

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

3                     Grand-Clement, E., Luscombe, D., Anderson, K., Gatis, N., Benaud, P., Brazier, R.E.

4     Grand-Clement, E. <sup>a</sup> \* ([e.grand-clement@exeter.ac.uk](mailto:e.grand-clement@exeter.ac.uk))

5     Luscombe, D. <sup>a</sup> ([D.J.Luscombe@exeter.ac.uk](mailto:D.J.Luscombe@exeter.ac.uk))

6     Anderson, K. <sup>b</sup> ([karen.anderson@exeter.ac.uk](mailto:karen.anderson@exeter.ac.uk))

7     Gatis, N. <sup>a</sup> ([nrl203@exeter.ac.uk](mailto:nrl203@exeter.ac.uk))

8     Benaud, P. <sup>a</sup> ([P.Benaud@exeter.ac.uk](mailto:P.Benaud@exeter.ac.uk))

9     Brazier, R.E. <sup>a</sup> ([r.e.brazier@exeter.ac.uk](mailto:r.e.brazier@exeter.ac.uk))

10    <sup>a</sup> Geography, College of Life and Environmental Sciences, Amory building, Rennes Drive, Exeter,  
11       Devon, EX4 4RJ, United Kingdom

12    <sup>b</sup> Environment and Sustainability Institute, University of Exeter , Penryn, Cornwall TR10 9FE, United  
13       Kingdom

14    \* Corresponding author: Tel: +44 (0)1392 72 3347

15 **Highlights:**

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

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

21 **Abstract**

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

## 42 **1. Introduction**

43 Peatlands and carbon-rich soils have been shown to be an important contributor of Dissolved  
44 Organic Carbon (DOC) in watercourses (e.g. Aitkenhead et al., 1999; Hope et al., 2004). Over the past  
45 three decades, large scale increases in DOC loss from peaty catchments has been observed in  
46 northern Europe (e.g. Evans et al., 2005; Freeman et al., 2001a; Hejzlar et al., 2003; Skjelkvåle *et al.*,  
47 2001) and North America (Driscoll *et al.*, 2003). This general trend suggests a systematic response to  
48 a combination of external drivers acting over large areas (Evans et al., 2005), such as a general  
49 increase in atmospheric CO<sub>2</sub> (Freeman *et al.*, 2004), a decrease in acidic deposition (Clark *et al.*,  
50 2005; Evans et al., 2005), or the influence of climate change (Freeman et al., 2001a). However, fine-  
51 scale or local factors (i.e. land use) can have an additional effect on the general trend, and therefore  
52 may help to enhance or mitigate DOC export in the short-term (Worrall et al., 2007b). In the UK,  
53 DOC losses from peaty catchments have come under particular scrutiny in recent years, partly  
54 because of the heavy damage peatlands have sustained since the nineteenth century due to  
55 drainage for agricultural reclamation and peat cutting (Holden et al., 2006), or from erosion (Evans  
56 et al., 2006). By lowering the water table, management practices have changed the hydrological  
57 functioning of peatlands, further affecting the provision of several ecosystem services (ES), such as  
58 the support of specific habitats, the provision of water or the storage of carbon (C) (Hubacek et al.,  
59 2009). DOC is of particular interest, firstly because it represents an important pathway for C losses to  
60 the ocean from what is usually considered to be a long-term terrestrial C sink; in-stream processes  
61 leading to evasion of CO<sub>2</sub>, however, mean that DOC will also have an impact on the radiative balance  
62 (Dinsmore et al., 2010). Secondly, DOC has been shown to have a strong effect on water quality and  
63 pollutant transport downstream (Thurman, 1985).

64 Water companies supplying drinking water from rivers or reservoirs that are fed by damaged upland  
65 catchments have to deal with the costly and complicated process of removing C from increasingly  
66 discoloured water supplies (Wallage et al., 2006), whilst ensuring that they meet environmental  
67 standards and regulations (e.g. EU Water Framework Directive 2000/60/EC). They also need to pre-  
68 empt the expected effects of upstream changes in land use, catchment characteristics and climate  
69 on both DOC concentrations and water quality, all of which are known to impact the treatability of  
70 water and the formation of carcinogen disinfection by-products (Ritson et al., 2014; Watts et al.,  
71 2001). As a result, water utilities in the UK (e.g. Severn Trent, United Utilities or South West Water)  
72 have been investing in long-term catchment management through the funding of peatland  
73 restoration projects, in order to avoid more costly, and relatively short-term, solutions downstream  
74 (Parry et al., 2014).

