aclands compared to Spooners, as observed in situations of extreme drought by Glatzel et al. (2006). However, differences in DOC concentrations were cancelled out by variations in discharge, causing similar losses of DOC export for the two catchments during the sampling period (Figure 3).

4.2. Importance of first order controls on water quality.

Several bodies of work point towards the importance of first order factors (e.g. temperature, pH, discharge) on DOC production or transport in northern peatlands (Clark et al., 2007, 2012; Dinsmore et al., 2013; Koehler et al., 2009). Therefore, it was hypothesised that such parameters would also influence the shallow, marginal peatlands in the south west of the UK (Hypothesis 2). Results presented here have shown that, amongst all factors considered, temperature had a strong correlation with DOC concentrations ($r = 0.53$, $P<0.01$), as observed elsewhere (e.g; Billett et al., 2006; Freeman et al., 2001a; 2001b; Kirschbaum, 1995), most likely because increased temperature stimulates microbial activity, which in turn can lead to increased decomposition. This finding also explains seasonal variations observed across the two catchments, with DOC concentrations being higher during summer months, as water table levels are drawn deeper compared to winter months (Figures 2, 5 and 6), and the microbial activity is stimulated by warm conditions (Bonnett et al., 2006; Dinsmore et al., 2013; Koehler et al., 2009; Scott et al., 1998). Similar conclusions were drawn in modelling work by Lumsdon et al. (2006) who found that temperature, used as a proxy for microbial activity, increases the solubility and hydrophilicity of DOC.

Discharge was found to be negatively related to DOC concentrations ($r = -0.33$, $P < 0.01$), as observed in Clark et al. (2008) and Billett et al. (2006) for catchments in Northern England and Scotland respectively. However, this relationship was weaker than that of temperature and DOC. This finding implies that DOC production has perhaps more importance than transport in controlling DOC concentrations. The negative relationship also confirmed that DOC concentrations decreased as the flow of water in the drain increased, caused by a dilution of peat water enriched in DOC with rainfall (Clark et al., 2007, 2008; Worrall et al., 2002).

Finally, there was a significant negative relationship between pH and DOC concentrations ($r = -0.58$, $P < 0.01$), which indicates that more acidic waters led to higher DOC concentrations. This negative correlation is in disagreement with the findings of Clark et al. (2005) who showed that DOC tends to increase at high flow because of its increased solubility as pH increases during rewetting after droughts. However, acidity has also been shown to be an indicator of the origin of water during flow events, with storm runoff from peaty water being more acidic compared to relatively alkaline water of groundwater origin (Soulsby et al. 2003). It could therefore be hypothesised that Aclands had a generally higher contribution of peaty water during storm events compared to Spooners, as found by Grocott (2011) in the same catchments, because of differences in peat properties and hydrological functioning. This would further suggest that DOC concentrations are related to water movements in the peat rather than changes in soil water chemistry. However, this assumption will be tested in further analysis (Grand-Clement et al., forthcoming).

4.3. Control of antecedent conditions over DOC concentrations

Antecedent conditions (depth to water table, temperature, discharge and rainfall) were considered here, both over short- (1 to 5 days) and long- (14 and 30 days) time-scales, in order to try to understand how environmental factors impacted on DOC concentrations (Hypothesis 3). These parameters were explored because they have been observed to influence either DOC production in soils or transport during rainfall events (e.g. Clark et al., 2009; Tipping et al., 1999; Wilson et al., 2011b) in deeper peat. The results from the stepwise linear regression model showed that both long-term (i.e. depth to water table in the 30 days prior to the event) and immediate changes (i.e. both temperature and discharge during the event) simultaneously affected DOC concentrations. This finding indicates that overall, long-term aeration due to low water table levels, was an important control on DOC concentrations ($r = 0.73$), confirming the idea that it stimulates microbial activity and aerobic production of DOC in shallow peatlands as well as deep peat (Glatzel et al., 2006). This also explains the higher concentrations of DOC measured at Aclands compared to Spooners, as Aclands was shown to be a significantly drier catchment, and seasonal variations with higher concentrations at times of deeper water table. Although neither pre-existing temperature, discharge nor rainfall were direct contributing variables to the model, water tables are generally influenced by water input (rainfall), temperature (controlling evapotranspiration), and movement through the peat; these factors are therefore likely to be indirectly considered in the model. pH was not included in the results of the stepwise regression either, which indicates that it did not exert a significant control over DOC concentrations in the peatlands of Exmoor, unlike findings by Clark et al. (2005; 2012) in conditions of flow recovery from drought. However, the lack of baseflow results in the present study prevents the inclusion of a pre-existing water pH variable in the statistical analysis, and therefore the full understanding of the role of pH in conditions of drought recovery.

