Sensitivity of peatland litter decomposition to changes in temperature and rainfall

AUTHORS AND AFFILIATIONS

Michael C. Bell[a],*, Jonathan P. Ritson[b,c], Anne Verhoef[a], Richard E. Brazier[d], Michael R. Templeton[c], Nigel J.D. Graham[c], Chris Freeman[e], Joanna M. Clark[a]

[a] Soil Research Centre, Department of Geography and Environmental Science, School of Archaeology, Geography and Environmental Science, The University of Reading, Whiteknights, PO Box 227, Reading RG6 6AB, UK

[b] Grantham Institute for Climate Change, Imperial College London, South Kensington, London SW7 2AZ, UK

[c] Department of Civil and Environmental Engineering, Imperial College London, South Kensington, London SW7 2AZ, UK

[d] Geography, College of Life and Environmental Sciences, University of Exeter, EX4 4RJ, UK

[e] Wolfson Carbon Capture Laboratory, School of Biological Sciences, Bangor University, Bangor, Gwynedd LL57 2UW, UK

[*]Corresponding author: Soil Research Centre, Department of Geography and Environmental Science, School of Archaeology, Geography and Environmental Science, The University of Reading, Whiteknights, PO Box 227, Reading RG6 6AB, UK. E-mail address: m.c.bell@pgr.reading.ac.uk

24 Abstract

25 Changes to climate are projected over the next 50 years for many peatland areas. As
26 decomposition of peat-forming vegetation is likely to be intrinsically linked to these changes in
27 climate, a clear understanding of climate-peat dynamics is required. There is concern that
28 increased temperature and decreased precipitation could increase the rate of decomposition
29 and put the carbon sink status of many peatlands at risk, yet few studies have examined the
30 impact of both climatic factors together. To better understand the sensitivity of peatland
31 decomposition to changes in both temperature and precipitation and their interaction, we
32 conducted a short-term laboratory experiment in which plant litters and peat soil were
33 incubated, in isolation, in a factorial design. Treatments simulated baseline and projected
34 climate averages derived from the latest UK climate change projections (UKCP09) for Exmoor,
35 a climatically marginal peatland in SW England. Regular carbon dioxide flux measurements
36 were made throughout the simulation, as well as total mass loss and total dissolved organic
37 carbon (DOC) leached. The largest effect on carbon loss in this multifactor experiment was
38 from substrate, with *Sphagnum*/peat releasing significantly less C in total during the
39 experiment than dwarf shrubs/graminoids. Climate effects were substrate specific, with the
40 drier rainfall treatment increasing the DOC leaching from *Calluna*, but decreasing it from
41 *Sphagnum*. Partitioning between CO_2 and DOC was also affected by climate, but only for the
42 peat and *Sphagnum* samples, where the future climate scenarios (warmer and drier) resulted
43 in a greater proportion of C lost in gaseous form. These results suggest that indirect effects of
44 climate through changes in species composition in peatlands could ultimately turn out to be
45 more important for litter decomposition than direct effects of climate change from increased
46 temperatures and decreased rainfall.

47 **Keywords**: decomposition; Exmoor; blanket peat; uplands; DOC; UK

48

49 1. Introduction

50 Northern peatlands are an important carbon store, holding around one third of the
51 global soil carbon stock (Gorham, 1991). For peatlands to accumulate organic matter, and thus
52 sequester carbon from the atmosphere, the overall loss of carbon from the system through
53 the combined decomposition of plant litter and peat must be lower than C input via litter
54 production and vascular plant root exudation (Frolking et al., 2010; Limpens et al., 2008).
55 Decomposition is the breakdown of organic matter. It can be due to one or a number of
56 physical, chemical or biological processes. Carbon dioxide (CO_2), dissolved organic carbon
57 (DOC), nutrients and stable hummus are among the principal final products of decomposition
58 (Bragazza et al., 2009). Carbon is primarily lost as CO_2 in peatlands (Billett et al., 2010).
59 However, additional losses in the form of methane (CH_4), produced during anaerobic
60 decomposition, and DOC to aquatic systems can be an important component of the peatland
61 carbon balance in some areas (Köehler et al., 2011). The speed and final product of the
62 decomposition process is dependent on the chemistry of the organic matter, and the
63 environment in which it decomposes (Limpens et al., 2008).

