

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

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

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

36 **1.0 Introduction**

37 Organic rich peat soils are a major global carbon (C) sink (Limpens et al., 2008) which have formed due to the
38 limited decay of recalcitrant plant litter found in peatland areas, coupled with anoxic conditions created by high
39 water-tables slowing decay (Billett et al., 2010; van Breemen, 1995). The extent to which conditions favourable
40 to peat formation exist are threatened by climate change (Clark et al., 2010; Gallego-Sala and Prentice, 2012)
41 and altered precipitation patterns and more frequent droughts may destabilise sequestered C (Evans and
42 Warburton, 2010; Fenner and Freeman, 2011; Freeman et al., 2001a).

43 Dissolved organic carbon (DOC) represents a significant flux of carbon from peatlands at around 24% of net
44 ecosystem exchange C uptake (Dinsmore et al., 2010) and can also lead to difficulties for downstream drinking
45 water treatment plants. DOC can cause colour, odour and taste problems in drinking water and so must be
46 removed as best as possible during treatment, commonly by coagulation, flocculation and
47 sedimentation/flotation. Any DOC which remains may act as a substrate for microbial growth in the distribution
48 system (Rodriguez and Sérodes, 2001) and can react during disinfection to form disinfection by-products
49 (DBPs) (Rook, 1974) which may have human health implications due to their potential genotoxicity and
50 carcinogenicity (Nieuwenhuijsen et al., 2009).

51 Droughts are projected to become more common under future climate conditions in the UK (Jenkins et al.,
52 2009). Droughts can have drastic consequences for peatland C storage and riverine DOC concentrations due to
53 the 'enzymatic latch' mechanism, whereby decomposition is suppressed due to the inhibitory effect of phenolic
54 compounds. Under drought conditions, the water table is lowered, creating oxic conditions which stimulates
55 phenol oxidase enzymes, thereby reducing the concentration of phenolics and their inhibitory effect on
56 hydrolase enzymes (Fenner and Freeman, 2011; Freeman et al., 2001a). Altered redox conditions can also
57 change the controls on DOC solubility, meaning organic C is not solubilised during the drought but instead
58 flushed from the system once redox conditions return to normal (Clark et al., 2006, 2005; Clark et al., 2011).
59 These processes have led to numerous observations of increased riverine DOC after droughts which may remain
60 elevated for years after the event (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall and Burt,
61 2004). How drought affects the treatability of dissolved organic matter (DOM) is less well understood although
62 some authors have noted an increase in the hydrophilic component during droughts and more hydrophobic
63 character post-drought (Clark et al., 2011; Scott et al., 1998; Watts et al., 2001). Hydrophobic DOM is
64 commonly regarded as being easier to remove via coagulation than the hydrophilic fraction (Bond et al., 2011;
65 Matilainen et al., 2010).

66 The impact of climate change on DOC production and drinking water treatment is complex and involves a
67 number of biogeochemical cycles (Ritson et al., 2014b). Vegetative change in peatlands has occurred in the
68 recent past (Chambers et al., 2007b) and is projected to continue with *Sphagnum* mosses, which are favoured for
69 peat formation, giving way to vascular plants (Fenner et al., 2007; Weltzin et al., 2003). Many grassland species
70 (*Juncus effusus*, *Molinia caerulea*) have encroached on peatland areas as a result of anthropogenic pressures
71 such as nutrient deposition and management practices (Berendse, 1994; Chambers et al., 2007a; McCorry and
72 Renou, 2003; Shaw et al., 1996). These species are adapted to higher nutrient availability (Aerts, 1999) and thus
73 can out-compete peatland species if nutrient levels are elevated through, for example, nitrogen deposition
74 (Berendse et al., 2001). Their rooting systems are also commonly deeper and more extensive than upland plant
75 species, facilitating colonisation of peatland areas with fluctuating water tables (Lazenby 1955, Loach, 1968).

