



1 **The effect of drought on dissolved organic carbon (DOC)**
2 **release from peatland soil and vegetation sources**
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15

16 **Abstract:** Drought conditions are expected to increase in frequency and severity as the climate changes,
17 representing a threat to carbon sequestered in peat soils. Downstream water treatment works are also at risk of
18 regulatory compliance failures and higher treatment costs due to the increase in riverine dissolved organic
19 carbon (DOC) often observed after droughts. More frequent droughts may also shift dominant vegetation in
20 peatlands from *Sphagnum* moss to more drought tolerant species. This paper examines the impact of drought on
21 the production and treatability of DOC from four vegetation litters (*Calluna vulgaris*, *Juncus effusus*, *Molinia*
22 *caerulea* and *Sphagnum spp.*) and a peat soil. We found that mild droughts caused a 39.6% increase in DOC
23 production from peat and that this DOC was harder to remove by conventional water treatment processes
24 (coagulation/flocculation). Drought had no effect on DOC production from vegetation litters, however large
25 variation was observed between typical peatland species (*Sphagnum* and *Calluna*) and drought tolerant
26 grassland species (*Juncus* and *Molinia*), with the latter producing more DOC per unit weight. This would
27 therefore suggest the increase in riverine DOC often observed post-drought is due entirely to soil microbial
28 processes and DOC solubility rather than litter-layer effects. Long term shifts in species diversity may,
29 therefore, be the most important impact of drought on litter layer DOC flux, whereas more immediate effects are
30 observed in peat soils. These results provide evidence in support of catchment management which increases the
31 resilience of peat soils to drought, such as ditch-blocking to raise water-tables.

32

33 **Keywords:** Dissolved organic carbon, DOC, drought, peat, drinking water treatment

34

35 **1.0 Introduction**

36 Organic rich peat soils are a major global carbon sink (Limpens et al., 2008) which have formed due to the
37 limited decay of recalcitrant plant litter found in peatland areas, coupled with anoxic conditions created by high



38 water-tables slowing decay (Billett et al., 2010; van Breemen, 1995). The locations in which these conditions
39 exist are threatened by climate change (Clark et al., 2010; Gallego-Sala and Prentice, 2012), and future climate
40 may also destabilise sequestered carbon (Evans and Warburton, 2010; Fenner and Freeman, 2011; Freeman et
41 al., 2001a).

42 Dissolved organic carbon (DOC) represents a significant flux of carbon from peatlands (Dinsmore et al., 2010)
43 and can also lead to difficulties for downstream drinking water treatment plants. DOC can cause colour, odour
44 and taste problems in drinking water and so must be removed as best as possible during treatment, commonly by
45 coagulation, flocculation and sedimentation/flotation. Any DOC which remains may act as a substrate for
46 microbial growth in the distribution system (Rodriguez and Sérodes, 2001) and can react during disinfection to
47 form disinfection by-products (DBPs) (Rook, 1974) which may have human health implications due to their
48 potential genotoxicity and carcinogenicity (Nieuwenhuijsen et al., 2009).

49 Droughts are projected to become more common under future climate conditions in the UK (Jenkins et al.,
50 2009). Droughts can have drastic consequences for peatland carbon storage and riverine DOC concentrations
51 due to the 'enzymatic latch' mechanism, whereby decomposition is suppressed due to the inhibitory effect of
52 phenolic compounds. Under drought conditions, the water table is lowered, creating oxic conditions which
53 stimulates phenol oxidase enzymes, thereby reducing the concentration of phenolics and their inhibitory effect
54 on hydrolase enzymes (Fenner and Freeman, 2011; Freeman et al., 2001a). Altered redox conditions can also
55 change the controls on DOC solubility, meaning organic carbon is not solubilised during the drought but instead
56 flushed from the system once redox conditions return to normal (Clark et al., 2006, 2005; Clark et al., 2011).

57 These processes have led to numerous observations of increased riverine DOC after droughts which may remain
58 elevated for years after the event (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall and Burt,
59 2004). How drought effects the treatability of DOC is less well understood although some authors have noted an
60 increase in the hydrophilic component during droughts and more hydrophobic character post-drought (Clark et
61 al., 2011; Scott et al., 1998; Watts et al., 2001). Hydrophobic DOC is commonly regarded as being easier to
62 remove via coagulation than the hydrophilic fraction (Bond et al., 2011; Matilainen et al., 2010).

63 The impact of climate change on DOC production and drinking water treatment is complex and involves a
64 number of biogeochemical cycles (Ritson et al., 2014b). Vegetative change in peatlands has occurred in the
65 recent past (Chambers et al., 2007b) and is projected to continue with *Sphagnum* mosses, which are favoured for
66 peat formation, giving way to vascular plants (Fenner et al., 2007; Weltzin et al., 2003). Many grassland species
67 (*Juncus effusus*, *Molinia caerulea*) have encroached on peatland areas as a result of anthropogenic pressures
68 such as nutrient deposition and management practices (Berendse, 1994; Chambers et al., 2007a; McCorry and
69 Renou, 2003; Shaw et al., 1996). These species are adapted to higher nutrient availability (Aerts, 1999) and thus
70 can out-compete peatland species if nutrient levels are elevated through, for example, nitrogen deposition
71 (Berendse et al., 2001).

