# 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 ~~this~~ 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 ~~more immediate effects are~~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

## 1.0 Introduction

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

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

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

The impact of climate change on DOC production and drinking water treatment is complex and involves a number of biogeochemical cycles (Ritson et al., 2014b). 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).

Vegetative change has implications for ~~carbon~~ C storage in peatlands, as *Sphagnum* is responsible for a number of mechanisms (e.g. the production of recalcitrant litter) which allow ~~carbon~~ C to be stored over long time periods (van Breemen, 1995). Conversely, many vascular plants can destabilise colonised peat, stimulating decomposition by adding labile ~~carbon~~ C at the surface and through their root systems (Fenner et al. 2007; Gogo et al. 2010). As such, a number of programmes have aimed to promote *Sphagnum* dominance for ~~carbon~~ C storage and other ecosystem services by blocking drainage ditches to re-establish high water tables (Grand-Clement et al., 2013). However, further evidence is needed on the water quality outcomes of such interventions and the implications for water treatment.

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 quantify the effect of drought on peatland DOC flux and any interaction with projected changes in litter input. 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 peatland species and invasive, drought tolerant vegetation produce different quantities and quality of DOC with respect to drinking water treatment.

## 2.0 Methodology

### 2.1 Field site and sample collection

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

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

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

**2.2 Experimental Design**

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

Data were obtained from regional historic climate records of the UK Meteorological Office for the south west of England for the period 1910-2013 (UK Met Office 2014) and these values were used to define three severities of drought and a control value. Data for the months of June, July and August (310 months in total) were used to find the 50th, 25th, 10th and 5th percentile for total monthly rainfall and these values (Table 1) have been used to set monthly rainfall values for control (79.0 mm), mild (51.5), moderate (34.7) and severe droughts (23.3), respectively.

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

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

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

**2.3 Experimental procedure and laboratory methods**

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

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

The samples were then placed in an incubator for six weeks with simulated rainfall applied eleven times per month at regular intervals using high purity reverse osmosis (RO) treated water as per Table 1, following the methodology of Ritson et al. (2016). Data on final water weight, available in the supplement, confirm degrees of dessication between the treatments.

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

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

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

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

**2.4 Data analysis and statistical methods**

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

**2.5 Repetition of the control group conditions**

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

**3.0 Results**

**3.1 Omnibus ANOVA**

A factorial ANOVA was performed exploring the source, drought and interactive effects on DOC, SUVA, DOC removal efficiency and the removal of SUVA (Table 1~~Table 2~~). Extractable DOC and SUVA had significant source, drought and source*drought effects suggesting that there is variation in the sensitivity of the sources to drought. No drought effects were observed for DOC removal or SUVA removal, although the source had strong effects on these parameters. For all significant results the effect size for the source was much greater than that for the drought treatment.

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

| Variable / Factor | Water extractable DOC | pH | SUVA | Peak C | Peak T | DOC removal | SUVA removal |
|---|---|---|---|---|---|---|---|
| **DOC source** | **<0.001 (0.945)** | **<0.001 (0.429)** | **<0.001 (0.422)** | **<0.001 (0.846)** | **<0.001 (0.675)** | **<0.001 (0.396)** | **<0.001 (0.331)** |
| **Drought** | **0.007** | 0.143 | **0.007** | **<0.001** | **<0.001** | 0.418 | 0.475 |

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| | **(0.004)** | | **(0.034)** | **(0.011)** | **(0.035)** | | |
| **DOC source*Drought** | **0.050** | 0.157 | **0.005** | **<0.001** | **<0.001** | 0.234 | 0.951 |
| | **(0.004)** | | **(0.054)** | **(0.095)** | **(0.177)** | | |

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### 3.2 Water extractable DOC

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

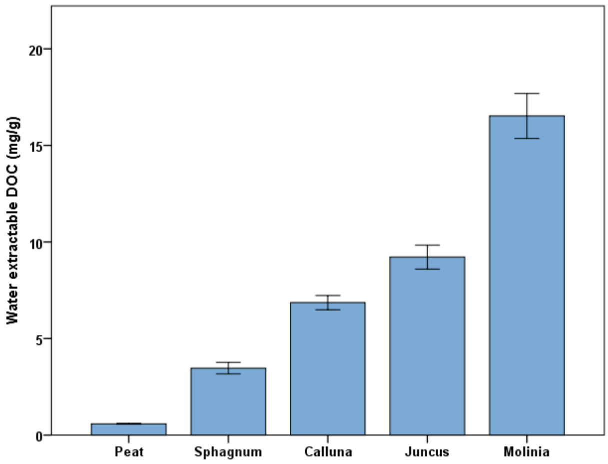


**Figure 1: Water extractable DOC of all samples across the different DOC sources (n=20 per source). Error bars at one standard error.**

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

~~**Table 3: ANOVA results testing the effect of drought on water extractable DOC from different sources. Significant effects (Holm-Šidák correction) are highlighted in bold with the $\omega^2$ estimate of effect size in brackets.**~~

| ~~DOC Source~~ | ~~p value (DOC extraction)~~ | ~~Alpha used for comparison~~ |
|---|---|---|
| ~~**Peat**~~ | ~~**0.010 (0.393)**~~ | ~~0.010~~ |
| ~~***Juncus***~~ | ~~0.038~~ | ~~0.013~~ |
| ~~***Sphagnum***~~ | ~~0.097~~ | ~~-~~ |
| ~~***Calluna***~~ | ~~0.418~~ | ~~-~~ |
| ~~***Molinia***~~ | ~~0.550~~ | ~~-~~ |