64 Understanding how peat and plant litter decomposition could be affected by climate
65 change, specifically changes in temperature and rainfall, is key to an improved understanding
66 of how the peatland carbon source/sink status could change during the 21st century. Northern
67 peatlands are typically dominated by remains of mosses of the genus *Sphagnum*, a bryophyte
68 (Turetsky, 2003). *Sphagnum* has played an important role in peatlands becoming such a large
69 carbon sink. Not only does the recalcitrance of its litter mean that it keeps C in the system for
70 longer, but the presence of *Sphagnum* maintains acidic, nutrient poor conditions which make
71 it difficult for plants with more labile litter to establish themselves (van Breemen, 1995).

72 Climate change may alter vegetation types in peatlands with vascular plants becoming more
73 dominant (Buttler et al., 2015; Dieleman et al., 2015; Fenner et al., 2007; Weltzin et al., 2003).
74 However, many ongoing catchment management programmes aim to encourage *Sphagnum*
75 species over vascular plants as part of peatland restoration programmes (Grand-Clement et
76 al., 2013).

77 While some authors have studied the effects of climate variables on the treatability of
78 water from different peatland plant species (e.g. Ritson et al., 2014; Tang et al., 2013), little
79 work has so far been conducted on the total flux of carbon and the partitioning between
80 gaseous and fluvial losses from different peatland plant species. This partitioning is an
81 important parameter to include in carbon cycle models, particularly for climate change
82 modelling as there is likely to be a lag between DOC release from the soil and its incorporation
83 into the atmospheric pool, as in-stream processing can lead to the temporary storage of C
84 within the aquatic system (Hope et al., 1994). An understanding of partitioning of carbon
85 losses between aquatic and gaseous fractions from different vegetation sources is also
86 important for predicting whether catchment management programmes aimed at restoring
87 certain species have the desired holistic effects of improving drinking water quality (including
88 enhanced C sequestration) and do not result in environmental problem-shifting.

89 Decomposition of litters in the field is traditionally measured using the litter bag
90 technique (Bragazza et al., 2009; Wieder and Lang, 1982). Litter of a known mass is enclosed
91 in mesh bags with openings large enough for decomposers to access the food source, but
92 small enough to prevent the physical loss of litters. Samples are incubated in the field, either
93 on, or just below the soil surface (Johnson and Damman, 1991; Moore et al., 2007) and
94 decomposition rate is quantified via mass loss or changing nutrient quotients of the litter
95 (Keuskamp et al., 2013). *In situ* litter decomposition studies, using this technique, have

96 suggested multiple drivers for increased decomposition rates in peatland systems including:
97 elevated nutrient additions (Bubier et al., 2007), water-table drawdown (Straková et al.,
98 2012), litter quality (Limpens and Berendse, 2003) and temperature (Moore et al., 2007).
99 However, these field-based studies are limited to a single measure of decomposition; mass
100 loss. Mass loss gives a valuable measure of net decomposition, which can be useful for
101 comparing between litters, but does not provide information on the final product of the
102 decomposition process. Carbon dioxide and DOC not only represent different flux pathways
103 (gaseous versus aquatic), but can also be indicative of different processes and stages of
104 decomposition. CO_2 is in effect representative of fully utilised carbon, whereas DOC could be
105 stored in the peat column or utilised by microbes and exported to the atmosphere via
106 respiration (Pastor et al., 2003; Turetsky, 2003).

107 Laboratory incubations of peatland litters to examine the relationship between
108 decomposition and climate have been limited to date. Studies that have been conducted have
109 tended to concentrate on a single measure of decomposition, have focussed solely on peat
110 rather than vegetation, or have just looked at one environmental variable, such as
111 temperature (e.g. Neff and Hooper 2002; Moore et al. 2008) or water table (e.g. Freeman et
112 al. 1993), in isolation. The effect of interactions between changes in temperature and rainfall
113 on the decomposition of peatland litter is not currently well understood (Breeuwer et al.,
114 2008). A gradient based mesocosm study measured increased C soil respiration in mesocosms
115 transplanted to a warmer, drier location (Bragazza et al., 2016). However, isolating the effects
116 of climatic variables such as temperature and rainfall from other confounding variables can
117 be difficult in the field as these factors naturally co-vary. It is also difficult to separate the
118 effects on different litters and measure the relative decomposition from different sources in
119 the field or in intact mesocosms. To address this, previous studies have incubated soils or

120 litters from wetland sites in isolation, notably Moore and Dalva (2001), Neff and Hooper
121 (2002) and Wickland et al. (2007). This was the approach taken here.