72 Vegetative change has implications for carbon storage in peatlands, as *Sphagnum* is responsible for a number of
73 mechanisms (e.g. the production of recalcitrant litter) which allow carbon to be stored over long time periods
74 (van Breemen, 1995). Conversely, many vascular plants can destabilise colonised peat, stimulating
75 decomposition by adding labile carbon at the surface and through their root systems (Fenner et al. 2007; Gogo et
76 al. 2010). As such, a number of programmes have aimed to promote *Sphagnum* dominance for carbon storage



77 and other ecosystem services (Grand-Clement et al., 2013). However, further evidence is needed on the water
78 quality outcomes of such interventions and the implications for water treatment.
79 Previous work has highlighted both the vegetative source and climate controls on production affecting the ease
80 of removal of DOC and the formation of DBPs (Gough et al., 2012; Reckhow et al., 2007; Ritson et al., 2014a;
81 Tang et al., 2013). The present research sought to quantify the effect of drought on peatland DOC flux and any
82 interaction with projected changes in litter input. To this end, climate simulations of varying drought severities
83 defined in terms of percentiles of mean monthly rainfall were performed on four typical peatland vegetation
84 types (*Calluna vulgaris*, *Juncus effusus*, *Molinia caerulea* and *Sphagnum spp.*) and a peat soil. After a six-week
85 drought simulation, the DOC released upon rewetting was analysed in terms of optical properties and
86 coagulation removal efficiency with ferric sulphate to determine: (a) whether drought conditions affect DOC
87 production from peatland litter and soil types and (b) whether peatland species and invasive, drought tolerant
88 vegetation produce different quantities and quality of DOC with respect to drinking water treatment.

89

90 **2.0 Methodology**

91 **2.1 Field site and sample collection**

92 Samples were collected from the Spooners site (51° 07'23.3" N 3° 45'11.8" W) in Exmoor National Park, UK at
93 approximately 400 m elevation. Further site details can be found in Ritson et al., (2014a). The site is part of the
94 MIREs project (Arnott, 2010) and was chosen as this area has been highlighted as a marginal peatland which
95 may be vulnerable to climate change (Clark et al., 2010).

96 Samples of vegetation and peat soil were collected in one day in May 2014 and were sealed in airtight bags in a
97 chilled container for transport from the field and stored in the dark at 4°C before use. For vascular plants, litter
98 was collected as standing dead biomass. As the decomposition of *Sphagnum* is a continuum process, the section
99 2-4 cm below the capitulum was taken as equivalent to freshly senesced "litter", as in other studies (e.g.
100 Bragazza et al., 2007). Samples were sorted to remove any vegetation not belonging to the target species and
101 then cut to 2 cm length and homogenised. Peat samples were collected using a screw auger and peat from 10-30
102 cm depth was used in the experiments. Peat samples were sorted to remove as many roots as possible but in sites
103 where *Molinia* was present some fine roots remained.

104 The start times of the drought simulations for different DOC sources were staggered by up to two weeks to
105 allow prompt analysis of water extracts at the end of the experiments. Preliminary work suggested chilled
106 storage gave no significant difference in the amount of water extractable DOC or UV absorbance properties
107 after three weeks of storage in the dark at 4°C.

108

109 **2.2 Experimental Design**

110 The vegetation and peat samples were homogenised by hand and randomly assigned a drought treatment in a
111 five (vegetation types) x four (drought treatments) design with five replicates per treatment, giving 100 samples
112 in total.

113 Data were obtained from regional historic climate records of the UK Meteorological Office for the south west of
114 England for the period 1910-2013 (UK Met Office 2014) and these values were used to define three severities of
115 drought and a control value. Data for the months of June, July and August (310 months in total) were used to



116 find the 50th, 25th, 10th and 5th percentile for total monthly rainfall and these values (Table 1) have been used to
 117 set control, mild, moderate and severe droughts, respectively.

118

119 **Table 1: Monthly rainfall for control group and three severities of drought**

Drought Treatment	Monthly rainfall total (mm)
Control (50 th percentile)	79.0
Mild (25 th percentile)	51.5
Moderate (10 th percentile)	34.7
Severe (5 th percentile)	23.3

120

121 The number of days of rain per month was fixed at a baseline value of eleven (regional average for June, July
 122 and August) and temperature ranged between the mean daily maximum of 18.9 for twelve hours and then and
 123 the mean daily minimum of 10.7 °C for twelve hours, calculated using the same historical UK Meteorological
 124 Office datasets for the south west of England.

125

126 **2.3 Experimental procedure and laboratory methods**

127 As in other decomposition studies, vegetation samples were air-dried to constant weight then mixed before
 128 subsampling (e.g. Latter et al., 1998). Five subsamples of each vegetation type were then oven-dried at 70 °C
 129 until constant weight, to determine the air-dry to oven-dry conversion factor. The peat samples were not air-
 130 dried before use as this would have changed the redox conditions within the peat and created a hydrophobic
 131 layer which can cause problems for re-wetting (Worrall et al., 2003). This will mean less accuracy in
 132 determining the starting weight of the peat sample as some variation in water content may exist, however this
 133 was minimised by effective homogenisation.

134 Buchner funnels fitted into amber-glass bottles were used to hold the sample and collect the simulated rainfall.
 135 Approximately 2 g dry-weight of air-dried vegetation/peat was used, however a lower weight of sample was
 136 used for *Sphagnum* (~0.65 g) and *Molinia* (~1.5 g) as this was enough to fill the Buchner funnel. The peat
 137 samples were spread over the area of the funnel so that a seal was created and the simulated rainwater infiltrated
 138 the peat rather than draining directly into the funnel.