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

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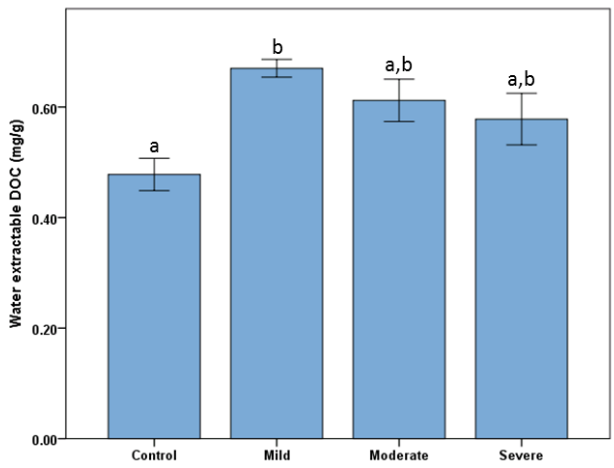


**Figure 2: DOC extracted from peat on rewetting following different severities of drought (n=5 per treatment). Letters indicate statistically similar groups from the Tukey test. Error bars at one standard error.**

~~A larger standard error in the moderate and severe drought treatments meant that these were not significantly different from the control (p=0.060 and p=0.204, respectively). Observations made throughout the experiment~~

suggested that in the severe treatment there was a large variation in the extent to which each replicate dried out. Once peat becomes dry, a hydrophobic layer forms (Spaccini et al. 2002; Worrall et al. 2003), meaning that less water will infiltrate the sample, therefore possibly increasing the severity of the drought beyond the experimental design.

Variation in peat water content during the experiment was not recorded; however the water content of the peat samples was measured at the end of the experiment. This averaged 16.11, 14.14, 15.11 and 5.95 g with standard errors of 7.7, 3.0, 15.9 and 28.1% for the peat control, mild, medium moderate and severe drought treatments respectively. The much larger standard error in final water content agrees with observations during the experiment and could perhaps explain some of the increased variation in extractable DOC for the severe drought treatment. This hypothesis was tested by comparing the variation from group mean in final water content for each sample with and the variation from group mean in extractable DOC. These two measures of variance were found to correlate (Spearman's ρ coefficient 0.484, p=0.031). suggesting some of the variation in DOC extracted may be explained by different water contents between the samples in each treatment. This could have been caused by small variations in the way rain was applied over the area of the sample or because shrinkage of the peat mass allowed water to pass through the funnel rather than infiltrate the peat, again possibly increasing the severity of drought beyond the experimental design. The source also had a significant effect (Table 2) on the pH of the samples with a Tukey test suggesting three statistical subsets with peat and *Calluna* < *Calluna* and *Molinia* < *Sphagnum* and *Juncus*. Mean values were in the order 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).

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### 3.3 SUVA and fluorescence

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

To investigate the source*drought interaction one-way ANOVAs were performed for drought effects on SUVA from each of the sources (Table 4) using a Holm-Šidák correction. Only *Molinia* was found to have a significant drought effect on the SUVA value (p=0.001, $\omega^2$=0.546).

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

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

Tukey's test suggested that both the moderate and severe drought treatments were significantly different than 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, ~~medium~~ moderate and severe treatment of the *Molinia* DOC, respectively. Figure 3 shows a graph of SUVA for *Molinia* DOC from the different treatment groups. ~~The SUVA value approximately doubles between the control and the moderate and severe droughts suggesting a large climatic control on the production of aromatic DOC DOM from *Molinia* litter~~. ~~Taken together, the main effects and interaction and $\omega^2$ values suggest that the source of DOC is the most important factor on SUVA and that the effect of drought is significant only for *Molinia* litter and not for the other vegetation types or the peat soil.~~

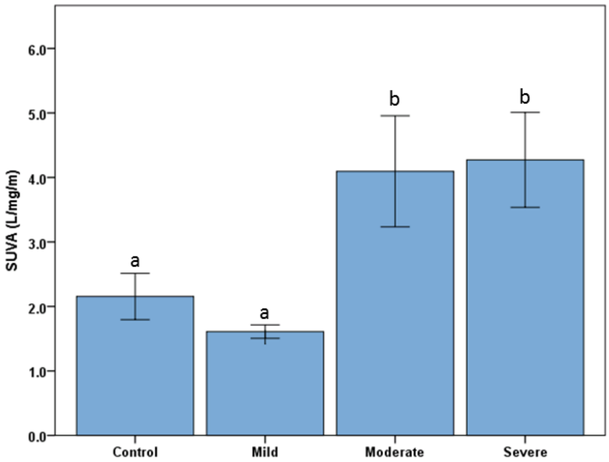


**Figure 3: SUVA value of *Molinia caerulea* derived DOC produced under differing severities of drought (n=5 per treatment) with error bars at one standard error. Letters indicate statistically similar groups from the Tukey test.**