The other two parameters included in the stepwise regression, temperature ($r = 0.46$) and discharge ($r = -0.52$), were considered over much shorter time scales, i.e. that of the storm event. The findings confirmed previous conclusions estimating that transport of the DOC available through the movement of water is essential, but also highlighted the impact of temperature at the time of the event. Water table drawdown has been shown to increase the temperature sensitivity of DOC production (Clark et al., 2007), therefore linking decomposition and transport processes. Moreover, Worrall et al. (2008) also state that physical processes forcing the movements of DOC within the soil profile, i.e. diffusion and sorption, are influenced by temperature. This would mean that, in the present case and at the timescale considered, temperature would be influencing DOC diffusion, and therefore transport, rather than DOC production. Therefore, the interaction between both production and transport of DOC also helped to explain the difference in the variability in DOC concentrations between summer and winter. In the winter, when water tables are higher, DOC concentrations are generally low across all sites. In the summer however, drier and warmer conditions will allow increased production of DOC, but DOC concentrations tend to be limited by production, i.e. how much is available to transport since the last rainfall event. This especially explains variations in DOC during the summer of the sampling period (Figure 5): exceptionally wet

June and July have led to increased water table and a subsequent drop in concentrations in July. Loads following high rainfall in June were high due to the large availability of decomposition product, but became limited by production in the following month (July 2012). The unusually wet summer during the year considered (2012) also means that DOC exports were not higher in the winter, but during the unusually wetter summer months.

Results presented herein underline the importance of the long-term production stage in DOC export in shallow peatlands. During the rainfall/runoff event, the effect of temperature on physical processes, such as hydrophilicity (Lumsdon et al., 2005) can facilitate this export. Finally, transport is the dominant control of DOC over short time scales, operating over the duration of a rainfall/runoff event. These factors are also likely to be relevant to deeper peat soils, with the drained layer promoting decomposition. As restoration has generally been observed to successfully increase water table levels and to decrease discharge (e.g. Wilson et al., 2010), there is potential for reducing, in the long-term, both DOC productions and export.

4.4. Changes in DOC characteristics

Hypothesis 4 addressed the quality of DOC, investigating whether greater DOC losses from increased decomposition would be characterised by a greater loss of less complex FAs. Overall, with humification ratios (E4/E6) consistently below 5 throughout the year, the DOC from Exmoor was predominantly composed of HAs. Similar results were measured in DOC from the geographically close (and also maritime) peatlands of Wales, albeit from deeper, restored environments (e.g. E4/E6 ranging between 1.5 and 4 immediately after restoration) (Wilson et al., 2011a). Further North in deeper peatlands, results from Moor House National Nature Reserve showed a predominance of FAs at low flow (E4/E6 between 5.5 and 7) only shifting towards HAs (E4/E6 ratios of about 3) during rainfall events (Worrall et al., 2002). This shift was explained by an exhaustion of the stock available for export. The samples in the present study were taken at high flow only, which prevents understanding of whether this process is important in shallow peatlands. However, the analysis of pore water by Wallage et al. (2006) in northern England showed significantly lower ratios in drained peatlands compared to pristine ones (medians of 5.56 and 6.67 respectively). If the values measured in stream water in the present study give an indication of the humification of the peat, the consistently low values (HAs dominated) and comparatively low proportion of FAs show that the peat studied here were perhaps more humified than other sites. This could suggest an influence of the dense drainage network on the humification process on Exmoor.