139 The samples were then placed in an incubator for six weeks with simulated rainfall applied eleven times per
 140 month using high purity reverse osmosis (RO) treated water as per Table 1, following the methodology of
 141 Ritson et al. (2016).

142 As the samples were collected from the field and had been in contact with litter and soil, no inoculation with
 143 microorganisms was required as a suitable decomposer community was likely to be present (Van Meeteren et
 144 al., 2007). In this experiment the action of invertebrates and other microfauna was excluded, however their role
 145 in the decay of peatland litter is minimal (Dickinson and Maggs, 1974), although their role in DOC production
 146 from peat soils may be more significant (Cole et al., 2002).

147 At the end of the six week simulation the samples were air-dried and weighed. Water extractable DOC from the
 148 air dried sample was taken to simulate re-wetting following the end of the drought. DOC was extracted from soil
 149 and vegetation samples using approximately 20:1 ratio of RO treated water to sample. Previous work has shown
 150 that the amount of water used to extract DOC and whether one extraction is performed or sequential extractions



151 to simulate multiple rainfall events gives no significant variation in DOC quality (Don and Kalbitz, 2005, Soong
152 et al., 2014), only changes in the total amount of carbon. DOC was measured as non-purgeable organic carbon
153 (NPOC) via a UV/persulphate oxidation method on a Shimadzu TOC-V instrument. The method detection limit
154 was determined by running five blank samples and using the value of three times the standard deviation. This
155 was found to be 0.05 mg l^{-1} .

156 UV and fluorescence analysis was undertaken before coagulation/flocculation jar testing. UV absorbance was
157 measured on a Perkin Elma Lambda 3 using a 1-cm pathlength quartz cuvette and the specific absorbance,
158 SUVA, was calculated as the absorbance at 254 nm in units of m^{-1} divided by the NPOC content (mgC l^{-1}).
159 Fluorescence analysis was completed using a Vary Eclipse fluorescence spectrophotometer where samples were
160 scanned at excitation wavelengths between 220 and 450 nm at 5 nm intervals and the resulting emission
161 recorded between 300 and 600 nm at 2 nm intervals. An R script was produced based on exiting scripts
162 (Lapworth and Kinniburgh, 2009) which performed a blank subtraction, masked out Rayleigh and Raman
163 scattering, visualised the data and calculated fluorescence indices. Data were normalised to the Raman
164 scattering peak of a RO water sample to allow comparison to other laboratories (Lawaetz and Stedmon, 2009).
165 The ‘peak C’ measure, related to humic-like character, and the tryptophan-like peak, ‘peak T’ were defined as in
166 Beggs et al., (2013).

167 Coagulation was performed on 350 ml of sample diluted to 3 mg l^{-1} DOC using a Phipps and Bird PB-700
168 paddled jar-tester (Phipps and Bird Ltd., Virginia, USA). After settling, the sample was filtered by Whatman
169 qualitative grade 2 filters to remove flocs before NPOC analysis. Preliminary work indicated the following
170 conditions gave effective DOC removal of similar samples: pH 5.5, 30.0 mg l^{-1} ferric sulphate dosed with 28.5
171 mg l^{-1} calcium hydroxide for pH control during a flash mix of one minute at 175 rpm, followed by a slow mix of
172 30 minutes at 60 rpm and then one hour of settling. Assessment of DBP formation was attempted, however
173 analysis within the two week period specified in the method was not possible due to instrument failure so data
174 quality could not be assured.

175

176 **2.4 Data analysis and statistical methods**

177 Statistical analysis was performed in the open source programming language, R, and SPSS version 21 (IBM).
178 Due to problems with normality and heteroscedasticity a Box-Cox transform (Box and Cox, 1964) was applied
179 to the variables before testing with a factorial ANOVA. A Tukey HSD post-hoc procedure was used for
180 pairwise comparisons between the DOC sources and drought conditions. Estimates of effect sizes were made
181 using ω^2 as this is suitable for small samples sizes (Keselman, 1975). Interactive effects from the omnibus
182 ANOVA were followed up using multiple one-way ANOVAs with a Holm-Šidák correction to control the
183 inflation of type one error (Holm, 1979; Šidák, 1967).

184

185 **2.5 Repetition of the control group**

186 To further investigate the effect of oxygenation of peat on DOC production and treatability, the control
187 condition of this experiment was repeated in August 2015 using peat samples collected from similar
188 ombrotrophic peatland sites in Dartmoor National Park (site details available in Ritson et al., 2016). Water
189 extractable DOC was taken from a subsample before the climate simulation began and analysed for fluorescence
190 and UV properties. Approximately 3.5 g dry weight of peat was then incubated using the same temperature and



191 rainfall as the control samples of the drought experiment with three replicates. After six weeks water extractable
 192 DOC was again taken for fluorescence and UV analysis to assess any changes in DOC quality.

193

194 3.0 Results

195 3.1 Omnibus ANOVA

196 A factorial ANOVA was performed exploring the source, drought and interactive effects on DOC, SUVA, DOC
 197 removal efficiency and the removal of SUVA (Table 2). Extractable DOC and SUVA had significant source,
 198 drought and source*drought effects suggesting that there is variation in the sensitivity of the sources to drought.
 199 No drought effects were observed for DOC removal or SUVA removal, although the source had strong effects
 200 on these parameters. For all significant results the effect size for the source was much greater than that for the
 201 drought treatment.