The fluorescence data suggests interactive effects between drought treatments and the source of the DOC (Table 2) and these was further interrogated using the using a Holm-Šidák method. This suggested that there was a 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) with the Tukey test suggesting that the severe drought treatment was significantly lower than the control (P<0.01). For the peak T fluorescence value drought had a significant effect on *Juncus* DOC (p<0.001, $\omega^2$ =0.634) with the Tukey test suggesting that the severe drought treatment was significantly lower than the control (P<0.01)

### 3.4 DOC removal efficiency

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

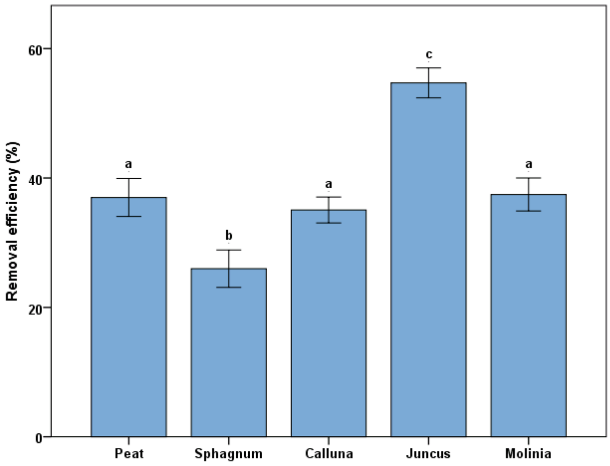


**Figure 4: DOC removal efficiency by coagulation/flocculation for different DOC sources (n=20 for each source, error bars at one standard error, letters indicate statistical subset according to Tukey test).**

### 3.5 SUVA removal efficiency

The removal of aromaticity, measured by SUVA, is of interest in drinking water treatment as aromatic compounds have a high propensity to form some of the regulated DBPs on chlorination (Bond et al., 2011). Large, aromatic compounds are selectively removed by coagulation/flocculation and as expected good removal (>70%) was observed for most of the samples. The mean values for the reduction in SUVA value following coagulation with ferric sulphate was in the order of peat (76.6 ± 1.8 %), *Sphagnum* (76.3 ± 2.5 %), *Molinia* (67.7 ± 4.7 %), *Calluna* (49.6 ± 5.3 %) and then *Juncus* (44.5 ± 2.3 %). The Tukey HSD test suggested that there were two subsets of DOC sources with similar means with peat, *Sphagnum* and *Molinia* > *Juncus* and *Calluna*. As with the overall DOC removal efficiency, there were no drought effects on SUVA removal (p=0.475). *Sphagnum* DOC showed good removal of SUVA despite relatively poor removal of total DOC, suggesting the aromatic compounds present in the sample are easily removed but that a large pool of aliphatic compounds are also present and these are more difficult to treat by conventional means.

### 3.6 Correlations between measures of DOC quality and treatability

A number of DOC quality indices based on absorbance and fluorescence measures were tested. The correlation coefficients for the different quality and treatability parameters are shown in Table 2~~Table 5~~. Peak C, a humic-like fluorescence peak, showed the best correlation with DOC removal efficiency while the ratio of humic-like to protein-like fluorescence (Peak C/T) gave a lower but still significant correlation coefficient. The magnitude of peak C values were in the order *Juncus*>*Molinia*>*Calluna*>peat>*Sphagnum* which is consistent with data on DOC removal efficiency. The SUVA value showed the best correlation with SUVA removal efficiency, suggesting that ~~DOC~~ DOM with a lower proportion of aromatic compounds (low SUVA value) contains aromatic compounds which are harder to remove by coagulation, possibly meaning they are either low molecular weight and/or also contain hydrophilic groups.

**Table 2~~5~~: Spearman's ρ for different DOC quality and treatability measures**

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

### 3.7 Repetition of ~~-~~the control group conditions

The data obtained from DOC extracted before and after the repeated simulation were analysed using student's t-test (equal variances assumed, confirmed using Levene's test) to assess whether the DOC extracted was significantly different following six weeks of exposure to oxygen without any experimental treatment. The results of this analysis are shown in Table 3~~Table 6~~.

**Table 3~~6~~: t-tests for pre and post-incubation peat samples (significant differences highlighted in bold)**

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

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

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## 4.0 Discussion

### 4.1 Water extractable DOC

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

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

The lack of a drought effect on DOC production from any of the vegetation types suggest the pulse in DOC observed post-drought elsewhere in catchment scale studies (Evans et al., 2005; Scott et al., 1998; Watts et al., 2001; Worrall and Burt, 2004) is likely to be due to the oxygenation of peat soils rather than any litter layer effects. Although there was no drought effect,~~,~~ ~~This~~ the increase in peat-derived DOC observed on oxygenation (Table 6) is significant for downstream water treatment as our previous work showed this has more environmental persistence than vegetation sources (Ritson et al., 2016) and the UV and fluorescence data suggested DOC from peat exposed to oxygen may be more difficult to remove by conventional treatment measures. High DOC production was noted for the vascular plants, suggesting they may be an important source of DOC within peatland catchments during the period of their senescence, although drought does not affect the amount they produce. Drought conditions may, however, precipitate a change in vegetation type favouring more drought-tolerant species (Bragazza, 2008), which may have longer term effects for peatland biogeochemistry.

