

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 \(Luscombe et al., 2014, Smith et al., 2014\).](#) ~~However,~~ Further evidence is
88 needed on the water quality outcomes of such interventions and the implications for water treatment [as the](#)
89 [timescales of restoration \(<5 years\) are short compared to both the period of drainage \(typically 10-100 years\)](#)
90 [and peat 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 quantify](#)
94 ~~the~~ [effect of oxygenation of peat and vegetation due to drought on peatland DOC flux and any interaction](#)
95 [with projected changes in litter input. The previous study had only assessed the DOC quality differences](#)
96 [between sources collected from the field with minimal degradation/oxygenation.](#) To this end, climate
97 simulations of varying drought severities defined in terms of percentiles of mean monthly rainfall were
98 performed on four typical peatland vegetation types (*Calluna vulgaris*, *Juncus effusus*, *Molinia caerulea* and
99 *Sphagnum spp.*) and a peat soil. After a six-week drought simulation, the DOC released upon rewetting was
100 analysed in terms of optical properties and coagulation removal efficiency with ferric sulphate to determine: (a)
101 whether drought conditions affect DOC production from peatland litter and soil types and (b) whether [the](#)
102 [differences in litter quality identified in Ritson et al. \(2016\) between typical peatland species \(*Sphagnum* and](#)
103 [Calluna\)](#) and invasive, drought tolerant vegetation (*Molinia* and *Juncus*) [cause different responses to drought in](#)
104 [terms of DOC production \(i.e. an interaction between the vegetation source and drought condition\).](#) ~~produce~~
105 [different quantities and quality of DOC with respect to drinking water treatment.](#)

107 2.0 Methodology

108 2.1 Field site and sample collection

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

113 Samples of vegetation and peat soil were collected in one day in May 2014 and were sealed in airtight bags in a
114 chilled container for transport from the field and stored in the dark at 4°C before use. For vascular plants, litter
115 was collected as standing dead biomass. As the decomposition of *Sphagnum* is a continuum process, the section

116 2-4 cm below the capitulum was taken as equivalent to freshly senesced “litter”, as in other studies (e.g.
117 Bragazza *et al.*, 2007). Samples were sorted to remove any vegetation not belonging to the target species and
118 then cut to 2 cm length and homogenised. Peat samples were collected using a screw auger and peat from 10-30
119 cm depth was used in the experiments. Peat samples were sorted to remove as many roots as possible but in sites
120 where *Molinia* was present some fine roots remained.

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

125

126 **2.2 Experimental Design**

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

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

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

142

143 **2.3 Experimental procedure and laboratory methods**

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

153 Buchner funnels fitted into amber-glass bottles were used to hold the sample and collect the simulated rainfall.

154 Approximately 2 g dry-weight of air-dried vegetation/peat was used, however a lower weight of sample was
155 used for *Sphagnum* (~0.65 g) and *Molinia* (~1.5 g) as this was enough to fill the Buchner funnel. The peat

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

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

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

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

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

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

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

190 Coagulation was performed on 350 ml of sample diluted to 3 mg l⁻¹ DOC using a Phipps and Bird PB-700
191 paddled jar-tester (Phipps and Bird Ltd., Virginia, USA). After settling, the sample was filtered by Whatman
192 qualitative grade 2 filters to remove flocs before NPOC analysis. Preliminary work indicated the following
193 conditions gave effective DOC removal of similar samples: pH 5.5, 30.0 mg l⁻¹ ferric sulphate dosed with 28.5
194 mg l⁻¹ calcium hydroxide for pH control during a flash mix of one minute at 175 rpm, followed by a slow mix of
195 30 minutes at 60 rpm and then one hour of settling. Assessment of DBP formation was attempted, however

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

198

199 **2.4 Data analysis and statistical methods**

200 Statistical analysis was performed in the open source programming language, R, and SPSS version 21 (IBM).
 201 Due to problems with normality and heteroscedasticity a Box-Cox transform (Box and Cox, 1964) was applied
 202 to the variables before testing with a factorial ANOVA. A Tukey HSD post-hoc procedure was used for
 203 pairwise comparisons between the DOC sources and drought conditions. Estimates of effect sizes were made
 204 using ω^2 as this is suitable for small samples sizes (Keselman, 1975). Interactive effects from the omnibus
 205 ANOVA were followed up using multiple one-way ANOVAs with a Holm-Šidák correction to control the
 206 inflation of type one error (Holm, 1979; Šidák, 1967). This method changes the value used for alpha, the
 207 significance level, based on how many comparisons have been performed starting with the source with lowest p
 208 value and moving to the next lowest until an insignificant comparison is found. Correlations between variables
 209 were tested using Spearman's ρ (Spearman, 1904) and differences between the start and end of the repetition of
 210 the control group were tested using Student's t test and Levene's test for equal variance (Levene, 1960; Student,
 211 1908).