202

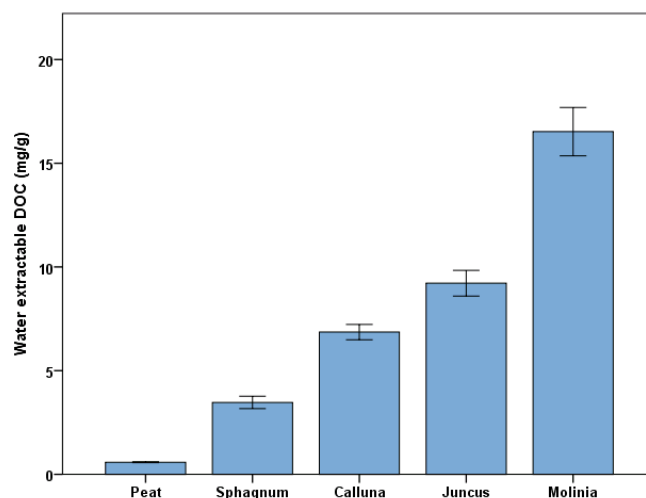
203 **Table 2: p-values from factorial ANOVA (significant values have been highlighted in bold and displayed**
 204 **with ω^2 estimate of effect size in brackets)**

Variable	Water extractable DOC	SUVA	DOC removal	SUVA removal
Factor				
DOC source	<0.001 (0.945)	<0.001 (0.422)	<0.001 (0.396)	<0.001 (0.331)
Drought	0.007 (0.004)	0.007 (0.034)	0.418	0.475
DOC source*Drought	0.050 (0.004)	0.005 (0.054)	0.234	0.951

205

206 3.2 Water extractable DOC

207 The omnibus ANOVA suggests both significant source and drought effects as well as an interaction, suggesting
 208 the effect of drought varies between the sources. The mean DOC extracted for all samples from each source is
 209 shown in Figure 1. The vegetation samples produced more DOC than the peat soil ($0.58 \pm 0.02 \text{ mg g}^{-1}$) with the
 210 peatland species, *Sphagnum* and *Calluna*, producing 3.47 ± 0.30 and $6.86 \pm 0.37 \text{ mg g}^{-1}$, respectively whereas
 211 the grassland species, *Juncus* and *Molinia*, produced much more at 9.21 ± 0.62 and $16.52 \pm 1.17 \text{ mg g}^{-1}$,
 212 respectively. A Tukey HSD test suggested that all DOC sources have significantly different means at the $p < 0.01$
 213 level except the *Calluna* - *Juncus* comparison which was significantly different at the $p < 0.05$ level.



214

215 **Figure 1: Water extractable DOC of all samples across the different DOC sources (n=20 per source).**216 **Error bars at one standard error.**

217

218 To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on each of
 219 the sources (Table 3) using a Holm-Šidák correction to control the inflation of type one error. This method
 220 changes the value used for alpha, the significance level, based on how many comparisons have been performed
 221 starting with the source with lowest p value and moving to the next lowest until an insignificant comparison is
 222 found.

223

224 **Table 3: ANOVA results testing the effect of drought on water extractable DOC from different sources.**

225 **Significant effects (Holm-Šidák correction) are highlighted in bold with the ω^2 estimate of effect size in**
 226 **brackets.**

227

DOC Source	p value (DOC extraction)	Alpha used for comparison
Peat	0.010 (0.393)	0.010
<i>Juncus</i>	0.038	0.013
<i>Sphagnum</i>	0.097	-
<i>Calluna</i>	0.418	-
<i>Molinia</i>	0.550	-

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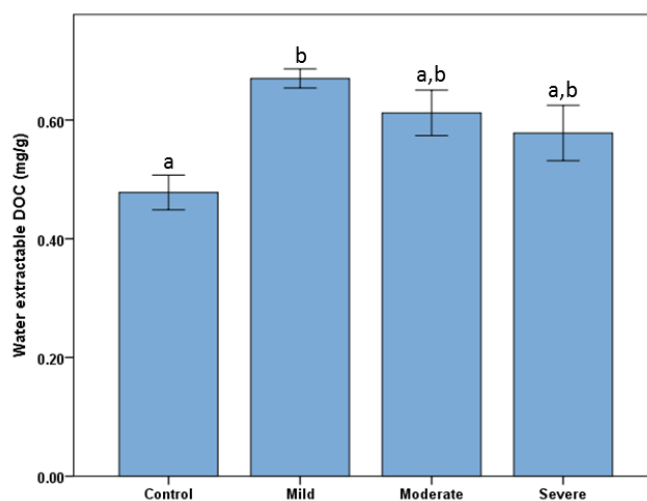
229 Due to the decrease in the level of significance of the p value in the Holm-Šidák method only the peat source
 230 was found to have a drought effect on water extractable DOC. The mean values were 0.48, 0.67, 0.61 and 0.58
 231 mg g⁻¹ for the control, mild, moderate and severe treatments, respectively, and this is shown in Figure 2. The
 232 mild drought treatment gave a significant increase in extractable DOC, indicated by a Tukey test for comparison
 233 to the control group (p=0.007). This corresponded to a 39.6% increase in DOC production for the mild drought



234 treatment. Taken together, the main effects and interaction and ω^2 values suggest that the source of DOC is the
235 most important factor on extractable DOC and that the effect of drought is significant only for the peat soil and
236 not for the vegetation.