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

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

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

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

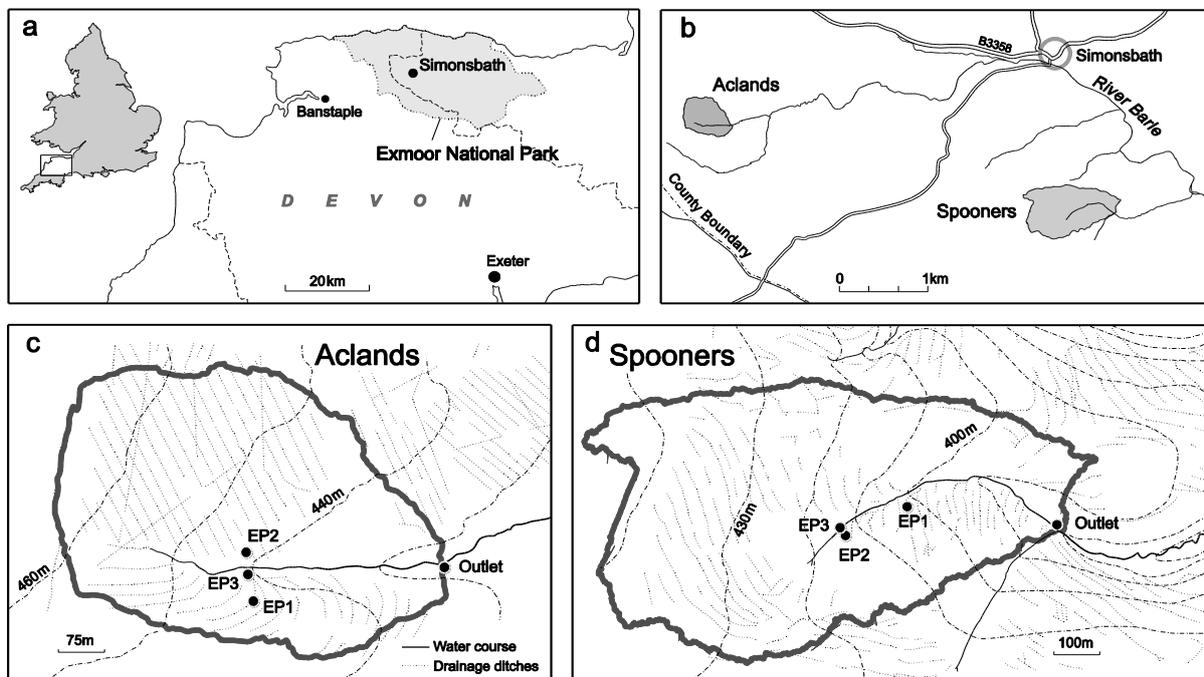
- 118 1. The heavily damaged upland peatlands of Exmoor National Park support poor water quality,  
119 which varies significantly between experimental catchments.
- 120 2. First order variables, including rainfall, air temperature and discharge, exert a strong control  
121 on DOC concentrations, which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

125 4. Quality of DOC, represented by the E4/E6 ratio, is directly related to DOC concentrations in  
126 runoff water, with higher DOC concentrations in the drains being characterised by a greater  
127 loss of fulvic acids (FAs).  
128

## 129 2. Material and methods

### 130 2.1. Study sites

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



146

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

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

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

155 **Table 1. Details of each location monitored as part of this study, with ditch depth and width measured at the sampling**  
 156 **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 <sup>2</sup> ) |
|----------|-------|-------------|----------------|-----------------|-----------------|-------------------------------------|
| 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                             |

157 **2.2. Water quality analysis**

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

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

169 DOC analyses were undertaken using UV spectrometry for chemical free substance analysis (TriOS  
 170 ProPS analyser, TriOS GmbH, Germany), as this enabled rapid and cost effective analysis of a large  
 171 number of samples (Glendell and Brazier, 2014; Sandford et al., 2010). The sensor was fitted with a  
 172 deuterium lamp and measured absorption spectra in the range 190-360 nm. The path lengths used  
 173 varied between 10 to 50 mm, depending on the colour of the samples. The spectra are used to  
 174 distinguish various chemical species and their concentration in the natural sample, and further

175 converted to DOC concentrations ( $\text{mg L}^{-1}$ ) using a multivariate software algorithm based on principal  
176 component analysis.

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

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

187 DOC composition is known to have an impact on spectral absorption properties (Dilling and Kaiser,  
188 2002), and the correlation between colour and chemical methods for measuring DOC has been  
189 shown to vary between sites and seasons (Wallage and Holden, 2010). Therefore, a selected number  
190 of samples from each rainfall/runoff event were sent to the South West Water (SWW) analytical  
191 facilities, where samples were analysed for DOC by thermal oxidation (Hach Lange TOC Analyser,  
192 USA) and colour (Segmented Flow Analysis, Skalar, The Netherlands). Spearman's Rank ( $r_s$ ) was used  
193 to investigate correlations between techniques. Coefficient correlations between DOC measured by  
194 spectrometry and thermal oxidation were 0.89 ( $P < 0.01$ ,  $n = 149$ ) and 0.83 ( $P < 0.01$ ,  $n = 182$ ) for  
195 Aclands and Spooners respectively; correlations between colour measurements (SWW and in-house  
196 UV-Vis spectrometry) varied between 0.98 ( $P < 0.01$ ,  $n = 149$ ) for Aclands, and 0.99 ( $P < 0.01$ ,  $n = 140$ )  
197 for Spooners, whilst coefficient correlations between in house absorbance and DOC concentrations  
198 (thermal oxidation method) ranged between 0.95 (Aclands,  $P < 0.01$  and  $n = 863$ ) and 0.98  
199 (Spooners,  $P < 0.01$ ,  $n = 780$ ). A significant overestimation of DOC measured by spectroscopy over  
200 chemical method was observed (Wilcoxon test,  $P < 0.01$ ,  $n = 376$ ). To address this issue,  
201 spectroscopic concentrations were recalculated using linear calibration curves between the two  
202 methods established for each rain event. For some events, this calibration was not considered  
203 adequate (i.e. when  $r_s < 0.85$ ); colour results, and the correlation between absorbance and DOC  
204 concentrations, were used instead. The linear correlation between recalculated DOC concentrations  
205 and results from thermal oxidation (SWW) showed an overall value of  $r_s = 0.94$  and 0.98 for Aclands  
206 ( $P < 0.01$ ,  $n = 149$ ) and Spooners ( $P < 0.01$ ,  $n = 182$ ) respectively.

### 207 2.3. Other data collected

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

217 rainfall data at 15 minute intervals. Rainfall data were collected using a 0.2 mm tipping-bucket rain  
218 gauge in each catchment.

#### 219 2.4. Data analysis

220 A wide range of rainfall/runoff events of magnitudes were sampled across all drains at both sites. To  
221 account for this temporal variability, data were summarized and analysed on an event basis. Event  
222 based data analysis has been widely undertaken at other peatland sites in the past (e.g. Austnes et  
223 al., 2010; Glendell et al., 2014; Worrall et al., 2008), however, no standard technique to define what  
224 constitutes a rainfall/runoff event has yet been developed for upland hydrology. Here, events were  
225 separated using the following criteria, based on Luscombe et al. (forthcoming, b) and Glendell et al.  
226 (2014). The start of a flow event was identified as the start of rainfall lasting over 15 minutes and  
227 with breaks of less than 60 minutes. In order to account for baseflow discharge and existing flow  
228 levels within each ditch, the instantaneous discharge at the start of the event was used as the  
229 baseflow level and subtracted from all discharges during the event. The event ended when the  
230 discharge returned to the initial, pre-event level. If the discharge did not return to its initial value,  
231 the event ended when flow reached its lowest value before the next increase in response to rainfall.  
232 Any rainfall break of over 3 hours marked the start of a new event.