122 A better understanding of the sensitivity of different peatland litters to changes in
123 temperature and rainfall regime is needed to enable predictions of the impact of climate
124 change on the stability of peatland carbon stocks, and to support better parameterisations of
125 models that simulate past, current and future climate (Frolking et al., 2010; Smith et al., 2010).
126 Therefore, the objectives of this research were as follows: (1) assess how litter decomposition
127 rates varied between common ombrotrophic peatland plant species (*Calluna vulgaris*, *Molinia*
128 *caerulea*, *Sphagnum* moss, and mixed litter) compared to peat; (2) determine the relative
129 importance (or partitioning) of gaseous (i.e. CO_2) versus aquatic (DOC) fluxes during
130 decomposition with respect to plant species and peat; (3) evaluate the importance of
131 simulated temperature and rainfall changes on controlling total decomposition, C fluxes and
132 partitioning between CO_2 and DOC. This final objective links to another study (Ritson et al.,
133 2014), which used the same experimental treatments to examine the impact of climate
134 change on the treatability (for potable water supply) of dissolved organic matter.
135

136 ## 2. Methods

137 ### *2.1. Field site and sample collection*

138 In the south-west UK, blanket peat covers large parts of the upland areas and
139 constitute an important store of C (Parry and Charman, 2013). These blanket peatlands
140 represent the southern-most blanket peat in the UK and are considered climatically marginal
141 (Clark et al., 2010). The shallow peat of Exmoor was heavily damaged by intensive drainage
142 during the 19th and 20th centuries, and recent efforts have been made to restore large areas

143 through a programme of ditch blocking (Grand-Clement et al., 2014, 2013). The field sites are
144 dominated by *Molinia caerulea* (purple moor grass) (Gatis et al., 2015) and are classified as UK
145 National Vegetation Classification M25: *Molinia caerulea* - *Polentilla erecta* mires (Rodwell,
146 1991). Paleoecological studies indicate that purple moor grass expansion corresponds with
147 the industrial revolution and prior to this, *Sphagnum* was more dominant species within this
148 region (Chambers et al., 1999). Exmoor typically receives precipitation of around 1800–2600
149 mm yr^{-1} with mean winter and summer temperatures of between 4.5–5.5 °C and 10–12 °C,
150 respectively (Met Office, 2014). Exmoor receives a relatively high input of nutrients through
151 atmospheric deposition, and the mean deposition of total nitrogen and oxidised sulphur for
152 the period 2008-2012 was estimated to be 15.5–16.16 kg N h^{-1} yr^{-1} and 4.41–4.86 kg S h^{-1} yr^{-}
153 ^{1}, respectively (DEFRA, 2015).

154 Samples of vegetation and peat were collected from two catchments, Aclands (51°
155 07’54.2” N 3° 48’43.3” W) and Spooners (51° 07’23.3” N 3° 45’11.8” W), within Exmoor
156 National Park, UK, during July 2013. A further description of these field sites, including maps,
157 can be found in Grand-Clement et al. (2014) and Luscombe et al. (2015). Five different
158 substrates were collected: *Calluna*, *Molina* and *Sphagnum*, mixed litter and peat. Fresh leaves
159 and branches were collected from *Calluna vulgaris* and *Molinia caerulea*, avoiding any plants
160 which had been partially eaten by herbivores. Mixed litter (predominantly *Molinia caerulea*
161 but also some *Eriphorum vaginatum*, both at the early stages of decomposition) was collected
162 from the bog surface. Intact *Sphagnum* spp. sods (entire plants) were collected from the
163 centre of stands and peat was collected from the top ca. 30 cm of the soil profile using a screw
164 auger. The samples were transported back to the laboratory in cool boxes within 8 hours of
165 collection, and stored at 4 °C prior to their preparation. Sample collection is described fully in
166 Ritson et al. (2014).

167

168 *2.2. Sample preparation*

169 Samples from each vegetation class (*Calluna vulgaris*, *Molinia caerulea*, mixed litter
170 and *Sphagnum* spp.), were cut into 2-3 cm sections and mixed thoroughly within their class.
171 Any material not from the target group was removed. Once sorted, cut and homogenised, the
172 vegetation samples were left to air-dry in the laboratory to constant mass (Moore et al., 2007).
173 The structure of peat is permanently altered when dried, becoming hydrophobic (Holden and
174 Burt, 2002). For this reason, the peat was treated differently to the other substrates and was
175 kept refrigerated and at field moist conditions prior to the experiment.
176 Air-dried sub-samples of each plant species and field moist peat (n = 5) were oven dried at 70
177 °C for 24 h to determine an air-dry to oven-dry conversion factor. This conversion factor was
178 applied to estimate the oven-dry weight of samples at the beginning of the simulation. These
179 oven-dry samples were analysed for litter quality (see methods below; Table 1).
180