237

238



239

240 **Figure 2: DOC extracted from peat on rewetting following different severities of drought (n=5 per**
241 **treatment). Letters indicate statistically similar groups from the Tukey test. Error bars at one standard**
242 **error.**

243

244 A larger standard error in the moderate and severe drought treatments meant that these were not significantly
245 different from the control ($p=0.060$ and $p=0.204$, respectively). Observations made throughout the experiment
246 suggested that in the severe treatment there was a large variation in the extent to which each replicate dried out.
247 Once peat becomes dry, a hydrophobic layer forms (Spaccini et al. 2002; Worrall et al. 2003), meaning that less
248 water will infiltrate the sample, therefore possibly increasing the severity of the drought beyond the
249 experimental design.

250 Variation in peat water content during the experiment was not recorded; however the water content of the peat
251 samples was measured at the end of the experiment. This averaged 16.11, 14.14, 15.11 and 5.95 g with standard
252 errors of 7.7, 3.0, 15.9 and 28.1% for the peat control, mild, medium and severe drought treatments respectively.
253 The much larger standard error in final water content agrees with observations during the experiment and could
254 perhaps explain some of the increased variation in extractable DOC for the severe drought treatment. This
255 hypothesis was tested by comparing the variation from group mean in final water content for each sample with
256 the variation from group mean in extractable DOC. These two measures of variance were found to correlate
257 (Spearman's ρ coefficient 0.484, $p=0.031$) suggesting some of the variation in DOC extracted may be explained
258 by different water contents between the samples in each treatment. This could have been caused by small
259 variations in the way rain was applied over the area of the sample or because shrinkage of the peat mass allowed



260 water to pass through the funnel rather than infiltrate the peat, again possibly increasing the severity of drought
 261 beyond the experimental design.

262

263 3.3 SUVA

264 Mean values of SUVA in $\text{L mg}^{-1} \text{m}^{-1}$ for the different sources were in the order *Molinia* (3.03 ± 0.38), peat (3.01
 265 ± 0.15), *Juncus* (2.04 ± 0.06), *Calluna* (1.66 ± 0.14) and then *Sphagnum* (1.34 ± 0.13). The Tukey HSD test
 266 suggested that the mean values for SUVA formed three subsets with peat and *Molinia* > group two *Calluna* and
 267 *Juncus* > *Calluna* and *Sphagnum*.

268

269 To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on SUVA
 270 from each of the sources (Table 4) using a Holm-Šidák correction.

271

272 **Table 4: ANOVA results testing the effect of drought on SUVA for different DOC sources. Significant**
 273 **effects (Holm-Šidák correction) are highlighted in bold with the ω^2 estimate of effect size in brackets**
 274

DOC Source	p value (SUVA)	Alpha used for comparison
<i>Molinia</i>	0.001 (0.546)	0.010
<i>Sphagnum</i>	0.278	0.013
<i>Calluna</i>	0.436	-
Peat	0.696	-
<i>Juncus</i>	0.741	-

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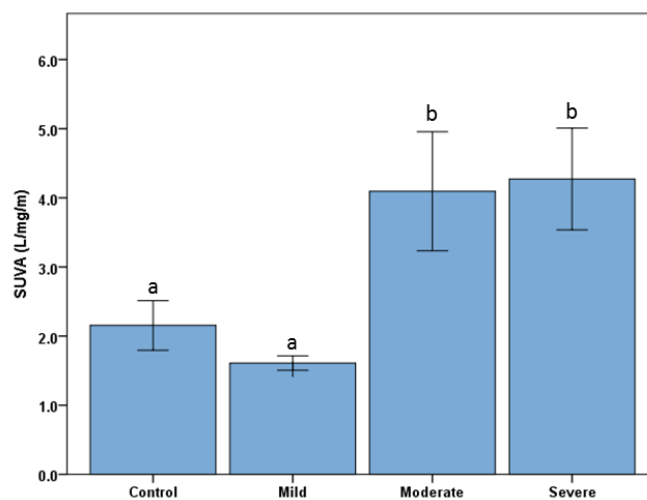
276 Tukey's test suggested that both the moderate and severe drought treatments were significantly different than
 277 the control ($p=0.045$ and 0.026 , respectively) with means of 2.15 , 4.09 and $4.27 \text{ L mg}^{-1} \text{m}^{-1}$ for the control,
 278 medium and severe treatment, respectively. Figure 3 shows a graph of SUVA for *Molinia* DOC from the
 279 different treatment groups. The SUVA value approximately doubles between the control and the moderate and
 280 severe droughts suggesting a large climatic control on the production of aromatic DOC from *Molinia* litter.

281 Taken together, the main effects and interaction and ω^2 values suggest that the source of DOC is the most
 282 important factor on SUVA and that the effect of drought is significant only for *Molinia* litter and not for the
 283 other vegetation types or the peat soil.