~~The amount of DOC extracted from *Sphagnum* was low, which may be due to the fact that its litter is recalcitrant to decay due to its high polyphenol content and numerous compounds with antimicrobial and antifungal properties (van Breemen, 1995). The other typically upland species, *Calluna*, produced the second least amount of DOC of the vegetation types, which also agrees with literature surrounding the recalcitrance of~~

its litter (Aerts, 1995; Huang et al., 1998) and field studies suggesting areas of *Calluna* produce more porewater DOC than *Sphagnum* (Armstrong et al., 2012). The two grassland species, *Molinia* and *Juncus*, produced much larger amounts of DOC per g of dry weight. This is in keeping with the growth strategy of these species, whereby they rapidly produce a large amount of above-ground biomass and produce litter which decays readily, providing a positive feedback to its strategy of rapid growth and fast nutrient cycling (Aerts, 1999; Mann and Wetzel, 2000). This growth strategy is in contrast to that of the upland species *Calluna* and *Sphagnum*, which have adapted to low nutrient availability and therefore grow slowly, have nutrient poor litter and invest fewer resources in material which cycles rapidly (Aerts, 1999). Correlations between litter C:N ratio, suggesting nutrient availability, and amount of extractable DOC have been found in our previous work (Ritson et al., 2016) and elsewhere in the literature (Soong et al, 2014), suggesting a shift to the drought tolerant *Molinia* and *Juncus* may increase DOC flux from the litter layer..

*Molinia* encroachment is a well acknowledged problem in Europe (Chambers et al., 2007b; Heil and Diemont, 1983; Hughes et al., 2007; Milligan et al., 2004) and nitrogen deposition and drier summers may mean more grassland species in the UK uplands in the future. The results of this study suggest the transition from *Sphagnum* to *Calluna* and *Molinia* observed in a paleoecological study of the area nearby our Exmoor site (Chambers, 1999) may have increased the amount of extractable DOC in the litter layer on g per g basis, as well as increased the seasonality of its export (Ritson et al., 2016). The much greater effect sizes for DOC source versus drought controls in this study and temperature and rainfall controls in previous work (Ritson et al., 2014a) suggest that the source of the DOC may be the primary driver of DOC quantity and quality in peatland litters, consistent with litter decomposition studies in boreal peatlands (Straková et al., 2011). This has important implications for overall soil carbon C stability in peatlands as the addition of labile carbon C from litter can stimulate the decomposition of older carbon C (Fontaine et al., 2007).

Studies concerning vegetation control of pore-water DOC are limited, but are reviewed in Ritson et al. (2016). Fenner et al. (2007) found elevated $CO_2$ caused a transition from *Sphagnum* to *Juncus* dominance on monoliths from flush peat which gave a 66% rise in DOC, attributed to an increase in above-ground biomass, more labile litter and stimulation of peat decomposition through root exudation. Vestgarden et al., (2010) found DOC in pore-waters beneath different vegetation types to be in the order *Molinia*>*Calluna*>*Sphagnum* in shallow samples but *Sphagnum* had higher concentrations than the vascular plants at depth and showed less seasonal variation. This has been linked to the seasonal growth cycles of vascular plants in peatlands which provide litter which decomposes rapidly and produces a large amount of DOC on a mg per g basis creating greater seasonality in DOC export (Ritson et al., 2016).

**4.2 SUVA and fluorescence**

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

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

A drought effect was observed for peak C (*Juncus* and *Molinia*) and peak T (*Juncus*) with lower values under severe drought. These indices have been described as 'humic-like' and 'protein-like', respectively, however meaningful interpretation of the moieties responsible is difficult as many compounds can fluorescence in these regions (Aiken, 2014). From Table 5, however, we can suggest that decreases in peak C caused by drought may decrease the amenability of DOC to removal by coagulation.

Taken together, the main effects and interaction and ω2 values suggest that the source of ~~DOC~~ DOM is the most important factor on SUVA and fluorescence and that the effect of drought is significant only for *Molinia* and *Juncus* litter and not for the other vegetation types or the peat soil. These results suggest encroachment of grassland species into the uplands will increase seasonal ~~DOC~~ DOM flux from the litter layer and increase the aromaticity of exported ~~DOC~~ DOM and create a small drought effect where *Molinia* or *Juncus* litter is present. The lack of a drought effect for peat SUVA suggests that short pulses of highly aromatic DOM are unlikely to be observed but ~~that the~~ long-term effects caused by water table drawdown identified elsewhere in the literature indicate elevated DOC concentration and SUVA values over periods of years following droughts.~~.~~ The effect of more frequent, repeated droughts and the ability of peat soils to recover remains an area for further research. ~~will likely be more important for DOC flux than the short-term effects studied here.~~

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### 4.3 DOC and SUVA removal

DOC removal for all sources were typical of literature values (Matilainen et al., 2010), with *Juncus* DOC proving the easiest to remove and *Sphagnum* DOC the hardest. *Sphagnum* DOC showed good removal of SUVA despite relatively poor removal of total DOC, suggesting the aromatic compounds present in the sample are easily removed but that a large pool of aliphatic compounds are also present and these are more difficult to treat by conventional means. Repeating the control condition and measuring DOC production and quality parameters allowed an estimate of the effect of oxygen exposure for peat samples. This showed a decrease in SUVA value and humic-like character (fluorescence Peak C) as well as a large increase in extractable DOC.