233 For each flow event, the following hydrological parameters were calculated: total precipitation ( $P$  in  
234 mm), peak rainfall ( $P_p$  mm h<sup>-1</sup>), total event discharge ( $Q$  in m<sup>3</sup>), peak  $Q$  (m<sup>3</sup> s<sup>-1</sup>), event duration ( $D$  in  
235 hours), and lag from peak rainfall to peak  $Q$  ( $L_p$  in min).

236 Sample collection did not always cover the whole duration of the event, and the number of samples  
237 and their spacing also varied between events and sites. In order to ensure a good representation of  
238 water quality during flow events, events with more than three samples collected, and covering over  
239 75% of the total discharge of the event were selected; other events were discarded from the  
240 analysis. The total number of events ranged between 5 and 13, for Aclands, and 9 and 13 for  
241 Spooners (Table 2). To account for variations in flow and number of samples between events, flow  
242 weighted mean concentrations (FWMC) were calculated for DOC (expressed in mg L<sup>-1</sup>) using  
243 equation (1) (Dinsmore et al., 2013), with  $C_i$  the instantaneous concentration,  $Q_i$  the instantaneous  
244 discharge, and  $t_i$  the time step between subsequent measurements.

$$FWMC = \frac{\sum(C_i \times t_i \times Q_i)}{\sum(t_i \times Q_i)} \quad (1)$$

245 Other parameters, i.e. Abs<sup>400</sup>, pH, C/C and E5/E6 ratios, were averaged per event.

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

$$F = K \times Q_r \times \left( \frac{\sum_{i=1}^n C_i \times Q_i}{\sum_{i=1}^n Q_i} \right) \quad (2)$$

249 with  $F$  the total DOC load carried over a time period,  $K$  the number of seconds in the time between  
250 samples,  $Q_r$  the mean discharge from the continuous record throughout the event,  $Q_i$  the  
251 instantaneous discharge,  $C_i$  the instantaneous concentration, and  $n$  the number of samples. Two

252 events in October 2011 were removed from the load analysis at Spooners' flume, as discharge  
253 calculations were shown to be unreliable for this time period, further affecting load calculations.

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

257 To investigate the influence of climatic parameters and hydrological changes on decomposition and  
258 DOC losses, and address hypothesis 3, antecedent conditions were calculated for the 1, 2, 5, 14 and  
259 30 days prior to the sampling time. These time ranges were chosen to explore the effects of  
260 hydrological changes occurring immediately before the event (1 and 2 days), or at longer timescales  
261 (5 to 30 days prior). For each sample taken, total rainfall and mean temperature were calculated  
262 over these time periods. Depth to water table (DWT) was averaged across all 16 dip wells at each  
263 ditch for the various time periods considered up to the start of the event, and normalised by ditch  
264 depth. This variable will be referred to as normalised DWT.

## 265 2.5. Statistical analysis

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

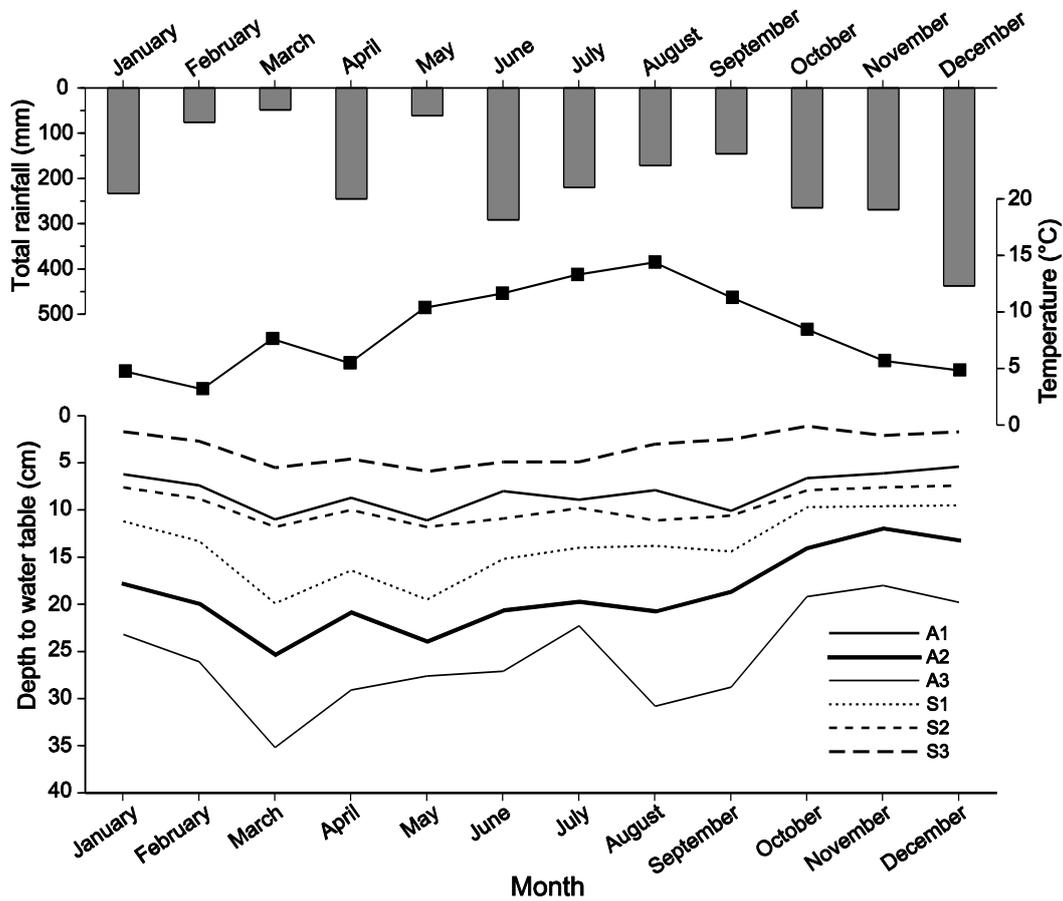
280 When boxplot diagrams are presented, the top box represents the third quartile and the bottom of  
281 the box represents the first quartile. Both boxes are separated by the median. The whiskers extend  
282 to the highest and lowest values within 1.5 interquartile ranges. Values outside the whiskers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