Results from Exmoor also showed a clear positive and linear relationship between DOC and E4/E6 ($r^2 = 0.92$ for both Aclands and Spooners), as well as seasonal variations and site differences. All this evidence points towards the products of increased microbial activity and decomposition (occurring both temporally and spatially) containing, comparatively, a higher proportion of more labile and less degraded FAs, despite being still predominantly composed of HAs. Our results agree with those of Worrall et al. (2002) in the deep blanket peat of Moor House NNR, where peaks in E4/E6 occur after the longest dry period and decrease as they are progressively flushed during storm events, whilst Clark et al. (2012) observed that drought produced more fractions that were less coloured. Results by Wallage et al. (2006) also showed significantly higher E4/E6 ratios in pore water at the surface (median = 6.23, range: 1.5-14) compared to deeper layers, explained by the presence of an upper layer of high microbial activity dominated by FAs from newly decomposed plant and litter, whereas deeper, the decreased decomposition process is producing more mature and coloured HAs. Overall the findings presented here indicate that the DOC on Exmoor is mostly composed of complex HAs compounds, but that dryness increases the input of less complex compounds due to increased decomposition.

4.5. Potential for restoration

A general trend of increasing DOC losses throughout the Northern Hemisphere has been observed (Evans et al., 2005; Freeman et al., 2001a). Recent modelling work has also shown that peatlands in the south west are likely to be affected by climate change, and could be outside their bioclimatic envelope as early as 2050 (Gallego-Sala et al., 2010), thereby compromising their ability to accumulate carbon. The direct impact of increased temperature on decomposition has generally been shown (Kirschbaum et al., 1995; Ritson et al. in review), and could affect both deep and shallow peatlands. However, the effect could be even greater in shallow and already dry peatlands, as temperature and long-term dryness were identified here to have a critical influence over water quality and the release of DOC. The greater proportion of the drained peat mass is also likely to make shallow peatlands less resilient to future climate change, compared to their deeper counterparts.

Moreover, temperature increase was shown to enhance the decomposition of more recalcitrant C compounds (Hilasvuori et al., 2013), and could therefore have an increased effect in the south west, with shallow peatlands already losing predominantly HAs. Restoration has generally been found to be a successful method to raise water table and increase water storage (Wilson et al., 2010; Worrall et al., 2007a). On Exmoor, it has also been shown to have the potential to improve a wide range of ecosystem services (Grand-Clement et al., 2013). However, the effects of higher water tables on changes in DOC concentrations are unclear (e.g. Wilson et al., 2011b; Worrall et al., 2007a). Maintaining consistently high water tables seems nonetheless key to increase water storage, and therefore decrease the export of fluvial C from these environments (Gibson et al., 2009).

5. Conclusion

The results presented here constitute a significant contribution to the understanding of DOC losses in shallow, damaged peatlands. More precisely, this work has shown that dryness is a critical factor controlling DOC concentrations, both through time and space. Long-term dryness, as seen here through the depth to water table 30 days before the storm event, impacted on DOC production, whilst discharge was the main control over transport at the time scale of the rainfall/runoff event. Temperature during events significantly affected concentrations, possibly acting on the solubility of DOC. Finally, DOC concentrations on Exmoor were overall dominated by complex HAs, but decomposition products led to an increased input of less complex and coloured FAs in summer months.

Considering the predicted impact of future climate change, it is likely that restoration of shallow peatland can, in the long-term, prevent increased peat decomposition, or at least in the short-term decrease the total fluvial flux of C from these environments. The results presented here will be a solid and invaluable base to understand how these shallow, marginal peatlands respond to restoration and then behave under changing climates.

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