These changes in quality parameters may provide an explanation of why poorer removal by coagulation was achieved for peat following this drought experiment than had been observed in our previous work (Ritson et al., 2016). In Ritson et al. 2016, coagulation experiments were performed on DOC extracted from fresh peat which had been exposed to a minimal amount of oxygenation during transport and very good removal by coagulation/flocculation was found. In contrast, the experiments reported here on peat exposed to oxygen showed comparatively poor removal via coagulation/flocculation. The repetition of the control group indicates that any exposure to oxygenation can decease the SUVA and Peak C values of DOC extracted from peat and both of these parameters have been linked to ease of treatability of DOC (Matilainen et al., 2011). ~~as less aromatic/humified material is likely to be harder to remove by coagulation (Bond et al. 2011).~~ Poorer removal was observed for *Sphagnum* than in our previous work; the effect of more oxygenated conditions on vegetation decomposition remains an area for further research, particularly as climate change may increase the likelihood of water table draw down in peatlands.

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

**5.0 Conclusions**

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

**Author contributions**

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

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## Response to reviewer comments and changes made

Reviewer #1

**Point 1: 'The study is based on the analysis of only 100 water samples for easily measureable parameters'**

Our response in the online discussion: "Although it would be desirable to include as many samples as possible in the experimental design this was limited to 5 replicates per vegetation/treatment for practical considerations. Similar studies looking at decomposition have used similar, or indeed lower, numbers of replicates. Soong et al. (2015) used three replicates per substrate in a laboratory decomposition experiment concerning DOC from fresh and pyrolysed litter. Fellman et al. (2015) also used three replicates per substrate in a litterbag study of litter decomposition whilst Cleveland et al. (2004) performed six DOC extractions per litter type and then bulked them to create three replicates. In a laboratory study on the decomposition of *Calluna Vulgaris*, Van Meeteren et al. (2007) used five replicates per treatment in a similar approach to our own study.

We feel five replicates, giving 100 samples in total, is a good balance between capturing natural variability in the samples and practicality given the samples filled three climate control cabinets and that manual irrigation of the samples (to ensure even wetting of the vegetation/soil) was necessary.
In the subsequent analysis 200 samples were analysed for TOC and UV properties (pre- and post-coagulation) as well as 100 fluorescence samples. The coagulation experiments themselves were time consuming as commercial jar-testing apparatus is limited to six samples per run and each run takes ~2hrs to perform. Although we were unable to present the data due to quality concerns resulting from instrument failure, 100 samples with two replicates (200 total) were also chlorinated, quenched and then extracted to assess disinfection by-product formation.

The reviewer notes the lack of any supporting water chemistry or litter chemistry data in the paper. We apologise for this oversight as we did measure pH of the extracts and will include these data in an updated version of the manuscript. We also measured the carbon and nitrogen content of a sub-sample of the starting soil/litter, however we did not include this in the manuscript as correlations between C:N and extractable DOC were shown in out 2016 paper in *Scientific Reports*. We instead referred to this paper in the discussion section. We will include the C:N data in an updated version of the manuscript. Although measuring $CO_2$ production during the experiment would have been desirable we already acknowledge the lack of these measurements as a weakness in our ability to confirm the cause of changes in extractable DOC between drought treatments (line 363)."

Corrections made:

Added to section 2.2: 'Similar experiments concerning the decomposition of litter have used three replicates per treatment (Fellman et al., 2013; Soong et al., 2015), suggesting our approach of using five samples per treatment is adequate to capture variability between samples.'

pH data added to Table 2 and section 3.2

Section 2.3 added: 'Elemental analysis on a subsample of the starting material revealed C:N to be in the order peat (29.9), *Molinia* (35.7), *Juncus* (42.2), *Calluna* (56.5) and *Sphagnum* (93.7) as reported in Ritson et al. (2016).'

**Point 2: The degree of desiccation after and during the 6 weeks was not measured, nor the biological status of the samples. Only for the peat samples some data on water contents at the end of irrigation (unit?) are given in line 251.**

Our response in the online discussion: "The unit of the final water content is grams and is given in the text. Data on final water content for the peat soil and *Sphagnum* litter are available and confirm the efficacy of the irrigation treatment in causing degrees of desiccation in the treatments. This can be included in the updated manuscript."

Corrections made:

Final water weight data added to the supplement and referred to in section 2.3.

**Point 3: The different intensity of irrigation should induce different leaching rates and different DOC fluxes from the samples. No information is given on that.**

Our response in the online discussion: "Unfortunately, DOC from each irrigation event was not recorded. We note in the method section that:

> 'Previous work has shown that the amount of water used to extract DOC and whether one extraction is performed or sequential extractions to simulate multiple rainfall events gives no significant variation in DOC quality (Don and Kalbtiz, 2005, Soong et al., 2014), only changes in the total amount of carbon'.

We would therefore suggest that any differences in DOC quality are captured by our approach. Rewetting following drought of interest as this has been highlighted in the literature (and discussed in our introduction) as a period of increased riverine DOC concentrations. One of the goals of the experiments was to ascertain whether litter layer DOC flux played a role in the increased DOC concentrations post-drought or whether this was entirely due to processes within the peat, hence our focus on rewetting."