284



285



286

287 **Figure 3: SUVA value of *Molinia caerulea* derived DOC produced under differing severities of drought**
 288 **(n=5 per treatment) with error bars at one standard error. Letters indicate statistically similar groups**
 289 **from the Tukey test.**

290

291

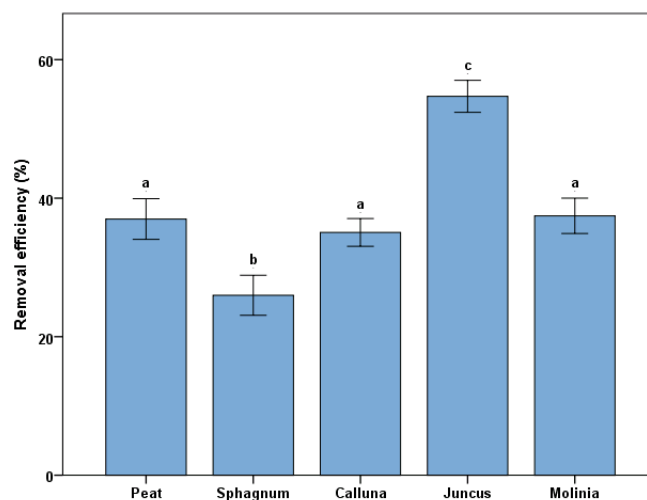
292 3.4 DOC removal efficiency

293 Mean values for DOC removal by coagulation with ferric sulphate were in the order of *Juncus* (54.7 ± 2.3 %),
 294 *Molinia* (37.5 ± 2.6 %), peat (37.0 ± 2.9 %), *Calluna* (35.1 ± 2.0 %) and then *Sphagnum* (26.0 ± 2.9 %). The
 295 Tukey HSD test suggested that the mean values for DOC removal efficiency fell into three subsets with similar
 296 means in the order *Juncus* > *Molinia*, peat and *Calluna* > *Sphagnum*. The factorial ANOVA suggested no drought
 297 effects on removal efficiency ($p=0.418$). The removal efficiency for all samples from each DOC source is
 298 shown in Figure 4. *Juncus* DOC proved to be the easiest to remove via coagulation/flocculation with peat,
 299 *Calluna* and *Molinia* all relatively easily removed at just under 40%. Comparatively poor removal was achieved
 300 for *Sphagnum* DOC (<30%) which may be attributable to the low SUVA and peak C measure also found.

301



302



303

304 **Figure 4: DOC removal efficiency by coagulation/flocculation for different DOC sources (n=20 for each**
 305 **source, error bars at one standard error, letters indicate statistical subset according to Tukey test).**

306

307 3.5 SUVA removal efficiency

308 The removal of aromaticity, measured by SUVA, is of interest in drinking water treatment as aromatic

309 compounds have a high propensity to form some of the regulated DBPs on chlorination (Bond et al., 2011).

310 Large, aromatic compounds are selectively removed by coagulation/flocculation and as expected good removal

311 (>70%) was observed for most of the samples. The mean values for the reduction in SUVA value following

312 coagulation with ferric sulphate was in the order of peat ($76.6 \pm 1.8\%$), *Sphagnum* ($76.3 \pm 2.5\%$), *Molinia*

313 ($67.7 \pm 4.7\%$), *Calluna* ($49.6 \pm 5.3\%$) and then *Juncus* ($44.5 \pm 2.3\%$). The Tukey HSD test suggested that

314 there were two subsets of DOC sources with similar means with peat, *Sphagnum* and *Molinia* > *Juncus* and

315 *Calluna*. As with the overall DOC removal efficiency, there were no drought effects on SUVA removal

316 ($p=0.475$). *Sphagnum* DOC showed good removal of SUVA despite relatively poor removal of total DOC,

317 suggesting the aromatic compounds present in the sample are easily removed but that a large pool of aliphatic

318 compounds are also present and these are more difficult to treat by conventional means.

319

320 3.6 Correlations between measures of DOC quality and treatability

321 A number of DOC quality indices based on absorbance and fluorescence measures were tested. The correlation

322 coefficients for the different quality and treatability parameters are shown in Table 5. Peak C, a humic-like

323 fluorescence peak, showed the best correlation with removal efficiency while the ratio of humic-like to protein-

324 like fluorescence (Peak C/T) gave a lower but still significant correlation coefficient. The magnitude of peak C

325 values were in the order *Juncus*>*Molinia*>*Calluna*>peat>*Sphagnum* which is consistent with data on removal

326 efficiency. The SUVA value showed the best correlation with SUVA removal efficiency, suggesting that DOC

327 with a lower proportion of aromatic compounds (low SUVA value) contains aromatic compounds which are



328 harder to remove by coagulation, possibly meaning they are either low molecular weight and/or also contain
 329 hydrophilic groups.

330

331 **Table 5: Spearman's ρ for different DOC quality and treatability measures**

DOC quality measure	Treatability measure	Spearman's ρ
Peak C	DOC removal %	0.578, $p < 0.001$
Peak C/T	DOC removal %	0.268, $p = 0.007$
SUVA	SUVA removal %	0.445, $p < 0.001$
Specific Peak C	SUVA removal %	0.235, $p = 0.019$

332

333

334 **3.7 Repetition of control group**

335 The data obtained from DOC extracted before and after the repeated simulation were analysed using student's t-
 336 test (equal variances assumed, confirmed using Levene's test) to assess whether the DOC extracted was
 337 significantly different following six weeks of exposure to oxygen without any experimental treatment. The
 338 results of this analysis are shown in Table 6.

339

340 **Table 6: t-tests for pre and post-incubation peat samples (significant differences highlighted in bold)**

Variable	t test	p value	% change
Extractable DOC	5.685	0.005	+41.6
Fluorescence peak C	8.168	0.011	-29.2
Fluorescence C/T	0.180	0.866	Not significant
SUVA	3.195	0.033	-23.0

341

342 Water extractable DOC increased significantly from 0.19 to 0.27 mg g⁻¹, an increase of 41.6%. The SUVA value
 343 decreased at the end of the simulation from 3.62 to 2.85 L mg m⁻¹, as did the fluorescence Peak C measure,
 344 which suggests a decrease in the level of aromaticity and humification of the DOC, respectively. This result may
 345 explain why poorer DOC removal for peat DOC was observed in this experiment than in our previous work
 346 (Ritson et al., 2016) as exposure to oxygen reduces the aromaticity of peat DOC and therefore its amenability to
 347 removal via coagulation.