## 284 3. Results

### 285 3.1. Differences in hydrological response and water quality.

286 General climatic factors are likely to impact on water quality during the period sampled, and were  
287 therefore investigated for the sampling period (2012). Figure 2 represents monthly climatic  
288 variations during the year sampled, as well as the resulting depth to water table measured across all  
289 EPs. The total rainfall measured in 2012 was 2,462 mm. The sampling year was characterised by an

290 unusually wet summer, with total monthly rainfall during the warmer summer months (June to  
 291 August) ranging between 291 mm and 171 mm in June and August respectively. This largely  
 292 impacted on water storage, with average depth to water table for all EPs being substantially higher  
 293 during usually drier times of the year (Figure 2). However, water table levels during the wet but  
 294 warm summers remained lower than during the winter months (i.e. November to January).



295  
 296 **Figure 2. Monthly variations of total rainfall (mm), mean temperature (°C) and average depth to water table for each EP**  
 297 **in 2012.**

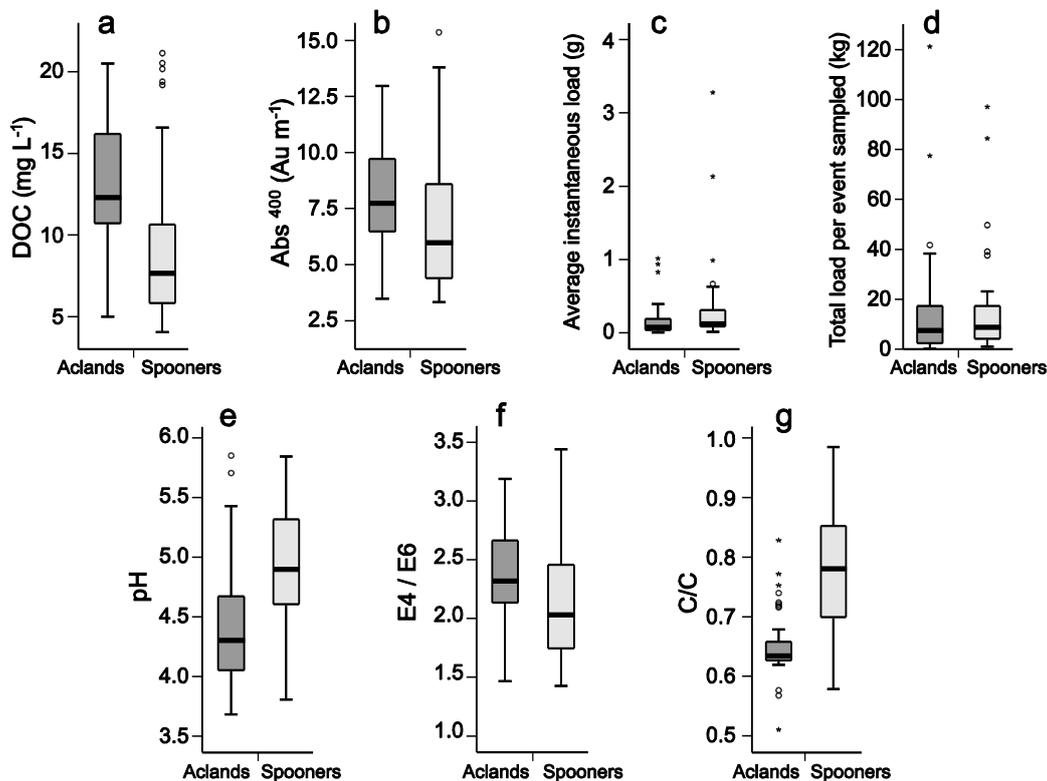
298 In this general climatic context, the hydrological response of each catchment to rainfall events was  
 299 examined to understand if they were behaving in the same way (Hypothesis 1). The summary of the  
 300 hydrological statistics of the events analysed for each of the eight sites is presented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

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

| Catchment | EP    | N  |        | P<br>(mm) | Pp<br>(mm h <sup>-1</sup> ) | Q<br>(m <sup>3</sup> ) | Peak Q<br>(m <sup>3</sup> s <sup>-1</sup> ) | D<br>(h) | Lp<br>(min) | Event<br>sampled<br>(%) |
|-----------|-------|----|--------|-----------|-----------------------------|------------------------|---|----------|-------------|-------------------------|
| 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                     |

312

313 The DOC concentrations measured for all EPs (Figure 3) ranged between 5 and 20.5 mg L<sup>-1</sup> for  
 314 Aclands, and 4 and 21 mg L<sup>-1</sup> for Spooners, with means of 13 mg L<sup>-1</sup> (SD = 4.5, n = 41) and 9 mg L<sup>-1</sup> (SD  
 315 = 4.8, n = 44) respectively. The difference between the two sites was statistically significant ( $P <$   
 316 0.05). A similar trend was observed for Abs<sup>400</sup>, where concentrations were significantly higher at  
 317 Aclands compared to Spooners ( $P <$  0.05), with means of 8.15 au m<sup>-1</sup> (SD = 3.13, n = 41) and 6.9 au m<sup>-1</sup>  
 318 (SD = 2.63, n = 44) respectively. pH measurements (Figure 3 e) were significantly higher at Spooners  
 319 (mean = 4.9) compared to Aclands (mean = 4.7). The difference between both catchments was also  
 320 highly significant for instantaneous loads (means of 0.3 g and 0.2 g per event for Spooners and  
 321 Aclands respectively,  $P <$  0.01), but not for total loads during the sampling period (means of 14.9 kg  
 322 for Aclands, 15.3 kg for Spooners,  $F = 1.905$ ,  $P = 0.171$ ).