212

213 **2.5 Repetition of the control group conditions**

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

221

222 **3.0 Results**

223 **3.1 Omnibus ANOVA**

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

230

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

Variable	Water	pH	SUVA	Peak	Peak	Peak	DOC	SUVA
	extractable			C	T	C/T	removal	removal
Factor	DOC							

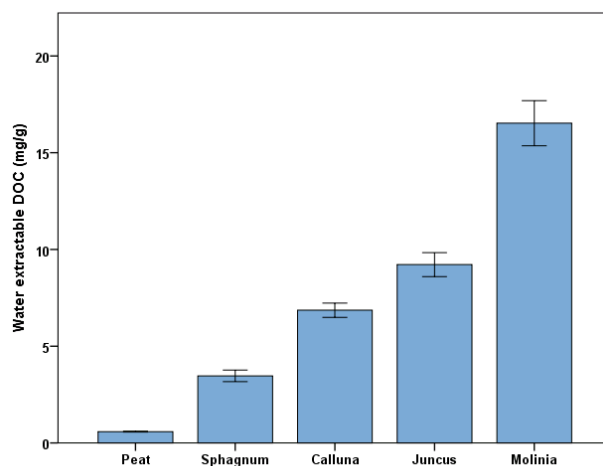
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DOC source	<0.001 (0.945)	<0.001 (0.429)	<0.001 (0.422)	<0.001 (0.846)	<0.001 (0.675)	<0.001 (0.691)	<0.001 (0.396)	<0.001 (0.331)
Drought	0.007 (0.004)	0.143	0.007 (0.034)	<0.001 (0.011)	<0.001 (0.035)	0.642	0.418	0.475
DOC source*Drought	0.050 (0.004)	0.157	0.005 (0.054)	<0.001 (0.095)	<0.001 (0.177)	0.096	0.234	0.951

233

234 3.2 Water extractable DOC

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



241

242 **Figure 1: Water extractable DOC of all samples across the different DOC sources (n=20 per source).**

243 **Error bars at one standard error.**

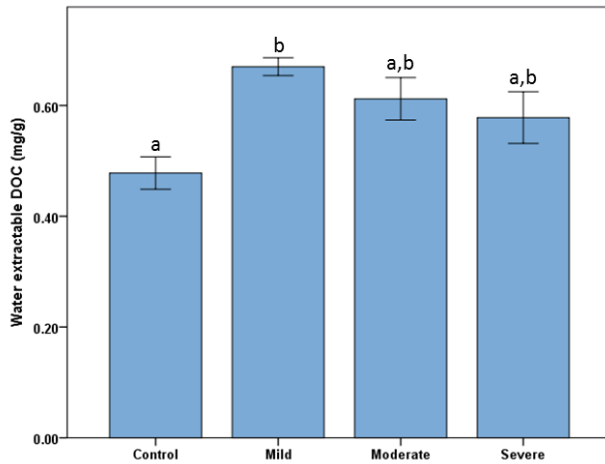
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245 To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on each of
 246 the sources using a Holm-Šidák correction to control the inflation of type one error.

247

248 Due to the decrease in the level of significance of the p value in the Holm-Šidák method only the peat source
 249 was found to have a drought effect on water extractable DOC ($p=0.010$, $\omega^2=0.393$). The mean values were 0.48,
 250 0.67, 0.61 and 0.58 mg g^{-1} for the control, mild, moderate and severe treatments of the peat DOC, respectively,
 251 and this is shown in Figure 2. The mild drought treatment gave a significant increase in extractable DOC,
 252 indicated by a Tukey test for comparison to the control group ($p=0.007$). This corresponded to a 39.6% increase

253 in DOC production for the mild drought treatment. A larger standard error in the moderate and severe drought
 254 treatments meant that these were not significantly different from the control ($p=0.060$ and $p=0.204$,
 255 respectively).
 256
 257



258
 259 **Figure 2: DOC extracted from peat on rewetting following different severities of drought (n=5 per**
 260 **treatment). Letters indicate statistically similar groups from the Tukey test. Error bars at one standard**
 261 **error.**