76 Our previous work (Ritson et al., 2016) has also shown that *Juncus* and *Molinia* may be create an increase in the
77 speed and seasonality of C cycling in peatland litter layers due to their annual cycle of production of a large
78 amount of relatively labile aboveground biomass,
79 Vegetative change has implications for C storage in peatlands, as *Sphagnum* is responsible for a number of
80 mechanisms (e.g. the production of recalcitrant litter) which allow C to be stored over long time periods (van
81 Breemen, 1995). Conversely, many vascular plants can destabilise colonised peat, stimulating decomposition by
82 adding labile C at the surface and through their root systems (Fenner et al. 2007; Gogo et al. 2010). As such, a
83 number of programmes have aimed to promote *Sphagnum* dominance for C storage and other ecosystem
84 services by blocking drainage ditches to re-establish high water tables (Grand-Clement et al., 2013). So far
85 preliminary results from ditch blocking schemes have shown a shift to vegetation species suited to wet
86 conditions and a decrease in peak flows in the restored catchment leading to a decrease in DOC load as
87 concentration has remained the same (Luscombe et al., 2014, Smith et al., 2014). Further evidence is needed on
88 the water quality outcomes of such interventions and the implications for water treatment as the timescales of
89 restoration (<5 years) are short compared to both the period of drainage (typically 10-100 years) and peat
90 formation (thousands of years).
91 Previous work has highlighted both the vegetative source and climate controls on production affecting the ease
92 of removal of DOC and the formation of DBPs (Gough et al., 2012; Reckhow et al., 2007; Ritson et al., 2014a;
93 Tang et al., 2013). The present research sought to build on the work of Ritson et al., 2016 by assessing the effect
94 of oxygenation of peat and vegetation due to drought on peatland DOC flux and any interaction with projected
95 changes in litter input. The previous study had only assessed the DOC quality differences between sources
96 collected from the field with minimal degradation/oxygenation. To this end, climate simulations of varying
97 drought severities defined in terms of percentiles of mean monthly rainfall were performed on four typical
98 peatland vegetation types (*Calluna vulgaris*, *Juncus effusus*, *Molinia caerulea* and *Sphagnum spp.*) and a peat
99 soil. After a six-week drought simulation, the DOC released upon rewetting was analysed in terms of optical
100 properties and coagulation removal efficiency with ferric sulphate to determine: (a) whether drought conditions
101 affect DOC production from peatland litter and soil types and (b) whether the differences in litter quality
102 identified in Ritson et al. (2016) between typical peatland species (*Sphagnum* and *Calluna*) and invasive,
103 drought tolerant vegetation (*Molinia* and *Juncus*) cause different responses to drought in terms of DOC
104 production (i.e. an interaction between the vegetation source and drought condition).

105

106 **2.0 Methodology**

107 **2.1 Field site and sample collection**

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

112 Samples of vegetation and peat soil were collected in one day in May 2014 and were sealed in airtight bags in a
113 chilled container for transport from the field and stored in the dark at 4°C before use. For vascular plants, litter
114 was collected as standing dead biomass. As the decomposition of *Sphagnum* is a continuum process, the section
115 2-4 cm below the capitulum was taken as equivalent to freshly senesced "litter", as in other studies (e.g.

116 Bragazza *et al.*, 2007). Samples were sorted to remove any vegetation not belonging to the target species and
117 then cut to 2 cm length and homogenised. Peat samples were collected using a screw auger and peat from 10-30
118 cm depth was used in the experiments. Peat samples were sorted to remove as many roots as possible but in sites
119 where *Molinia* was present some fine roots remained.

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

124

125 **2.2 Experimental Design**

126 The vegetation and peat samples were homogenised by hand and randomly assigned a drought treatment in a
127 five (vegetation types) x four (drought treatments) design with five replicates per treatment, giving 100 samples
128 in total. Similar experiments concerning the decomposition of litter have used three replicates per treatment
129 (Fellman *et al.*, 2013; Soong *et al.*, 2015), suggesting our approach of using five samples per treatment is
130 adequate to capture variability between samples.

131 Data were obtained from regional historic climate records of the UK Meteorological Office for the south west of
132 England for the period 1910-2013 (UK Met Office 2014) and these values were used to define three severities of
133 drought and a control value. Data for the months of June, July and August (310 months in total) were used to
134 find the 50th, 25th, 10th and 5th percentile for total monthly rainfall and these values have been used to set
135 monthly rainfall values for control (79.0 mm), mild (51.5), moderate (34.7) and severe droughts (23.3),
136 respectively.

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

141

142 **2.3 Experimental procedure and laboratory methods**

143 As in other decomposition studies, vegetation samples were air-dried to constant weight then mixed before
144 subsampling (e.g. Latter *et al.*, 1998). Five subsamples of each vegetation type were then oven-dried at 70 °C
145 until constant weight, to determine the air-dry to oven-dry conversion factor. The peat samples were not air-
146 dried before use as this would have changed the redox conditions within the peat and created a hydrophobic
147 layer which can cause problems for re-wetting (Worrall *et al.*, 2003). This will mean less accuracy in
148 determining the starting weight of the peat sample as some variation in water content may exist, however this
149 was minimised by effective homogenisation. Elemental analysis on a subsample of the starting material revealed
150 C:N to be in the order peat (29.9), *Molinia* (35.7), *Juncus* (42.2), *Calluna* (56.5) and *Sphagnum* (93.7) as
151 reported in Ritson *et al.* (2016).

152 Buchner funnels fitted into amber-glass bottles were used to hold the sample and collect the simulated rainfall.
153 Approximately 2 g dry-weight of air-dried vegetation/peat was used, however a lower weight of sample was
154 used for *Sphagnum* (~0.65 g) and *Molinia* (~1.5 g) as this was enough to fill the Buchner funnel. The peat

155 samples were spread over the area of the funnel so that a seal was created and the simulated rainwater infiltrated
156 the peat rather than draining directly into the funnel.

157 The samples were then placed in an incubator for six weeks with simulated rainfall applied eleven times per
158 month at regular intervals using high purity reverse osmosis (RO) treated water, following the methodology of
159 Ritson et al. (2016). Data on final water weight, available in the supplement, confirm degrees of desiccation
160 between the treatments. RO or deionised water has been used in similar degradation studies (Cortez et al., 1996,
161 Soong et al. 2014) and is employed so that no organic carbon is added to the samples and for the extraction step
162 is considered to be representative of soil solutions collected *in situ* (Chantigny et al., 2007).