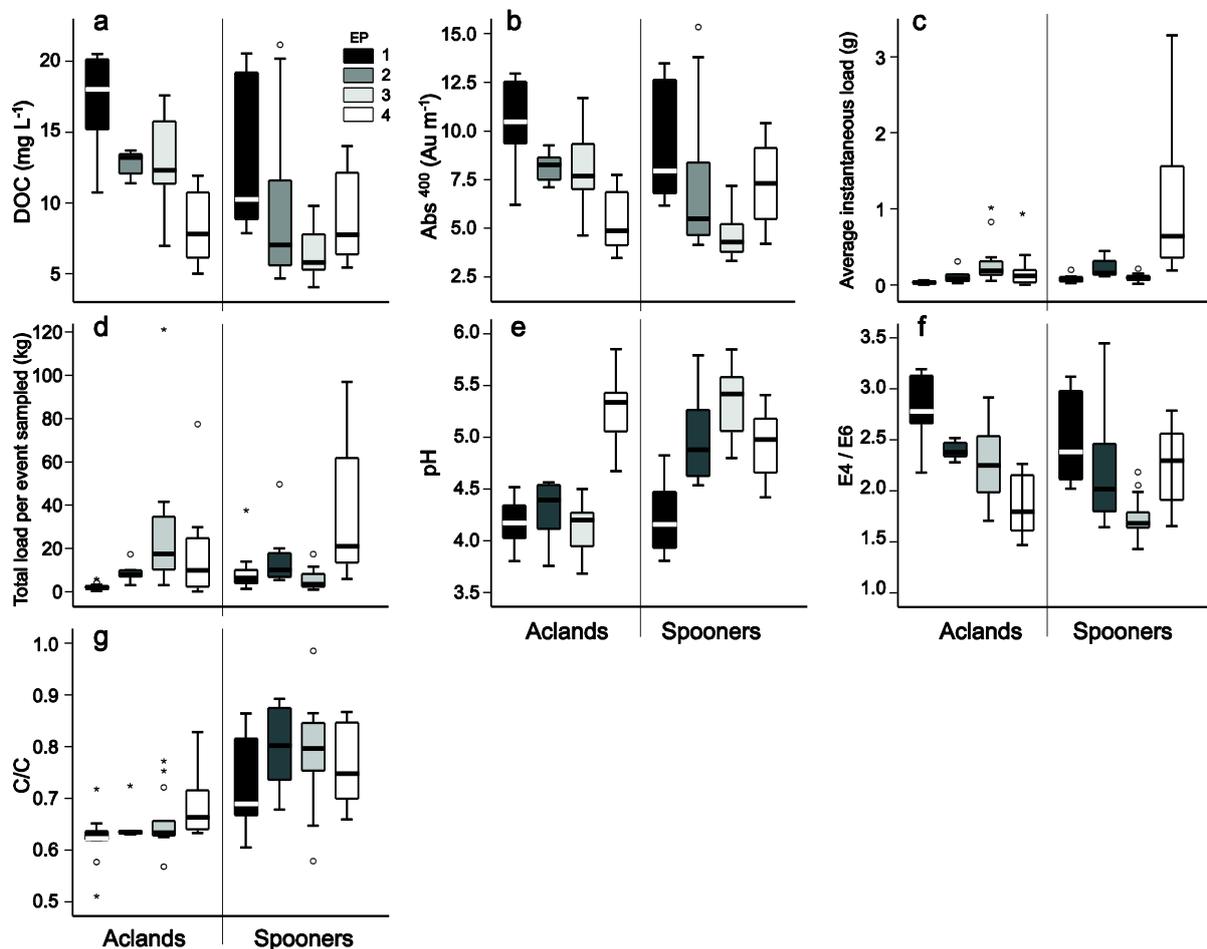
323

324 **Figure 3.** Boxplot diagrams of DOC - FWMC (a), Abs<sup>400</sup> (b), average instantaneous load per event (c), total load per event  
 325 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).

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

333 Differences in water quality were also noticeable within catchments, as presented in Figure 4. Both  
 334 sites showed a scaling effect with drain size, with DOC, Abs<sup>400</sup> and E4/E6 decreasing with increasing  
 335 drain size. At Aclands, the highest concentrations were measured in the smallest drain (EP1), and

336 lowest concentrations occurred in the main channel (e.g. DOC ranging between 17.3 and 8 mg L<sup>-1</sup>;  
 337 mean Abs<sup>400</sup> decreasing between 10.5 and 5.4 au m<sup>-1</sup>). The difference between sites was statistically  
 338 significant for DOC (F = 16.38, df = 3, P < 0.01), Abs<sup>400</sup> (F = 13.42, df = 3, P < 0.01), and E4/E6 (Kruskall  
 339 Wallis test, P < 0.01). A similar trend was also observed at Spooners, although the lowest  
 340 concentrations for all variables studied occurred on the main channel (EP3). Differences between  
 341 sites were statistically different for DOC (F = 4.96, df = 3, P < 0.01), Abs<sup>400</sup> (F = 5.48, df = 3, P < 0.05)  
 342 and E4/E6 ratio (Kruskall Wallis, P < 0.01). Despite higher concentrations, the small drains on both  
 343 catchments experienced lowest DOC loads due to lower discharge (Figure 4 c and d), whilst most  
 344 export of DOC was measured at the outlet of the catchment. Loads for the events sampled were  
 345 especially high at Spooners' outlet (mean of 37 kg and maximum 97 kg). The difference at the EP  
 346 scale was statistically significant for both Aclands (F = 8.1, P < 0.01) and Spooners (F = 21.7, P < 0.01)  
 347 for instantaneous loads, and total loads during the time period sampled (F = 9.2, P < 0.01 and F = 7.1,  
 348 P < 0.01 for Aclands and Spooners respectively).