**Point 4: Following the 6 weeks of irrigation, all samples were air dried before water extraction (line 148) which does not make sense to me: If all samples were air dried before extraction, the pre irrigation to induce different degrees of desiccation seems meaningless. The rewetting of air dried soil samples cause specific effects (Birch effects) that my override the aimed irrigation effect.**

Our response in the online discussion: "Air-drying was performed so that accurate estimates of extractable DOC could be determined on a mgC $g^{-1}$ basis. Whilst air drying the samples after the irrigation simulations may have increased the homogeneity between the sample treatments, we feel this is likely to be minor as this occurred for approximately 2-3 days compared to a 42 day simulation. Also, during the simulation all samples will have been exposed to periods with no irrigation multiple times due to the number of days of rainfall being fixed across all treatments. The differences between treatments, therefore, are the extent of decomposition and DOC production during the 42 day simulation due to desiccation rather than the final water content."

**Point 5: a) The data presentation needs substantial revision: The content of tables 1 – 6 and the main message can easily be given in text form (tables 1-6 can be omitted).**

Our response in the online discussion: "We can reduce the number of tables in the manuscript if the editor feels this is necessary. Table 1 can be described easily in the text so may be removed, however Table 2 contains twelve p values as well as eight $\omega^2$ values so we feel a table is appropriate to summarise this information for the reader. It would also be possible to incorporate Tables 5 and 6 into the text if necessary."

Corrections made: Table 1, 3, 4 now described in the text.

**Point 5: b) Fig. 1 gives DOC release from the 5 sources, Fig. 2 gives drought effects on only peat samples, Fig 3 gives SUVA only for Molinia, Fig 4 gives removal efficiency for the 5 sources, but without drought effects. Hence, the presentation is confusing and inconsistent.**

Our response in the online discussion: The reasoning for this is explained in the text as treatment and/or interactive effects are interrogated. In Fig 2 drought effects were shown only for peat as this was the only DOC source with significant drought effects. Similarly, only *Molinia* was included in Fig 3 as this was the only source with a significant drought effect on SUVA. Finally, drought effects were not included in Fig 4 as there were no significant drought effects for removal efficiency.

**Point 6: The conclusions on effects of climate and vegetation change on peatland biogeochemistry are highly speculative in view of this short term laboratory study.**

Please see the online discussion for a point-by-point defence of our conclusions section. The discussions section has been significantly shortened to focus on the drought effects we observed rather than making broader comments about vegetative change in peatlands. We feel this helps differentiate this manuscript further from Ritson et al 2016 and avoids the over-interpretation the reviewer suggests.

Reviewer #2

**Point 1: The abstract states in line 29- 30 that "more immediate effects are observed in peat soils". This is correct, but if drought events will be more frequently observed in the future, these pulses of DOC can also be regarded as a long- term effect, in that they will be occurring more frequently, potentially giving a steady increase in DOC concentration.**

Corrections made:

Sentence now reads: "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."

**Point 2: It is somewhat surprising that drought effect was only observed with the mild treatment. This is explained by large variability in the other treatments, possibly because some samples became drier than intended (line 244- 261). The arguments are mainly repeated in lines 359- 363, but I miss a discussion of the implications of this. Do these results indicate that there is an "optimum" drought frequency for DOC release, i.e. that DOC release will not increase with increasing drought frequency and severity, but will increase to a certain point and then decline?**

Our response in the online discussion: 'Yes, we hypothesise that this is due to 'water scarcity limiting microbial activity (Toberman et al., 2008) and/or increased hydrophobic protection decreasing the extractable DOC on rewetting'. We would suggest that at very severe levels of drought DOC production is limited by water scarcity, however this would not stop oxygenation of peat and therefore greater potential for increased DOC production in the future due to the enzymatic latch mechanism. We will add a more detailed explanation of the implication of this finding to the amended manuscript.'

Corrections made:

Further discussion has been added to section 4.1 on this matter.

**Point 3: Line 423- 426: Are you suggesting that drought causes permanently altered biogeochemical controls so that the released DOM becomes gradually more aromatic? The literature usually argues that more aromatic DOM is released after single drought events, but that increased frequency of these will give increased aromaticity over time. Please explain in more detail in which way you suggest your single rewetting differs from field studies and how this may have affected the results.**

Our response in the online discussion: "In this section we discuss the lack of an increase in SUVA value for peat from the drought simulation, in contrast to field studies. The literature often suggests that DOC is elevated for many years after drought events. As we were monitoring a single rewetting event we suggest that one of the possible explanations for conflicting results could be that many of the longer term processes involved in increased DOC concentration and aromaticity (enzymatic latch, recovery from sulphate acidification from oxygenation) may not have had time to occur. We will explain this more clearly in the updated manuscript."

Corrections made:

Further discussion has been added to section 4.2 on this matter.