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

168 At the end of the six week simulation the samples were air-dried and weighed. Water extractable DOC from the
169 air dried sample was taken to simulate re-wetting following the end of the drought. DOC was extracted from soil
170 and vegetation samples using approximately 20:1 ratio of RO treated water to sample. The samples were then
171 filtered with pre-ashed GF/F filters (Whatman) and the pH measured. Previous work has shown that the amount
172 of water used to extract DOC and whether one extraction is performed or sequential extractions to simulate
173 multiple rainfall events gives no significant variation in DOC quality, only changes in the total amount of C
174 (Don and Kalbitz, 2005; Soong et al., 2014). DOC was measured as non-purgeable organic carbon (NPOC) via a
175 UV/persulphate oxidation method on a Shimadzu TOC-V instrument. The method detection limit was
176 determined by running five blank samples and using the value of three times the standard deviation. This was
177 found to be 0.05 mgC l⁻¹.

178 UV and fluorescence analysis was undertaken before coagulation/flocculation jar testing. UV absorbance was
179 measured on a Perkin Elma Lambda 3 using a 1-cm pathlength quartz cuvette and the specific absorbance,
180 SUVA, was calculated as the absorbance at 254 nm in units of m⁻¹ divided by the NPOC content (mgC l⁻¹).

181 Fluorescence analysis was completed using a Vary Eclipse fluorescence spectrophotometer where samples were
182 scanned at excitation wavelengths between 220 and 450 nm at 5 nm intervals and the resulting emission
183 recorded between 300 and 600 nm at 2 nm intervals. An R script was produced based on existing scripts
184 (Lapworth and Kinniburgh, 2009) which performed a blank subtraction, masked out Rayleigh and Raman
185 scattering, visualised the data and calculated fluorescence indices. Data were normalised to the Raman
186 scattering peak of a RO water sample to allow comparison to other laboratories (Lawaetz and Stedmon, 2009).

187 The 'peak C' measure, related to humic-like character, and the tryptophan-like peak, 'peak T' were defined as in
188 Beggs et al., (2013).

189 Coagulation was performed on 350 ml of sample diluted to 3 mg l⁻¹ DOC using a Phipps and Bird PB-700
190 paddled jar-tester (Phipps and Bird Ltd., Virginia, USA). After settling, the sample was filtered by Whatman
191 qualitative grade 2 filters to remove flocs before NPOC analysis. Preliminary work indicated the following
192 conditions gave effective DOC removal of similar samples: pH 5.5, 30.0 mg l⁻¹ ferric sulphate dosed with 28.5
193 mg l⁻¹ calcium hydroxide for pH control during a flash mix of one minute at 175 rpm, followed by a slow mix of
194 30 minutes at 60 rpm and then one hour of settling. Assessment of DBP formation was attempted, however

195 analysis within the two week period specified in the method was not possible due to instrument failure so data
196 quality could not be assured.

197

198 **2.4 Data analysis and statistical methods**

199 Statistical analysis was performed in the open source programming language, R, and SPSS version 21 (IBM).
200 Due to problems with normality and heteroscedasticity a Box-Cox transform (Box and Cox, 1964) was applied
201 to the variables before testing with a factorial ANOVA. A Tukey HSD post-hoc procedure was used for
202 pairwise comparisons between the DOC sources and drought conditions. Estimates of effect sizes were made
203 using ω^2 as this is suitable for small samples sizes (Keselman, 1975). Interactive effects from the omnibus
204 ANOVA were followed up using multiple one-way ANOVAs with a Holm-Šidák correction to control the
205 inflation of type one error (Holm, 1979; Šidák, 1967). This method changes the value used for alpha, the
206 significance level, based on how many comparisons have been performed starting with the source with lowest p
207 value and moving to the next lowest until an insignificant comparison is found. Correlations between variables
208 were tested using Spearman's ρ (Spearman, 1904) and differences between the start and end of the repetition of
209 the control group were tested using Student's t test and Levene's test for equal variance (Levene, 1960; Student,
210 1908).

211

212 **2.5 Repetition of the control group conditions**

213 To further investigate the effect of oxygenation of peat on DOC production and treatability, the control
214 condition of this experiment was repeated in August 2015 using peat samples collected from similar
215 ombrotrophic peatland sites in Dartmoor National Park (site details available in Ritson et al., 2016). Water
216 extractable DOC was taken from a subsample before the climate simulation began and analysed for fluorescence
217 and UV properties. Approximately 3.5 g dry weight of peat was then incubated using the same temperature and
218 rainfall as the control samples of the drought experiment with three replicates. After six weeks water extractable
219 DOC was again taken for fluorescence and UV analysis to assess any changes in DOC quality.