349

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

353 Differences between pH levels at the catchment and EP scale were also evident, with Aclands  
 354 showing low pH on small to large drains (mean pH between 4.1 and 4.3 for drain 2 and 3  
 355 respectively), whereas pH at the outlet of the catchment ranged between 4.6 and 5.8. For Spooners,

356 the lowest pH was measured on EP1 (3.7 to 4.8), whereas values from all three other sampling  
357 locations ranged between 4.5 and 5.7. Clear differences between catchments in terms of C/C were  
358 consistent at the EP level, with more coloured DOC lost consistently at Spooners (C/C between 0.6  
359 and 0.9) compared to all EPs at Aclands (mean of 0.65 across EP1, 2 and 3), whereas greater  
360 variability was measured at the outlet of the catchment.

### 361 3.2. First order control of water quality variables

362 To address Hypothesis 2, Table 3 describes the relationships between water quality parameters and  
363 first order controls. There was a strong positive correlation between Ln DOC and temperature ( $r =$   
364  $0.53, P < 0.01$ ), and a strong negative correlation between Ln DOC and Ln Total Q per event ( $r = -$   
365  $0.33, P < 0.01$ ), but no relationship between DOC and Ln total rainfall during the event. Because of  
366 close inter-correlation between DOC,  $Abs^{400}$  and C/C, similar relationships were found between first  
367 order control parameters and colour and C/C. This analysis also showed that the type of DOC  
368 correlated strongly with all three water quantity variables, as indicated by the E4/E6 ratio. Finally,  
369 there was a good correlation between pH and other water quality parameters (i.e.  $r = -0.58$  for DOC,  
370  $r = -0.53$  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  
371 with temperature or discharge.

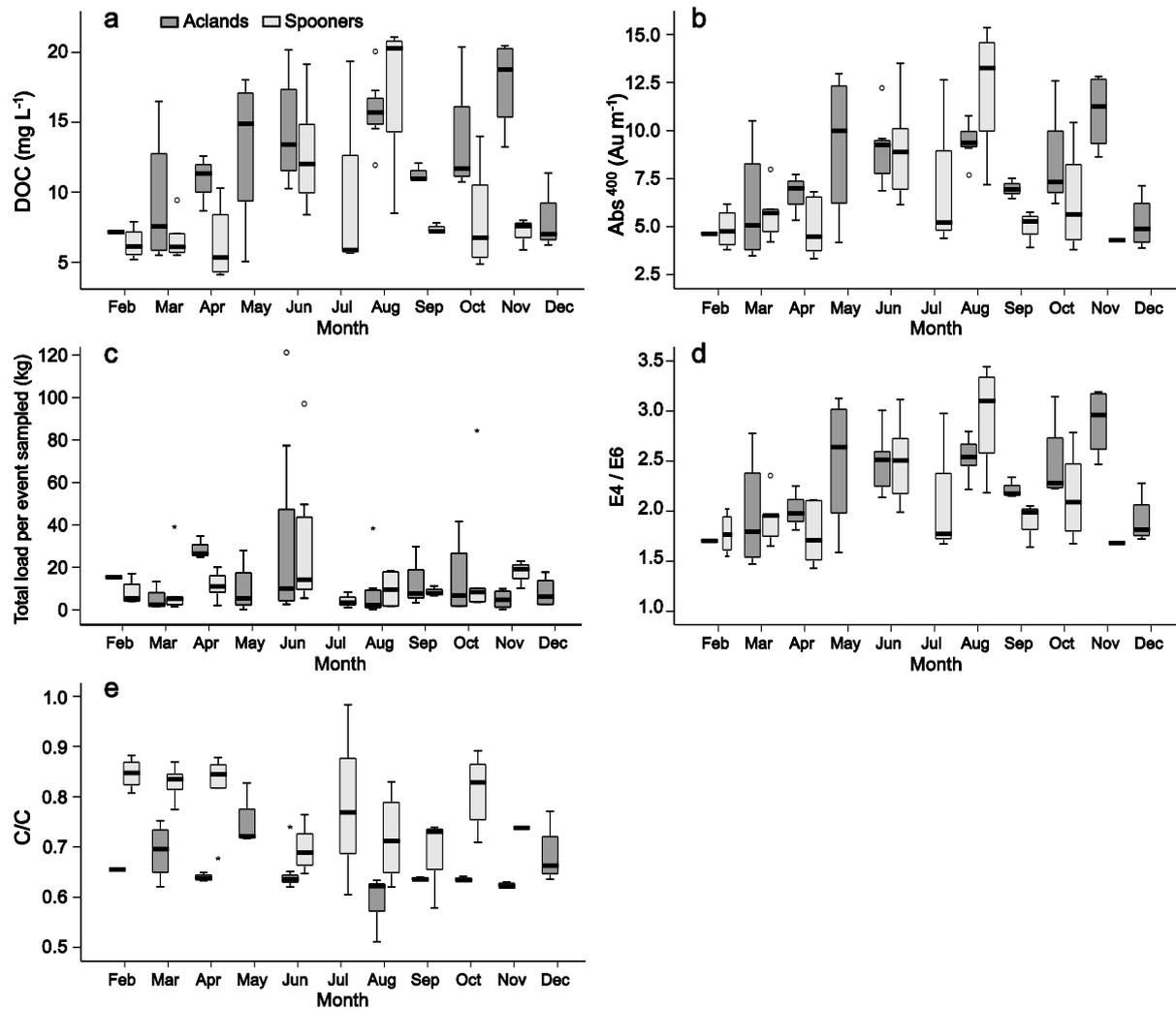
372 Broad seasonal trends of DOC and  $Abs^{400}$  were observed on both sites (Figure 5). Generally, DOC and  
373  $Abs^{400}$  values on each catchment increased between April and August, coinciding with higher  
374 temperature and lower water tables (Figure 2). However, a drop in concentrations occurred at  
375 Spooners in July, a substantially wetter month. The evolution of E4/E6 throughout the year (Figure 5  
376 d) showed that the humification index follows DOC and  $Abs^{400}$  very closely. Both sites tended to  
377 release comparatively more FAs during the summer months. Finally, the marked difference in C/C  
378 between both catchments was also visible throughout the year, with DOC being more discoloured at  
379 Spooners compared to Aclands, but also more variable during the summer. Seasonal DOC loads  
380 variations showed relatively high values in the autumn, but also the impact of a particularly wet June  
381 2012 (mean total DOC load during the sampling period of 33.9 kg for Aclands and 29.7 kg for  
382 Spooners) in contrast with drier periods in the rest of the summer.