262
 263
 264 Variation in peat water content during the experiment was not recorded; however the water content of the peat
 265 samples was measured at the end of the experiment. This averaged 16.11, 14.14, 15.11 and 5.95 g with standard
 266 errors of 7.7, 3.0, 15.9 and 28.1% for the peat control, mild, moderate and severe drought treatments
 267 respectively. The much larger standard error in final water content agrees with observations during the
 268 experiment and the variation from group mean in final water content for each sample and the variation from
 269 group mean in extractable DOC were found to correlate (Spearman's ρ coefficient 0.484, $p=0.031$). The source
 270 also had a significant effect (Table 1) on the pH of the samples with a Tukey test suggesting three statistical
 271 subsets with peat and *Calluna* < *Calluna* and *Molinia* < *Sphagnum* and *Juncus*. Mean values were in the order
 272 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).
 273

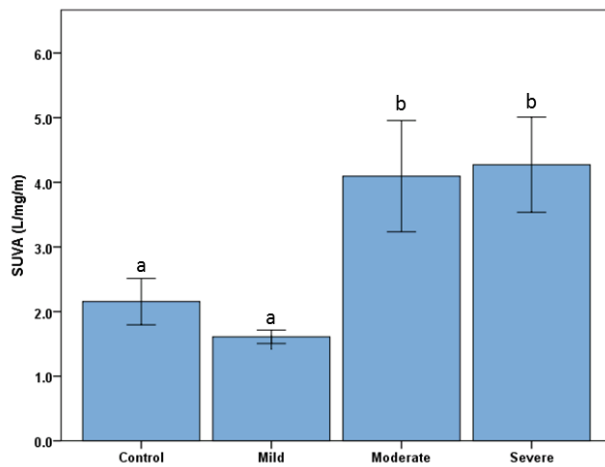
274 3.3 SUVA and fluorescence

275 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
 276 ± 0.15), *Juncus* (2.04 ± 0.06), *Calluna* (1.66 ± 0.14) and then *Sphagnum* (1.34 ± 0.13). The Tukey HSD test
 277 suggested that the mean values for SUVA formed three subsets with peat and *Molinia* > *Calluna* and *Juncus* >
 278 *Calluna* and *Sphagnum*.

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

282 Tukey's test suggested that both the moderate and severe drought treatments were significantly different than
283 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,
284 moderate and severe treatment of the *Molinia* DOC, respectively. Figure 3 shows a graph of SUVA for *Molinia*
285 DOC from the different treatment groups.

286



287

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

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

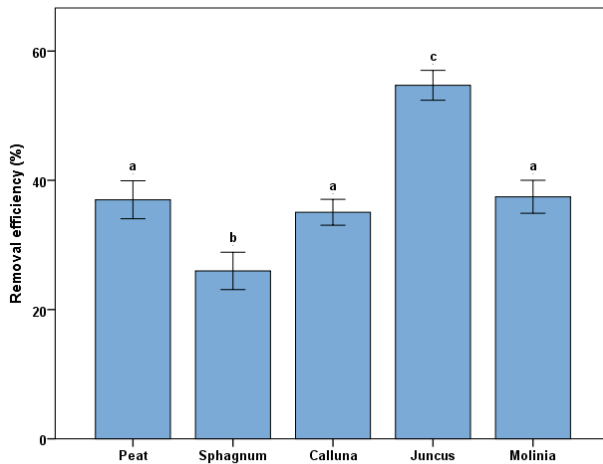
300

301 3.4 DOC removal efficiency

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

306 *Molinia*, peat and *Calluna*>*Sphagnum*. The removal efficiency for all samples from each DOC source is shown
307 in Figure 4.

308
309



310
311 **Figure 4: DOC removal efficiency by coagulation/flocculation for different DOC sources (n=20 for each**
312 **source, error bars at one standard error, letters indicate statistical subset according to Tukey test).**

313

314 3.5 SUVA removal efficiency

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

324

325 3.6 Correlations between measures of DOC quality and treatability

326 A number of DOC quality indices based on absorbance and fluorescence measures were tested. The correlation
327 coefficients for the different quality and treatability parameters are shown in Table 2. Peak C, a humic-like
328 fluorescence peak, showed the best correlation with DOC removal efficiency while the ratio of humic-like to
329 protein-like fluorescence (pPeak C/T) gave a lower but still significant correlation coefficient. The magnitude of
330 peak C values were in the order *Juncus*>*Molinia*>*Calluna*>peat>*Sphagnum* which is consistent with data on
331 DOC removal efficiency. The SUVA value showed the best correlation with SUVA removal efficiency,

332 suggesting that DOM with a lower proportion of aromatic compounds (low SUVA value) contains aromatic
 333 compounds which are harder to remove by coagulation, possibly meaning they are either low molecular weight
 334 and/or also contain hydrophilic groups.