220

221 **3.0 Results**

222 **3.1 Omnibus ANOVA**

223 A factorial ANOVA was performed exploring the source, drought and interactive effects on DOC, SUVA, DOC
224 removal efficiency and the removal of SUVA (Table 1). Extractable DOC and SUVA had significant source,
225 drought and source*drought effects suggesting that there is variation in the sensitivity of the sources to drought.
226 No drought effects were observed for DOC removal or SUVA removal, although the source had strong effects
227 on these parameters. For all significant results the effect size for the source was much greater than that for the
228 drought treatment.

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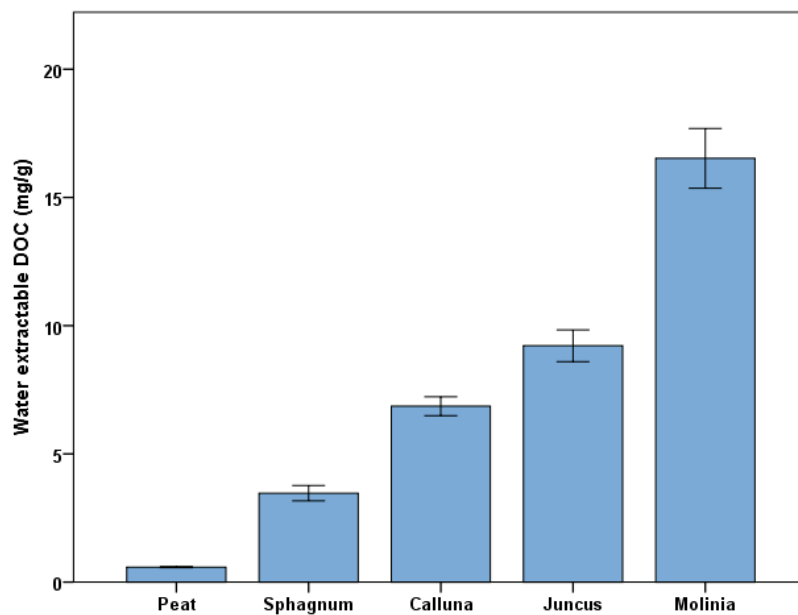
232 **Table 1: p-values from factorial ANOVA (significant values have been highlighted in bold and displayed**
 233 **with ω^2 estimate of effect size in brackets)**

Variable	Water extractable DOC	pH	SUVA	Peak C	Peak T	Peak C/T	DOC removal	SUVA removal
Factor	DOC							
DOC source	<0.001 (0.945)	<0.001 (0.429)	<0.001 (0.422)	<0.001 (0.846)	<0.001 (0.675)	<0.001 (0.691)	<0.001 (0.396)	<0.001 (0.331)
Drought	0.007 (0.004)	0.143	0.007 (0.034)	<0.001 (0.011)	<0.001 (0.035)	0.642	0.418	0.475
DOC source*Drought	0.050 (0.004)	0.157	0.005 (0.054)	<0.001 (0.095)	<0.001 (0.177)	0.096	0.234	0.951

234

235 3.2 Water extractable DOC

236 The mean DOC extracted for all samples from each source is shown in Figure 1. The vegetation samples
 237 produced more DOC than the peat soil ($0.58 \pm 0.02 \text{ mg g}^{-1}$) with the peatland species, *Sphagnum* and *Calluna*,
 238 producing 3.47 ± 0.30 and $6.86 \pm 0.37 \text{ mg g}^{-1}$, respectively whereas the grassland species, *Juncus* and *Molinia*,
 239 produced much more at 9.21 ± 0.62 and $16.52 \pm 1.17 \text{ mg g}^{-1}$, respectively. A Tukey HSD test suggested that all
 240 DOC sources have significantly different means at the $p < 0.01$ level except the *Calluna* - *Juncus* comparison
 241 which was significantly different at the $p < 0.05$ level.



242

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

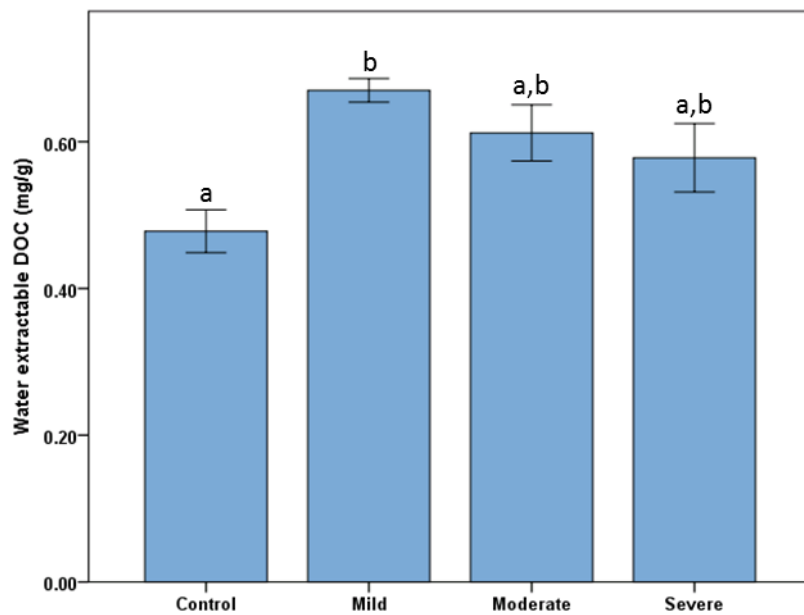
245

246 To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on each of
 247 the sources using a Holm-Šidák correction to control the inflation of type one error.