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

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

385 <sup>a</sup>  $P < 0.05$

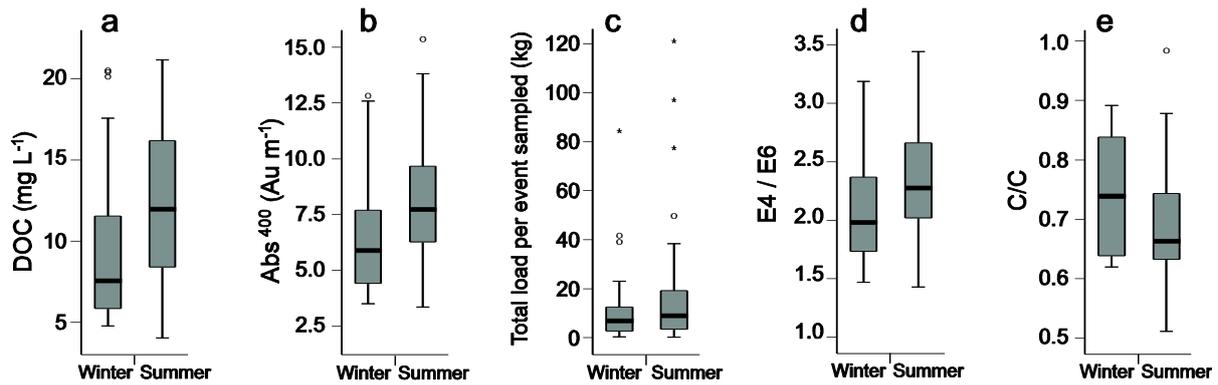
386 <sup>b</sup>  $P < 0.01$



387

388 **Figure 5. Temporal variations of DOC FWMC (a), Abs<sup>400</sup> (b), total loads per event sampled (c), E4/E5 (d) and C/C (e), for**  
 389 **Aclands (n = 41) and Spooners (n= 44).**

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



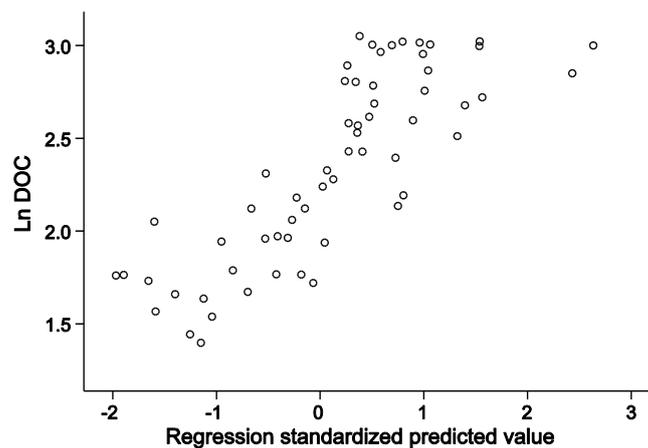
396

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

399 3.3. Importance of antecedent conditions in the control of DOC concentrations in runoff

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

406 Amongst the three variables included, depth to water table presented the best partial correlation ( $r$   
 407 = 0.73,  $P < 0.01$ ), followed by total Q during the event ( $r = -0.52$ ,  $P < 0.01$ ), and current air  
 408 temperature ( $r = 0.46$ ,  $P < 0.01$ ). It is worth noticing that neither pH nor any of the rainfall  
 409 parameters were included in the model. Residuals were normally distributed ( $P = 0.20$ ), and using Z  
 410 scores for all variables successfully dealt with co-linearity (VIF between 1 and 1.08).

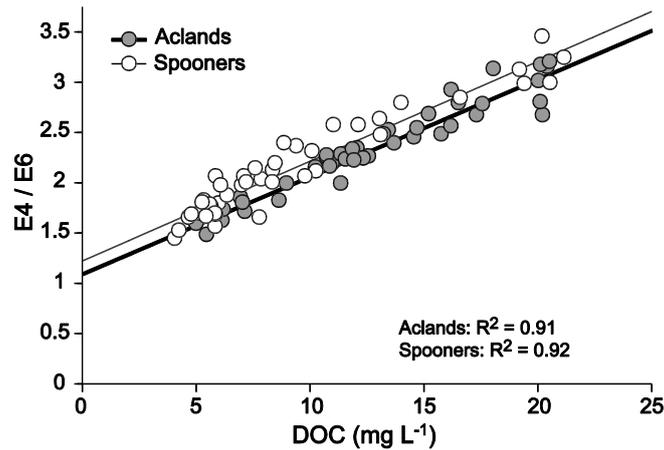


411

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

414 3.4. Variations of fulvic to humic acid ratio with DOC concentrations

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



421

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

424 **4. Discussion**

425 4.1. Impact of local spatial differences on DOC losses.