335

336 **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 pPeak C	SUVA removal %	0.235, $p = 0.019$

337

338

339 3.7 Repetition of the control group conditions

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

344

345 **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

346

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

353

354 4.0 Discussion

355 4.1 Water extractable DOC

356 Taken together, the main effects and interaction ω^2 values suggest that the source of DOC is the most important
 357 factor on extractable DOC and that the effect of drought is significant only for the peat soil and not for the
 358 vegetation. The peat soil was affected by the drought treatment with higher extractable DOC observed at the
 359 mild severity. This finding is consistent with the 'enzymatic latch' hypothesis that increased oxygenation of peat
 360 engages a biogeochemical cascade whereby increased phenol oxidase activity ends the phenol-induced

361 inhibition of hydrolase enzymes, thus increasing overall organic matter decomposition (Freeman et al., 2001a).
362 This is also confirmed by the replication of the control treatment which showed exposure to oxygen even in the
363 absence of drought increased extractable DOC and decreased DOM aromaticity. This finding has implications
364 for all laboratory studies which remove peat from anoxic conditions as these may not be representative of in-situ
365 conditions.

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

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

393

394 **4.2 SUVA and fluorescence**

395 The SUVA value has been linked to the aromaticity of DOM (Weishaar et al., 2003) and is of interest as a
396 predictor of coagulation removal efficiency and DBP formation (Matilainen et al., 2011) in water treatment. The
397 highest SUVA value was observed for the peat soil and *Molinia* litter, and the lowest value for the statistical
398 subset of *Sphagnum* and *Calluna*. In a similar trend to DOM production, it appears that the grassland species
399 produce DOM of greater aromaticity than the peatland species. *Molinia* also showed an interactive effect with
400 the drought treatment, with a greater flux of aromatic compounds at the moderate and severe treatments,

401 suggesting dry conditions are favourable for the breakdown and/or solubilisation of aromatic compounds in
402 *Molinia* litter. *Molinia* DOM may, therefore, contribute to the increase in the aromaticity of peatland DOC
403 observed after droughts at the catchment scale (Scott et al., 1998; Watts et al., 2001), although solubility
404 controls on peat-derived DOM may be more important (Clark et al., 2006, 2005; Clark et al., 2011).
405 No drought effect was found for the SUVA value of peat which is in contrast to field studies which have shown
406 a decrease in aromaticity of DOM during drought due to solubility controls and an increase in aromaticity on
407 rewetting (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall et al., 2004). This may be explained
408 by the fact that field studies have shown an increase in DOM aromaticity over many years, whereas this study
409 examined a single rewetting event following drought, so the altered biogeochemical controls on DOM
410 aromaticity may not have had enough time to exert a significant effect. Comparing our results to field findings,
411 then, suggest that a sharp pulse in high aromaticity DOM on rewetting is unlikely but that elevated amounts may
412 be present over longer timescales. The laboratory conditions may also have played a part, as the control sample
413 is likely to have been exposed to more oxygenation through sample collection and setup of the experiment than
414 undisturbed peat in the field, therefore increasing its similarity to the treatment conditions. The changes in DOM
415 properties when the control group was repeated would appear to confirm this hypothesis.
416 A drought effect was observed for peak C (*Juncus* and *Molinia*) and peak T (*Juncus*) with lower values under
417 severe drought. These indices have been described as ‘humic-like’ and ‘protein-like’, respectively, however
418 meaningful interpretation of the moieties responsible is difficult as many compounds can fluoresce in these
419 regions (Aiken, 2014). From Table 2, however, we can suggest that decreases in peak C caused by drought may
420 decrease the amenability of DOC to removal by coagulation.
421 Taken together, the main effects and interaction and ω_2 values suggest that the source of DOM is the most
422 important factor on SUVA and fluorescence and that the effect of drought is significant only for *Molinia* and
423 *Juncus* litter and not for the other vegetation types or the peat soil. These results suggest encroachment of
424 grassland species into the uplands will increase seasonal DOM flux from the litter layer and increase the
425 aromaticity of exported DOM and create a small drought effect where *Molinia* or *Juncus* litter is present. The
426 lack of a drought effect for peat SUVA suggests that short pulses of highly aromatic DOM are unlikely to be
427 observed but long-term effects caused by water table drawdown identified elsewhere in the literature indicate
428 elevated DOC concentration and SUVA values over periods of years following droughts. The effect of more
429 frequent, repeated droughts and the ability of peat soils to recover remains an area for further research.