248

249 Due to the decrease in the level of significance of the p value in the Holm-Šidák method only the peat source
 250 was found to have a drought effect on water extractable DOC ($p=0.010$, $\omega^2=0.393$). The mean values were 0.48,
 251 0.67, 0.61 and 0.58 mg g^{-1} for the control, mild, moderate and severe treatments of the peat DOC, respectively,
 252 and this is shown in Figure 2. The mild drought treatment gave a significant increase in extractable DOC,
 253 indicated by a Tukey test for comparison to the control group ($p=0.007$). This corresponded to a 39.6% increase
 254 in DOC production for the mild drought treatment. A larger standard error in the moderate and severe drought
 255 treatments meant that these were not significantly different from the control ($p=0.060$ and $p=0.204$,
 256 respectively).

257
 258



259
 260 **Figure 2: DOC extracted from peat on rewetting following different severities of drought (n=5 per**
 261 **treatment). Letters indicate statistically similar groups from the Tukey test. Error bars at one standard**
 262 **error.**

263
 264

265 Variation in peat water content during the experiment was not recorded; however the water content of the peat
 266 samples was measured at the end of the experiment. This averaged 16.11, 14.14, 15.11 and 5.95 g with standard
 267 errors of 7.7, 3.0, 15.9 and 28.1% for the peat control, mild, moderate and severe drought treatments
 268 respectively. The much larger standard error in final water content agrees with observations during the
 269 experiment and the variation from group mean in final water content for each sample and the variation from
 270 group mean in extractable DOC were found to correlate (Spearman's ρ coefficient 0.484, $p=0.031$). The source
 271 also had a significant effect (Table 1) on the pH of the samples with a Tukey test suggesting three statistical
 272 subsets with peat and *Calluna* < *Calluna* and *Molinia* < *Sphagnum* and *Juncus*. Mean values were in the order
 273 peat (5.92 ± 0.04), *Calluna* (5.98 ± 0.01), *Molinia* (6.03 ± 0.01), *Sphagnum* (6.14 ± 0.02) and *Juncus* (6.17 ± 0.02).
 274

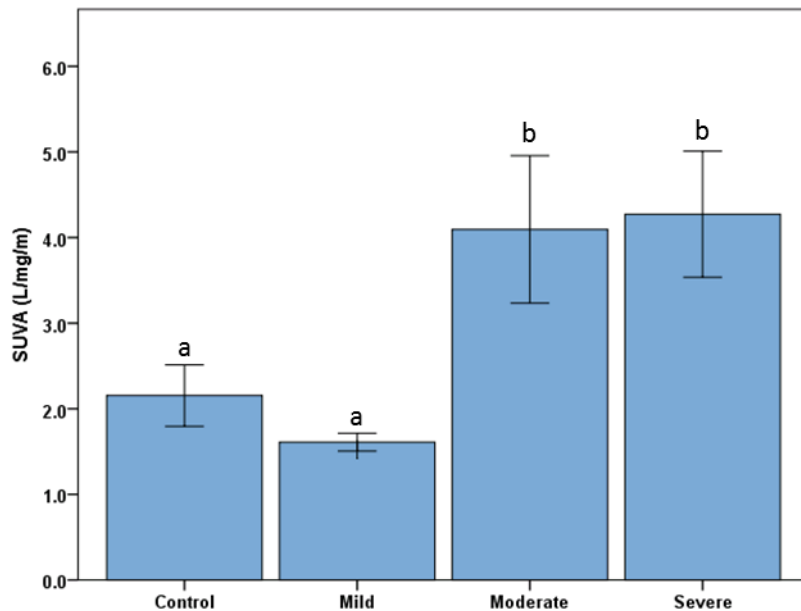
275 **3.3 SUVA and fluorescence**

276 Mean values of SUVA in $L\ mg^{-1}\ m^{-1}$ for the different sources were in the order *Molinia* (3.03 ± 0.38), peat (3.01
277 ± 0.15), *Juncus* (2.04 ± 0.06), *Calluna* (1.66 ± 0.14) and then *Sphagnum* (1.34 ± 0.13). The Tukey HSD test
278 suggested that the mean values for SUVA formed three subsets with peat and *Molinia* > *Calluna* and *Juncus* >
279 *Calluna* and *Sphagnum*.

280 To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on SUVA
281 from each of the sources using a Holm-Šidák correction. Only *Molinia* was found to have a significant drought
282 effect on the SUVA value ($p=0.001$, $\omega^2=0.546$).

283 Tukey's test suggested that both the moderate and severe drought treatments were significantly different than
284 the control ($p=0.045$ and 0.026 , respectively) with means of 2.15, 4.09 and $4.27\ L\ mg^{-1}\ m^{-1}$ for the control,
285 moderate and severe treatment of the *Molinia* DOC, respectively. Figure 3 shows a graph of SUVA for *Molinia*
286 DOC from the different treatment groups.