**Point 4: In line 431- 435 the results on both DOC and SUVA seem to be summarized. Do you consider that there was a "lack of drought effect for peat" or are you here only talking about SUVA? And again, you argue that the experiment simply investigates short- term effects. It is true, in the sense that only one single drought event is mimicked. But are there arguments that long- term effects of drought go beyond the sum of many single events, that there are more permanent changes going on? This is what you indicate, but you do not explain or express it clearly.**

Our response in the online discussion: "Yes, as this is in the section headed 'SUVA' we were only referring to effects on SUVA in this statement. We will clarify this in the updated manuscript. The reviewer is correct that our intention was to suggest that frequent droughts could create long term changes in peatland biogeochemistry, but that our experiment did not cover this. Again, we would be happy to clarify this in the updated manuscript."

Corrections made:

Clarified that we were referring only to SUVA and reworded concluding statement at the end of section 4.2.

**Point 5: Line 186- 192: Please explain why peat samples for this additional test were collected at a different site. And explain more clearly why this extra experiment was performed? Was it simply because in the main experiment there was no extraction prior to treatment, so you did this to look at changes over the course of the experiment?**

Our response in the online discussion: "The reasoning behind performing the extra experiment was to interrogate the possibility that *any* oxygenation of peat could affect DOC quantity and quality and thus explain differences between the results found here and our previous work. The reviewer is correct that this could have been achieved by extracting DOC from a sub-sample prior to the start of the original experiment, however as this was not done we performed this short experiment. The samples were collected from an ombrotrophic peatland with a comparable mixture of vegetation (*Juncus*, *Molinia*, *Sphagnum*, *Calluna*, *Eriophorum*) and were of the same level of humification (von Post scale). Although not identical to the peat collected in the original experiment, we feel these samples are similar enough to test the hypothesis that the control conditions used in the original experiment give enough oxygenation to alter DOC properties."

**Point 6: Line 439- 447: The discussion comes here, but it is not clear. Yes, you show that DOC removal may decline with time due to change in DOM properties, but it is not clear why this suggests that DOC removal was lower in this experiment than in Ritson et al. (2016). As far as I can see the control samples in the current experiment underwent exactly the same treatment as the peat samples in the previous experiment. Figure 4 shows DOC removal across treatments, but the results for the control group given in the supplement should be directly comparable to Figure 1 in the 2016 paper – which shows a big difference in DOC removal. I cannot see that this follow- up experiment explains why there is such a big difference. This is important, as you argue (e.g. in the abstract) that DOC from peat is harder to remove, but in Ritson et al. (2016) it is the easiest to remove. Please elaborate.**

Our response in the online discussion: "The confusion here lies in the experiment we are referring to in Ritson et al. (2016) as there are multiple experiments in this paper. The control group of this paper is directly comparable to the experiment entitled 'Litter decomposition in the laboratory' in the Ritson et al. 2016 paper where only data on amount of DOC extracted were presented. The comparison we were intending to make, however, is to the first experiment from the 2016 paper entitled 'Ease of DOC removal during the treatment process for different peatland sources'.

In the 2016 coagulation experiments DOC was extracted from fresh peat which had had minimal exposure to oxygen. We suggest a reason why the peat DOC in the 2017 paper showed poorer removal by coagulation was that it had been exposed to oxygen over the length of the simulation and this may have altered the treatability of the extracted DOC. The repetition of the control group conditions provides evidence for this as it shows exposure to oxygen causes a decrease in Peak C and SUVA, both of which have been correlated with ease of removal via coagulation in the literature.

We will explain this in greater detail in an updated version of the manuscript and make it clear that when we say in the abstract that that peat DOC is harder to remove we mean peat that has been exposed to oxygen compared to peat which has not."

Corrections made:

Abstract editing to clarify we mean peat DOC which has been exposed to oxygen is harder to remove. Section 4.3 expanded to explain the differences between samples in this experiment and Ritson et al. 2016 and therefore why we feel oxygenation of peat leads to DOC which is harder to remove via coagulation/flocculation.

**Point 7: Section 3.6: The fluorescence data are only presented in connection with coagulation. But what about difference in fluorescence properties related to drought treatment or vegetation type? Why are these results not presented and discussed?**

Our response in the online discussion: "These data are available and can be included in the updated manuscript. The data suggest a drought effect on Peak C (humic-like) fluorescence for both *Molinia* and *Juncus* and an effect on Peak T (protein-like) fluorescence for *Juncus*."

Corrections made:

Addition to Table 2 of ANOVA results for peak C and peak T. Section 3.3 expanded to include results from SUVA and fluorescence. Section 4.2 expanded to include discussion of both SUVA and fluorescence with the addition of the following paragraph:

'A drought effect was observed for peak C (Juncus and Molinia) and peak T (Juncus) with lower values under severe drought. These indices have been described as 'humic-like' and 'protein-like', respectively, however meaningful interpretation of the moieties responsible is difficult as many compounds can fluorescence in these regions (Aiken, 2014). From Table 5, however, we can suggest that decreases in peak C caused by drought may decrease the amenability of DOC to removal by coagulation.'

**Point 8: Line 367- 369: This probably relates to the results given in table 6, but it does not fit with the lack of drought effect on peat SUVA. I suggest just briefly mentioning this here, but refer to the lack of drought effect for peat discussed in section 4.2**

Corrections made:

Altered for clarity

**Point 9: Line 460- 462: You could mention the drought effect on SUVA for Molinia, which may partly counteract the oxygenation effect of peat (lower aromaticity).**

Corrections made:

Conclusions section has been amended to add this point in.