430

431 **4.3 DOC and SUVA removal**

432 DOC removal for all sources were typical of literature values (Matilainen et al., 2010), with *Juncus* DOC
433 proving the easiest to remove and *Sphagnum* DOC the hardest. *Sphagnum* DOC showed good removal of
434 SUVA despite relatively poor removal of total DOC, suggesting the aromatic compounds present in the sample
435 are easily removed but that a large pool of aliphatic compounds are also present and these are more difficult to
436 treat by conventional means. Repeating the control condition and measuring DOC production and quality
437 parameters allowed an estimate of the effect of oxygen exposure for peat samples. This showed a decrease in
438 SUVA value and humic-like character (fluorescence pPeak C) as well as a large increase in extractable DOC.
439 These changes in quality parameters may provide an explanation of why poorer removal by coagulation was
440 achieved for peat following this drought experiment than had been observed in our previous work (Ritson et al.,

441 2016). In Ritson et al. 2016, coagulation experiments were performed on DOC extracted from fresh peat which
442 had been exposed to a minimal amount of oxygenation during transport and very good removal by
443 coagulation/flocculation was found. In contrast, the experiments reported here on peat exposed to oxygen
444 showed comparatively poor removal via coagulation/flocculation. The repetition of the control group indicates
445 that any exposure to oxygenation can decrease the SUVA and pPeak C values of DOC extracted from peat and
446 both of these parameters have been linked to ease of treatability of DOC (Matilainen et al., 2011). Poorer
447 removal was observed for *Sphagnum* than in our previous work; the effect of more oxygenated conditions on
448 vegetation decomposition remains an area for further research, particularly as climate change may increase the
449 likelihood of water table draw down in peatlands.

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

457

458 **5.0 Conclusions**

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

471

472 **Author contributions**

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

475

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[Reviewer comments in normal text, author response in bold]

Response to reviewer 1

While the revisions appear to address most of my initial concerns, I still found it difficult to disentangle this study from Ritson et al. 2016. I recognize that there are a number of different analyses between papers but the purpose of both papers seem nearly identical and have many overlapping results. There is a brief section in the Discussion (Lines 424-427) that highlights how Ritson 2016 differed from the current paper as Ritson 2016 extracted DOC from peat that had been exposed to a minimal amount of oxygenation during transport whereas the current study reports on peat exposed to oxygenation. I think the authors should point out this experimental difference early in the Introduction as this is an extremely important difference and the reader needs to be aware of it straightaway (to avoid the same confusion I had).

Added to introduction: “The present research sought to build on the work of Ritson et al., 2016 by assessing the effect of oxygenation of peat and vegetation due to drought on peatland DOC flux and any interaction with projected changes in litter input. The previous study had only assessed the DOC quality differences between sources collected from the field with minimal degradation/oxygenation.”

Authors highlight previous studies and define objectives of this new study, but fail to provide hypotheses regarding their choice for peatland vegetation. They do a fine enough job articulating why different plant species should be tested but without hypotheses for expected effects, the experimental design with these specific plant species remains too speculative for justification. Why did the authors choose these three specific vascular plant species? Is there a reason why these particular plant species might affect DOC differently such that they needed to be tested? Use your results from Ritson 2016 to provide hypotheses for the current study. This would also help you rationalize this study as a follow-up to Ritson 2016 and why it would make a valuable addition to the scientific community. Please include hypotheses at the end of the Introduction to address this.