348

349 **4.0 Discussion**

350 **4.1 Water extractable DOC**

351 The peat soil was affected by the drought treatment with higher extractable DOC observed at the mild severity.
 352 This finding is consistent with the 'enzymatic latch' hypothesis that increased oxygenation of peat engages a
 353 biogeochemical cascade whereby increased phenol oxidase activity ends the phenol-induced inhibition of
 354 hydrolase enzymes, thus increasing overall organic matter decomposition (Freeman et al., 2001a). This is also
 355 confirmed by the replication of the control treatment which showed exposure to oxygen even in the absence of
 356 drought increased DOC production and decreased DOC aromaticity. This finding has implications for all



357 laboratory studies which remove peat from anoxic conditions as these may not be representative of in-situ
358 conditions.

359 No effect was observed with the moderate and severe drought treatments which may be explained by water
360 scarcity limiting microbial activity (Toberman et al., 2008) and/or increased hydrophobic protection decreasing
361 the extractable DOC on rewetting. The very low final water content of the severe treatment and observations of
362 drying out and shrinkage of the peat mass throughout the experiment add weight to these possible explanations,
363 although actual rates of microbial respiration were not monitored during the experiment.

364 The lack of a drought effect on DOC production from any of the vegetation types suggest the pulse in DOC
365 observed post-drought elsewhere in catchment scale studies (Evans et al., 2005; Scott et al., 1998; Watts et al.,
366 2001; Worrall and Burt, 2004) is likely to be due to the oxygenation of peat soils rather than any litter layer
367 effects. This increase in peat-derived DOC is significant for downstream water treatment as our previous work
368 showed this has more environmental persistence than vegetation sources (Ritson et al., 2016) and the UV and
369 fluorescence data suggested DOC from peat exposed to oxygen may be more difficult to remove by
370 conventional treatment measures. High DOC production was noted for the vascular plants, suggesting they may
371 be an important source of DOC within peatland catchments during the period of their senescence, although
372 drought does not affect the amount they produce. Drought conditions may, however, precipitate a change in
373 vegetation type favouring more drought-tolerant species (Bragazza, 2008), which may have longer term effects
374 for peatland biogeochemistry.

375 The amount of DOC extracted from *Sphagnum* was low, which may be due to the fact that its litter is
376 recalcitrant to decay due to its high polyphenol content and numerous compounds with antimicrobial and
377 antifungal properties (van Breemen, 1995). The other typically upland species, *Calluna*, produced the second
378 least amount of DOC of the vegetation types, which also agrees with literature surrounding the recalcitrance of
379 its litter (Aerts, 1995; Huang et al., 1998) and field studies suggesting areas of *Calluna* produce more porewater
380 DOC than *Sphagnum* (Armstrong et al., 2012). The two grassland species, *Molinia* and *Juncus*, produced much
381 larger amounts of DOC per g of dry weight. This is in keeping with the growth strategy of these species,
382 whereby they rapidly produce a large amount of above-ground biomass and produce litter which decays readily,
383 providing a positive feedback to its strategy of rapid growth and fast nutrient cycling (Aerts, 1999; Mann and
384 Wetzel, 2000). This growth strategy is in contrast to that of the upland species *Calluna* and *Sphagnum*, which
385 have adapted to low nutrient availability and therefore grow slowly, have nutrient poor litter and invest fewer
386 resources in material which cycles rapidly (Aerts, 1999). Correlations between litter C:N ratio, suggesting
387 nutrient availability, and amount of extractable DOC have been found in our previous work (Ritson et al., 2016)
388 and elsewhere in the literature (Soong et al, 2014).

389 *Molinia* encroachment is a well acknowledged problem in Europe (Chambers et al., 2007b; Heil and Diemont,
390 1983; Hughes et al., 2007; Milligan et al., 2004) and nitrogen deposition and drier summers may mean more
391 grassland species in the UK uplands in the future. The results of this study suggest the transition from
392 *Sphagnum* to *Calluna* and *Molinia* observed in a paleoecological study of the area nearby our Exmoor site
393 (Chambers, 1999) may have increased the amount of extractable DOC in the litter layer on g per g basis, as well
394 as increased the seasonality of its export (Ritson et al., 2016). The much greater effect sizes for DOC source
395 versus drought controls in this study and temperature and rainfall controls in previous work (Ritson et al.,
396 2014a) suggest that the source of the DOC may be the primary driver of DOC quantity and quality in peatland



397 litters, consistent with litter decomposition studies in boreal peatlands (Straková et al., 2011). This has important
398 implications for overall soil carbon stability in peatlands as the addition of labile carbon from litter can stimulate
399 the decomposition of older carbon (Fontaine et al., 2007).