Technical corrections

**Line 463- 464: It is claimed that drought (oxygenation) deceases aromaticity, while the drought experiment itself did not show effects on DOM quality for peat soils. You argue why this may be so in section 4.2, but please repeat it briefly here and modify the conclusions (make them less firm).**

Done

**Line 76: You may mention what kind of programmes/how Sphagnum dominance is promoted**

Done

**Line 139: I assume the intervals between the rainfall simulation were the same, but please specify this**

Done

**Line 152: I assume the extracts were filtered before further analysis? Please explain**

Yes, added in that extracts were filtered using re-ashed GF/F filters (Whatman)

**Line 167: Was the coagulation performed on filtered samples? Incase, please justify this**

Yes, as we were working with model waters with no turbidity, filtration was performed to standardise the extracts and remove the small pieces of vegetation in the leachate.

**Line 207- 208: Move and merge into 3.1 to avoid repeating this information here**

Done

**Line 219- 222: Move the more detailed explanation of the method to section 2.4**

Done

**Line 230- 231: Specify that you are talking about the peat soil**

Done

**Line 276- 278: Specify that you are talking about the Molinia samples**

Done

**Section 3.4: Move the sentence in line 296- 297 (on drought effects) to the beginning of the section.**

Done

**Line 299- 300 simply repeats line 293- 294 – move and merge.**

Done

**Line 308- 310: Move to the discussion (section 4.2)**

Done

**Line 139: Space between "applied" and "eleven" missing.**

Corrected

**Line 151- 2: "Kalbitz" incorrectly spelled, and both references missing in the reference list. And why is the reference not put at the end of the sentence? Is the latter part the author's own interpretation?**

Citation corrected and moved to the end of the sentence.

**Line 155: Unit misspelled, should be mgC l- 1.**

Corrected

**Line 266: Delete "group two Calluna and"**

Done

**Line 278: Replace "medium" with "moderate", as this is the term used elsewhere**

Done

**Line 323: Add DOC before "removal efficiency"**

Done

**Line 344+line 346 and similar places: When talking about the properties of the actual molecules in question, use DOM, not DOC. DOC is just a notation for what is actually analysed and for which we can talk about changes in concentration etc, but DOC cannot be more or less aromatic or humified.**

Done

**Line 433: Add "SUVA" before peat**

Done

**References: Sometimes access date is added, sometimes not. In general web page and access date should not be necessary for published papers, but at least be consistent.**

Apologies, this formatting was done with the automatic style for *Biogesciences* through Mendeley. The references have now been altered to be consistent (DOI, web page and access date removed).

**Line 337: I would change "without any experimental treatment" to "at control conditions"**

Done

**Line 344- 347: Delete this type of discussion text from the results chapter**

Done

Reviewer #3

**The authors do tend to over-interpret the magnitude of their results on future drought effects given this short-term laboratory study, but I still find merit in this study and recommend publication following revisions on the comments listed below.**

The discussions section has been significantly shortened to focus on the drought effects we observed rather than making broader comments about vegetative change in peatlands. We feel this helps differentiate this manuscript further from Ritson et al 2016 and avoids the over-interpretation the reviewer suggests.

Specific Comments

**Lines 38-41: Vague sentences that aren't useful to a reader as written.**

Altered to 'The extent to which conditions favourable to peat formation exist are threatened by climate change (Clark et al., 2010; Gallego-Sala and Prentice, 2012) and altered precipitation patters and more frequent droughts may also destabilise sequestered carbon (Evans and Warburton, 2010; Fenner and Freeman, 2011; Freeman et al., 2001a).'

**Line 42: "represents a significant flux of carbon from peatlands (Dinsmore et al. 2010)" - Provide a range of flux values rather than another vague sentence. Don't make the reader dig into every one of your citations to find useful information that could have easily been supplied.**

Done. Added that DOC is around 24% of NEE C uptake (Dinsmore et al. 2010).

**Line 76-77: Vague sentence. Provide useful information from this citation that explains which programmes are being promoted to increase Sphagnum dominance.**

Done. Added 'by blocking drainage ditches to re-establish high water tables'.

**Line 219-222: Description of Holm-Sidak correction should be moved to Methods section "2.4 Data analysis and statistical methods"**

Done. This was added at the first stage of revisions as in the initial submission it was queried why *Juncus* was not classed as significant in this section.

**Line 234-236: Not a result. Move to Discussion.**

Done.

**Line 245-249: Not a result. Move to Discussion.**

Done.

**Line 253-254: Not a result. Move to Discussion.**

Done.

**Line 258-261: Not a result. Move to Discussion.**

Done.

**Line 281-283: Not a result. Move to Discussion.**

Done.

**Line 316-318: Not a result. Move to Discussion.**

Done.

**Line 335-337: Do not introduce a new statistical test in the Results. Move this entire description to the Methods section "2.4 Data analysis and statistical methods"**

Citations for Sperman's, Student's and Levene's techniques added to methods section.

Technical Corrections

**Inconsistent use of "carbon" and "C" throughout the manuscript. Write "carbon (C)" the first time it is used and "C" afterwards.**

Done.

**Line 59: Change "effects" to "affects"**

Done.