287



288

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

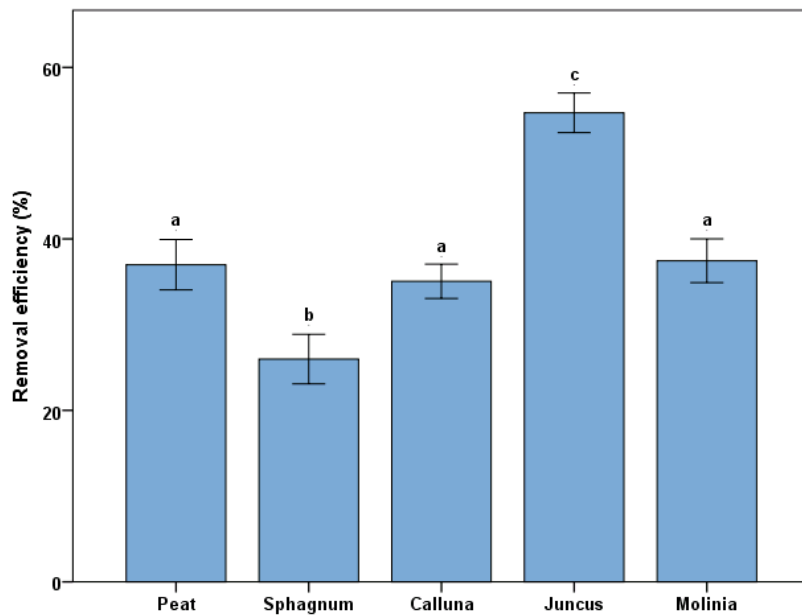
292 The fluorescence data suggests interactive effects between drought treatments and the source of the DOC (Table
293 1) and these was further interrogated using the using a Holm-Šidák method. This suggested that there was a
294 significant effect of drought on peak C for both *Juncus* ($p<0.001$, $\omega^2=0.840$) and *Molinia* ($p<0.001$, $\omega^2=0.760$)
295 with the Tukey test suggesting that the severe drought treatment was significantly lower than the control
296 ($P<0.01$). For the peak T fluorescence value drought had a significant effect on *Juncus* DOC ($p<0.001$, ω^2
297 $=0.634$) with the Tukey test suggesting that the severe drought treatment was significantly lower than the
298 control ($P<0.01$). The ratio of fluorescence peak C to T was showed no drought effect ($p>0.05$) but there were
299 significant differences between the sources with a Tukey test suggesting that *Sphagnum* < *Calluna*, *Juncus* and
300 *Molinia* < peat.

301

302 **3.4 DOC removal efficiency**

303 The factorial ANOVA suggested no drought effects on removal efficiency ($p=0.418$). Mean values for DOC
304 removal by coagulation with ferric sulphate were in the order of *Juncus* (54.7 ± 2.3 %), *Molinia* (37.5 ± 2.6 %),
305 peat (37.0 ± 2.9 %), *Calluna* (35.1 ± 2.0 %) and then *Sphagnum* (26.0 ± 2.9 %). The Tukey HSD test suggested
306 that the mean values for DOC removal efficiency fell into three subsets with similar means in the order *Juncus*>
307 *Molinia*, peat and *Calluna*> *Sphagnum*. The removal efficiency for all samples from each DOC source is shown
308 in Figure 4.

309
310



311
312 **Figure 4: DOC removal efficiency by coagulation/flocculation for different DOC sources (n=20 for each**
313 **source, error bars at one standard error, letters indicate statistical subset according to Tukey test).**

314

315 **3.5 SUVA removal efficiency**

316 The removal of aromaticity, measured by SUVA, is of interest in drinking water treatment as aromatic
317 compounds have a high propensity to form some of the regulated DBPs on chlorination (Bond et al., 2011).
318 Large, aromatic compounds are selectively removed by coagulation/flocculation and as expected good removal
319 (>70%) was observed for most of the samples. The mean values for the reduction in SUVA value following
320 coagulation with ferric sulphate was in the order of peat (76.6 ± 1.8 %), *Sphagnum* (76.3 ± 2.5 %), *Molinia*
321 (67.7 ± 4.7 %), *Calluna* (49.6 ± 5.3 %) and then *Juncus* (44.5 ± 2.3 %). The Tukey HSD test suggested that
322 there were two subsets of DOC sources with similar means with peat, *Sphagnum* and *Molinia* > *Juncus* and
323 *Calluna*. As with the overall DOC removal efficiency, there were no drought effects on SUVA removal
324 ($p=0.475$).