400 Studies concerning vegetation control of pore-water DOC are limited, but are reviewed in Ritson et al. (2016).
401 Fenner et al. (2007) found elevated CO₂ caused a transition from *Sphagnum* to *Juncus* dominance on monoliths
402 from flush peat which gave a 66% rise in DOC, attributed to an increase in above-ground biomass, more labile
403 litter and stimulation of peat decomposition through root exudation. Vestgarden et al., (2010) found DOC in
404 pore-waters beneath different vegetation types to be in the order *Molinia*>*Calluna*>*Sphagnum* in shallow
405 samples but *Sphagnum* had higher concentrations than the vascular plants at depth and showed less seasonal
406 variation. This has been linked to the seasonal growth cycles of vascular plants in peatlands which provide litter
407 which decomposes rapidly and produces a large amount of DOC on a mg per g basis creating greater seasonality
408 in DOC export (Ritson et al., 2016).

409

410 4.2 SUVA

411 The SUVA value has been linked to the aromaticity of DOC (Weishaar et al., 2003) and is of interest as a
412 predictor of coagulation removal efficiency and DBP formation (Matilainen et al., 2011) in water treatment. The
413 highest SUVA value was observed for the peat soil and *Molinia* litter, and the lowest value for the statistical
414 subset of *Sphagnum* and *Calluna*. In a similar trend to DOC production, it appears that the grassland species
415 produce DOC of greater aromaticity than the peatland species. *Molinia* also showed an interactive effect with
416 the drought treatment, with a greater flux of aromatic compounds at the moderate and severe treatments,
417 suggesting dry conditions are favourable for the breakdown and/or solubilisation of aromatic compounds in
418 *Molinia* litter. *Molinia* DOC may, therefore, contribute to the increase in the aromaticity of peatland DOC
419 observed after droughts at the catchment scale (Scott et al., 1998; Watts et al., 2001), although solubility
420 controls on peat-derived DOC may be more important (Clark et al., 2006, 2005; Clark et al., 2011).

421 No drought effect was found for the SUVA value of peat which is in contrast to field studies which have shown
422 a decrease in aromaticity of DOC during drought due to solubility controls and an increase in aromaticity on
423 rewetting (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall et al., 2004). This may be explained
424 by the fact that field studies have shown an increase in DOC aromaticity over many years, whereas this study
425 examined a single rewetting event following drought, so the altered biogeochemical controls on DOC
426 aromaticity may not have had enough time to exert a significant effect. The laboratory conditions may also have
427 played a part, as the control sample is likely to have been exposed to more oxygenation through sample
428 collection and setup of the experiment than undisturbed peat in the field, therefore increasing its similarity to the
429 treatment conditions. The changes in DOC properties when the control group was repeated would appear to
430 confirm this hypothesis.

431 These results suggest encroachment of grassland species into the uplands will increase seasonal DOC flux from
432 the litter layer and increase the aromaticity of exported DOC and create a drought effect where *Molinia* litter is
433 present. The lack of a drought effect for peat suggests that the long-term effects caused by water table
434 drawdown identified elsewhere in the literature will likely be more important for DOC flux than the short-term
435 effects studied here.

436



437 **4.3 DOC and SUVA removal**

438 DOC removal for all sources were typical of literature values (Matilainen et al., 2010), with *Juncus* DOC
439 proving the easiest to remove and *Sphagnum* DOC the hardest. Repeating the control condition and measuring
440 DOC production and quality parameters allowed an estimate of the effect of oxygen exposure for peat samples.
441 This showed a decrease in SUVA value and humic-like character (fluorescence Peak C) as well as a large
442 increase in extractable DOC. These changes in quality parameters may provide an explanation of why poorer
443 removal by coagulation was achieved for peat following this drought experiment than had been observed in our
444 previous work (Ritson et al., 2016) as less aromatic/humified material is likely to be harder to remove by
445 coagulation (Bond et al. 2011). Poorer removal was observed for *Sphagnum* than in our previous work; the
446 effect of more oxygenated conditions on vegetation decomposition remains an area for further research,
447 particularly as climate change may increase the likelihood of water table draw down in peatlands.
448 The coagulation removal efficiency could best be explained by the Peak C fluorescence index, suggesting humic
449 substances content was the strongest predictor of DOC removal. This is in contrast to our previous work which
450 found the ratio of humic to protein-like DOC to be the most important predictor (Ritson et al. 2014b). Our
451 previous work used DOC collected throughout a two-month simulation rather than a single re-wetting event at
452 the end. The samples will, therefore, have likely undergone microbial processing during this simulation and
453 consequently an increase in the amount of autochthonous DOC, hence the greater importance of the
454 fluorescence measure of protein-like DOC.

455

456 **5.0 Conclusions**

457 Climate projections for the UK vary, however most agree the likelihood of droughts in the future is set to
458 increase. The results of this research suggest the dominant effect of drought on peatland DOC sources is to
459 increase the amount and decrease the treatability of DOC from peat soils. This is likely due to the ‘enzymatic
460 latch’ mechanism increasing decomposition when oxic conditions prevail. No drought effect on different
461 vegetation litters was found, suggesting that the greatest effect of drought for vegetation may be facilitating
462 shifts to drought-tolerant species dominance rather than altering decomposition processes in the short term.
463 Oxygenation of peat appears to greatly increase extractable DOC whilst also decreasing the aromaticity and
464 humification, which may mean it is more difficult to remove at the treatment works. These results provide
465 support for catchment management programmes seeking to increase resilience to drought by raising peatland
466 water tables as a strategy for mitigating against high riverine DOC concentrations following droughts.

467

468 **Author contributions**

469 All authors developed the experimental design and advised on the subsequent analysis. Ritson performed the
470 experiments and data analysis. The manuscript was written by Ritson with contributions from all co-authors.

471

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 478
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