Justification of choice of species expanded in introduction so now reads: “Vegetative change in peatlands has occurred in the recent past (Chambers et al., 2007b) and is projected to continue with Sphagnum mosses, which are favoured for peat formation, giving way to vascular plants (Fenner et al., 2007; Weltzin et al., 2003). Many grassland species (Juncus effusus, Molinia caerulea) have encroached on peatland areas as a result of anthropogenic pressures such as nutrient deposition and management practices (Berendse, 1994; Chambers et al., 2007a; McCorry and Renou, 2003; Shaw et al., 1996). These species are adapted to higher nutrient availability (Aerts, 1999) and thus can out-compete peatland species if nutrient levels are elevated through, for example, nitrogen deposition (Berendse et al., 2001). Their rooting systems are also commonly deeper and more extensive than upland plant species, facilitating colonisation of peatland areas with fluctuating water tables (Lazenby 1955, Loach, 1968). Our previous work (Ritson et al., 2016) has also shown that Juncus and Molinia may be create an increase in the speed and seasonality of C cycling in peatland litter layers due to their annual cycle of production of a large amount of relatively labile aboveground biomass”

Wrt modifying hypothesis, the final paragraph now reads: “Previous work has highlighted both the vegetative source and climate controls on production affecting the ease of removal of DOC and the formation of DBPs (Gough et al., 2012; Reckhow et al., 2007; Ritson et al., 2014a; Tang et al., 2013). The present research sought to build on the work of Ritson et al., 2016 by assessing the effect of oxygenation of peat and vegetation due to drought on peatland DOC flux and any interaction with projected changes in litter input. The previous study had only assessed the DOC quality differences between sources collected from the field with minimal degradation/oxygenation. To this end, climate simulations of varying drought severities defined in terms of percentiles of mean monthly rainfall were performed on four typical peatland vegetation types (Calluna vulgaris, Juncus effusus, Molinia caerulea and Sphagnum spp.) and a peat soil. After a six-week drought simulation, the DOC released upon rewetting was analysed in terms of optical properties and coagulation removal efficiency with ferric sulphate to determine: (a) whether drought conditions affect DOC production from peatland litter and soil types and (b) whether

the differences in litter quality identified in Ritson et al. (2016) between typical peatland species (Sphagnum and Calluna) and invasive, drought tolerant vegetation (Molinia and Juncus) cause different responses to drought in terms of DOC production (i.e. an interaction between the vegetation source and drought condition).

Line 145-147: A potential limitation to this study (and Ritson 2016) is the use of RO treated water to simulate rainfall. Several previous studies on rainfall simulation in peatland experiments utilize “artificial rainwater” with chemistry that matches natural rainwater. Natural (or artificial) rainwater may play a role in DOC quality that cannot be distinguished from this study. Have you considered this? **Added to Section 2.3 “RO or deionised water has been used in similar degradation studies (Cortez et al., 1996, Soong et al. 2014) and is employed so that no organic carbon is added to the samples and for the extraction step is considered to be representative of soil solutions collected *in situ* (Chantigny et al., 2007).”**

Line 169: Change “exiting” to “existing” **Done**

Line 334: Change “it” to “its” **Done**

Line 451-453: It appears that the authors’ ultimate justification is to provide support for catchment management programmes on peatland water table levels. This justification seems to always be mentioned fleetingly and no additional information about these programmes is ever provided. Additional details (either within Intro or Discussion) about these programmes and their effectiveness at managing catchments (i.e., provide specific examples where these have been implemented) and how they can (or have) minimize(d) costs and resources at water treatment plants would be nice to see. In its current form, this justification reads more as an attempt to scale your results without provided sufficient evidence for this rationale.

Evidence of minimised costs at treatment works are essentially the holy grail of this field of research and are, at present, lacking so hence the need for short-term studies such as this which suggest how ditch blocking may affect water treatment in the future. Many ditch blocking schemes have occurred in the UK however the timescales of blocking (<5 years) are small compared to the period of draining (typically 10-100 years) and the duration of peat formation (in the thousands of years). The introduction has been updated of include the preliminary results from the Mires project (lower peak flows in the catchment and shift to vegetation more tolerant of wet conditions).

Response to reviewer 2

The authors have addressed my remarks to the manuscript to my satisfaction, and I recommend publishing the manuscript. My only scientific remarks is that the authors may want to report fluorescence effects on Peak C/Peak T (Line 313-319), if it adds to the understanding.

Added to Table 1 and Section 3.3.

Some technical remarks:

Line 41 Spelling error «patterns» **Corrected**

Line 314 “were” **Changed to ‘are’**

Line 317 Capital P in peak, for consistency **All references to fluorescence peaks have been made lower case for consistency (except when at the start of a sentence)**

Table 2 and 3 Use same notation for the fluorescence variables **Done**

Line 478 “fluoresce” **Corrected**

Line 506 “decrease”? **Corrected**