325

326 **3.6 Correlations between measures of DOC quality and treatability**

327 A number of DOC quality indices based on absorbance and fluorescence measures were tested. The correlation
 328 coefficients for the different quality and treatability parameters are shown in Table 2. Peak C, a humic-like
 329 fluorescence peak, showed the best correlation with DOC removal efficiency while the ratio of humic-like to
 330 protein-like fluorescence (peak C/T) gave a lower but still significant correlation coefficient. The magnitude of
 331 peak C values are in the order *Juncus*>*Molinia*>*Calluna*>peat>*Sphagnum* which is consistent with data on DOC
 332 removal efficiency. The SUVA value showed the best correlation with SUVA removal efficiency, suggesting
 333 that DOM with a lower proportion of aromatic compounds (low SUVA value) contains aromatic compounds
 334 which are harder to remove by coagulation, possibly meaning they are either low molecular weight and/or also
 335 contain hydrophilic groups.

336

337 **Table 2: Spearman’s ρ for different DOC quality and treatability measures**

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

338

339

340 **3.7 Repetition of the control group conditions**

341 The data obtained from DOC extracted before and after the repeated simulation were analysed using student’s t-
 342 test (equal variances assumed, confirmed using Levene’s test) to assess whether the DOC extracted was
 343 significantly different following six weeks of exposure to oxygen without any experimental treatment. The
 344 results of this analysis are shown in Table 3.

345

346 **Table 3: 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

347

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

354

355 4.0 Discussion

356 4.1 Water extractable DOC

357 Taken together, the main effects and interaction ω^2 values suggest that the source of DOC is the most important
358 factor on extractable DOC and that the effect of drought is significant only for the peat soil and not for the
359 vegetation. The peat soil was affected by the drought treatment with higher extractable DOC observed at the
360 mild severity. This finding is consistent with the 'enzymatic latch' hypothesis that increased oxygenation of peat
361 engages a biogeochemical cascade whereby increased phenol oxidase activity ends the phenol-induced
362 inhibition of hydrolase enzymes, thus increasing overall organic matter decomposition (Freeman et al., 2001a).
363 This is also confirmed by the replication of the control treatment which showed exposure to oxygen even in the
364 absence of drought increased extractable DOC and decreased DOM aromaticity. This finding has implications
365 for all laboratory studies which remove peat from anoxic conditions as these may not be representative of in-situ
366 conditions.

367 No effect was observed with the moderate and severe drought treatments which may be explained by water
368 scarcity limiting microbial activity (Toberman et al., 2008) and/or increased hydrophobic protection decreasing
369 the extractable DOC on rewetting. Observations made throughout the experiment suggested that in the severe
370 treatment there was a large variation in the extent to which each replicate dried out. Once peat becomes dry, a
371 hydrophobic layer forms (Spaccini et al. 2002; Worrall et al. 2003), meaning that less water will infiltrate the
372 sample, therefore possibly increasing the severity of the drought beyond the experimental design. The very low
373 final water content of the severe treatment and observations of drying out and shrinkage of the peat mass
374 throughout the experiment add weight to these possible explanations, although actual rates of microbial
375 respiration were not monitored during the experiment. The correlation between variance in final water content
376 and extractable DOC also suggests the source of variance may be either the application of rainfall or the extent
377 to which each sample dried out. Although hydrophobic protection may limit DOC concentrations on rewetting,
378 in the longer term the effect of oxygenation, described by the enzymatic latch mechanism, will likely mean
379 higher DOC production (Freeman et al., 2001a).

380 The lack of a drought effect on DOC production from any of the vegetation types suggest the pulse in DOC
381 observed post-drought elsewhere in catchment scale studies (Evans et al., 2005; Scott et al., 1998; Watts et al.,
382 2001; Worrall and Burt, 2004) is likely to be due to the oxygenation of peat soils rather than any litter layer
383 effects. Although there was no drought effect, the increase in peat-derived DOC observed on oxygenation
384 (Table 3) is significant for downstream water treatment as our previous work showed this has more
385 environmental persistence than vegetation sources (Ritson et al., 2016) and the UV and fluorescence data
386 suggested DOC from peat exposed to oxygen may be more difficult to remove by conventional treatment
387 measures. High DOC production was noted for the vascular plants, suggesting they may be an important source
388 of DOC within peatland catchments during the period of their senescence, although drought does not affect the
389 amount they produce. Drought conditions may, however, precipitate a change in vegetation type favouring more
390 drought-tolerant species (Bragazza, 2008), which may have longer term effects for peatland biogeochemistry.
391 Correlations between litter C:N ratio, suggesting nutrient availability, and amount of extractable DOC have been
392 found in our previous work (Ritson et al., 2016) and elsewhere in the literature (Soong et al, 2014), suggesting a
393 shift to the drought tolerant *Molinia* and *Juncus* may increase DOC flux from the litter layer.

394

395 **4.2 SUVA and fluorescence**

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

406 No drought effect was found for the SUVA value of peat which is in contrast to field studies which have shown
407 a decrease in aromaticity of DOM during drought due to solubility controls and an increase in aromaticity on
408 rewetting (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall et al., 2004). This may be explained
409 by the fact that field studies have shown an increase in DOM aromaticity over many years, whereas this study
410 examined a single rewetting event following drought, so the altered biogeochemical controls on DOM
411 aromaticity may not have had enough time to exert a significant effect. Comparing our results to field findings,
412 then, suggest that a sharp pulse in high aromaticity DOM on rewetting is unlikely but that elevated amounts may
413 be present over longer timescales. The laboratory conditions may also have played a part, as the control sample
414 is likely to have been exposed to more oxygenation through sample collection and setup of the experiment than
415 undisturbed peat in the field, therefore increasing its similarity to the treatment conditions. The changes in DOM
416 properties when the control group was repeated would appear to confirm this hypothesis.