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

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

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

#### 454 4.2. Importance of first order controls on water quality.

455 Several bodies of work point towards the importance of first order factors (e.g. temperature, pH,  
456 discharge) on DOC production or transport in northern peatlands (Clark et al., 2007, 2012; Dinsmore  
457 et al., 2013; Koehler et al., 2009). Therefore, it was hypothesised that such parameters would also  
458 influence the shallow, marginal peatlands in the south west of the UK (Hypothesis 2). Results  
459 presented here have shown that, amongst all factors considered, temperature had a strong  
460 correlation with DOC concentrations ( $r = 0.53$ ,  $P < 0.01$ ), as observed elsewhere (e.g; Billett et al.,  
461 2006; Freeman et al., 2001a; 2001b; Kirschbaum, 1995), most likely because increased temperature  
462 stimulates microbial activity, which in turn can lead to increased decomposition. This finding also  
463 explains seasonal variations observed across the two catchments, with DOC concentrations being  
464 higher during summer months, as water table levels are drawn deeper compared to winter months  
465 (Figures 2, 5 and 6), and the microbial activity is stimulated by warm conditions (Bonnett et al., 2006;  
466 Dinsmore et al., 2013; Koehler et al., 2009; Scott et al., 1998). Similar conclusions were drawn in  
467 modelling work by Lumsdon et al. (2006) who found that temperature, used as a proxy for microbial  
468 activity, increases the solubility and hydrophilicity of DOC.

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

476 Finally, there was a significant negative relationship between pH and DOC concentrations ( $r = -0.58$ ,  
477  $P < 0.01$ ), which indicates that more acidic waters led to higher DOC concentrations. This negative  
478 correlation is in disagreement with the findings of Clark et al. (2005) who showed that DOC tends to  
479 increase at high flow because of its increased solubility as pH increases during rewetting after  
480 droughts. However, acidity has also been shown to be an indicator of the origin of water during flow  
481 events, with storm runoff from peaty water being more acidic compared to relatively alkaline water  
482 of groundwater origin (Soulsby et al. 2003). It could therefore be hypothesised that Aclands had a  
483 generally higher contribution of peaty water during storm events compared to Spooners, as found

484 by Grocott (2011) in the same catchments, because of differences in peat properties and  
485 hydrological functioning. This would further suggest that DOC concentrations are related to water  
486 movements in the peat rather than changes in soil water chemistry. However, this assumption will  
487 be tested in further analysis (Grand-Clement et al., forthcoming).

#### 488 4.3. Control of antecedent conditions over DOC concentrations

489 Antecedent conditions (depth to water table, temperature, discharge and rainfall) were considered  
490 here, both over short- (1 to 5 days) and long- (14 and 30 days) time-scales, in order to try to  
491 understand how environmental factors impacted on DOC concentrations (Hypothesis 3). These  
492 parameters were explored because they have been observed to influence either DOC production in  
493 soils or transport during rainfall events (e.g. Clark et al., 2009; Tipping et al., 1999; Wilson et al.,  
494 2011b) in deeper peat. The results from the stepwise linear regression model showed that both  
495 long-term (i.e. depth to water table in the 30 days prior to the event) and immediate changes (i.e.  
496 both temperature and discharge during the event) simultaneously affected DOC concentrations. This  
497 finding indicates that overall, long-term aeration due to low water table levels, was an important  
498 control on DOC concentrations ( $r = 0.73$ ), confirming the idea that it stimulates microbial activity and  
499 aerobic production of DOC in shallow peatlands as well as deep peat (Glatzel et al., 2006). This also  
500 explains the higher concentrations of DOC measured at Aclands compared to Spooners, as Aclands  
501 was shown to be a significantly drier catchment, and seasonal variations with higher concentrations  
502 at times of deeper water table. Although neither pre-existing temperature, discharge nor rainfall  
503 were direct contributing variables to the model, water tables are generally influenced by water input  
504 (rainfall), temperature (controlling evapotranspiration), and movement through the peat; these  
505 factors are therefore likely to be indirectly considered in the model. pH was not included in the  
506 results of the stepwise regression either, which indicates that it did not exert a significant control  
507 over DOC concentrations in the peatlands of Exmoor, unlike findings by Clark et al. (2005; 2012) in  
508 conditions of flow recovery from drought. However, the lack of baseflow results in the present study  
509 prevents the inclusion of a pre-existing water pH variable in the statistical analysis, and therefore the  
510 full understanding of the role of pH in conditions of drought recovery.

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

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

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

#### 540 4.4. Changes in DOC characteristics

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

558 Results from Exmoor also showed a clear positive and linear relationship between DOC and E4/E6 ( $r^2$   
559 = 0.92 for both Aclands and Spooners), as well as seasonal variations and site differences. All this  
560 evidence points towards the products of increased microbial activity and decomposition (occurring  
561 both temporally and spatially) containing, comparatively, a higher proportion of more labile and less  
562 degraded FAs, despite being still predominantly composed of HAs. Our results agree with those of  
563 Worrall et al. (2002) in the deep blanket peat of Moor House NNR, where peaks in E4/E6 occur after  
564 the longest dry period and decrease as they are progressively flushed during storm events, whilst  
565 Clark et al. (2012) observed that drought produced more fractions that were less coloured. Results  
566 by Wallage et al. (2006) also showed significantly higher E4/E6 ratios in pore water at the surface  
567 (median = 6.23, range: 1.5-14) compared to deeper layers, explained by the presence of an upper  
568 layer of high microbial activity dominated by FAs from newly decomposed plant and litter, whereas

569 deeper, the decreased decomposition process is producing more mature and coloured HAs. Overall  
570 the findings presented here indicate that the DOC on Exmoor is mostly composed of complex HAs  
571 compounds, but that dryness increases the input of less complex compounds due to increased  
572 decomposition.

#### 573 4.5. Potential for restoration

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

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

## 594 **5. Conclusion**

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

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

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