417 A drought effect was observed for peak C (*Juncus* and *Molinia*) and peak T (*Juncus*) with lower values under
418 severe drought. These indices have been described as ‘humic-like’ and ‘protein-like’, respectively, however
419 meaningful interpretation of the moieties responsible is difficult as many compounds can fluoresce in these
420 regions (Aiken, 2014). From Table 2, however, we can suggest that decreases in peak C caused by drought may
421 decrease the amenability of DOC to removal by coagulation.

422 Taken together, the main effects and interaction and ω_2 values suggest that the source of DOM is the most
423 important factor on SUVA and fluorescence and that the effect of drought is significant only for *Molinia* and
424 *Juncus* litter and not for the other vegetation types or the peat soil. These results suggest encroachment of
425 grassland species into the uplands will increase seasonal DOM flux from the litter layer and increase the
426 aromaticity of exported DOM and create a small drought effect where *Molinia* or *Juncus* litter is present. The
427 lack of a drought effect for peat SUVA suggests that short pulses of highly aromatic DOM are unlikely to be
428 observed but long-term effects caused by water table drawdown identified elsewhere in the literature indicate
429 elevated DOC concentration and SUVA values over periods of years following droughts. The effect of more
430 frequent, repeated droughts and the ability of peat soils to recover remains an area for further research.

431

432 **4.3 DOC and SUVA removal**

433 DOC removal for all sources were typical of literature values (Matilainen et al., 2010), with *Juncus* DOC
434 proving the easiest to remove and *Sphagnum* DOC the hardest. *Sphagnum* DOC showed good removal of

435 SUVA despite relatively poor removal of total DOC, suggesting the aromatic compounds present in the sample
436 are easily removed but that a large pool of aliphatic compounds are also present and these are more difficult to
437 treat by conventional means. Repeating the control condition and measuring DOC production and quality
438 parameters allowed an estimate of the effect of oxygen exposure for peat samples. This showed a decrease in
439 SUVA value and humic-like character (fluorescence peak C) as well as a large increase in extractable DOC.
440 These changes in quality parameters may provide an explanation of why poorer removal by coagulation was
441 achieved for peat following this drought experiment than had been observed in our previous work (Ritson et al.,
442 2016). In Ritson et al. 2016, coagulation experiments were performed on DOC extracted from fresh peat which
443 had been exposed to a minimal amount of oxygenation during transport and very good removal by
444 coagulation/flocculation was found. In contrast, the experiments reported here on peat exposed to oxygen
445 showed comparatively poor removal via coagulation/flocculation. The repetition of the control group indicates
446 that any exposure to oxygenation can decrease the SUVA and peak C values of DOC extracted from peat and
447 both of these parameters have been linked to ease of treatability of DOC (Matilainen et al., 2011). Poorer
448 removal was observed for *Sphagnum* than in our previous work; the effect of more oxygenated conditions on
449 vegetation decomposition remains an area for further research, particularly as climate change may increase the
450 likelihood of water table draw down in peatlands.

451 The coagulation removal efficiency could best be explained by the peak C fluorescence index, suggesting humic
452 substances content was the strongest predictor of DOC removal. This is in contrast to our previous work which
453 found the ratio of humic to protein-like DOC to be the most important predictor (Ritson et al. 2014b). Our
454 previous work used DOC collected throughout a two-month simulation rather than a single re-wetting event at
455 the end. The samples will, therefore, have likely undergone microbial processing during this simulation and
456 consequently an increase in the amount of autochthonous DOM, hence the greater importance of the
457 fluorescence measure of protein-like DOM.

458

459 **5.0 Conclusions**

460 Climate projections for the UK vary, however most agree the likelihood of droughts in the future is set to
461 increase. The results of this research suggest the dominant effect of drought on peatland DOC sources is to
462 increase the amount and decrease the treatability of DOC from peat soils. This is likely due to the ‘enzymatic
463 latch’ mechanism increasing decomposition when oxic conditions prevail. No drought effect on the amount of
464 DOC from different vegetation litters was found, although an increase in SUVA value from *Molinia* DOC was
465 observed and could offset decreases in peat DOC. The greatest effect of drought for vegetation may be
466 facilitating shifts to drought-tolerant species dominance rather than altering decomposition processes in the short
467 term. Oxygenation of peat appears to greatly increase extractable DOM and whilst no drought effect was
468 observed, extracts before and after oxygenations showed decreased aromaticity and humification, which may
469 mean it is more difficult to remove at the treatment works. These results provide support for catchment
470 management programmes seeking to increase resilience to drought by raising peatland water tables as a strategy
471 for mitigating against high riverine DOC concentrations following droughts.

472

473

474

475 **Author contributions**

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

478

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