181 *2.3. Experimental design*

182 *2.3.1. Experimental set up*

183 Polypropylene Buchner funnels (Thermo Scientific, USA) were filled with
184 approximately 2 g dry-weight of air-dry vegetation or 10 g homogenised peat. The stem of the
185 funnel was packed with acid washed glass wool to ensure no loss of particulates, and each
186 Buchner funnel was placed above an amber-glass bottle to collect leachate, for separate
187 analysis (see Ritson et al., 2014). The climate control facilities comprise two versatile
188 environmental test chambers (Panasonic MLR-352H). The incubators were set to cycle
189 between 12 h at the mean daily maximum and 12 h at the mean daily minimum temperature.

190 Deionised water was applied in amounts equivalent to the monthly rainfall, with a dispenser
191 set to the required volume based on the area of the Buchner funnel top. This was applied
192 gradually and evenly, over approximately 30 seconds, taking care not to disturb the samples.
193
194 *2.3.2. Experimental design*
195 The experiment was set up as a factorial ANOVA design, where substrate, temperature
196 and rainfall were the treatment factors in a 5 x 2 x 2 design. Five replicates of each treatment
197 were conducted, giving a total of 100 samples (see Ritson et al., 2014). Climate treatments
198 were based on (i) baseline (1961-1990; Met Office, 2013) mean minimum and mean maximum
199 daily temperature and mean rainfall totals for July and August for Exmoor National Park, UK,
200 and (ii) a projection from the UKCP09 high emissions scenario for 2080s (2070-2100). All four
201 possible combinations of baseline and projected temperature and rainfall were applied as
202 treatments. Mean minimum daily temperatures were set to 11.0 °C (±0.3 °C for test chamber
203 error) for the baseline, and 15.4 °C (±0.3 °C) for the UKCP09 treatment. Mean maximum daily
204 temperatures were set to 18.2 °C (±0.3 °C) for the baseline treatment and 23.7 °C (±0.3 °C) for
205 the UKCP09 treatment. Rainfall totalled 100.9 and 117.5 mm for the baseline treatment for
206 July and August, respectively, and 75.4 and 67.2 mm for the UKCP09 treatment. Overall, this
207 was equivalent to a ca. 5.0 °C increase in temperature and ca. 35 % decrease in rainfall for the
208 UKCP09 treatments. The relative humidity (to program the test chambers) and number of rain
209 days were set at mean values from the baseline period for all samples (for relative humidity:
210 80 % in July, 79 % in August; for rain days: 12 in July and 14 in August). The rainfall total for
211 each month was split evenly between the rain days (resulting in irrigation amounts ranging
212 between 4.2 mm and 8.4 mm per event, or 19 and 38 ml, depending on treatment and month),

and the amounts were applied every 2-4 days. The conversion from mm to ml was based on the area of the funnel.

2.4. Measurements

2.4.1. Carbon dioxide evolution

At eight points during the experiment (on days 2, 7, 10, 17, 31, 45, 50, and 60 after the start of the incubation) samples were analysed for CO_2 efflux. Samples were taken out of the incubators individually and the top part of the Buchner funnel, containing the sample, was removed and placed into an airtight container (Lock&Lock, South Korea) which was connected to an infra-red gas analyser, IRGA (8100A, LI-COR, USA). Samples were removed for measurement in a random order to avoid the introduction of systematic measurement error. Observations with the IRGA lasted for 2 minutes during which time the concentration of CO_2 in the chamber (water vapour compensated) was measured every second, and the samples were out of the incubators for a maximum of 5 minutes. The rate of change in CO_2 concentration in the headspace during the 2-minute measurement period was used to calculate the instantaneous flux by applying a linear regression. The IRGA system was allowed to purge for a minute between samples, and a 30 second deadband (a period where the IRGA is running without the measurements being used in the flux estimate) was introduced at the beginning of each measurement to allow for adequate mixing of air in the headspace. The CO_2 time series for each sample was analysed separately, and the deadband was adjusted where necessary. All flux estimates were derived from a minimum of 60 consecutive CO_2 concentration measurements (i.e. 60 seconds). Individual flux estimates were converted to mg CO_2-C g C^{-1} day^{-1}. Cumulative CO_2 flux over the course of the two month experiment was

236 calculated for each sample based on a linear interpolation of fluxes between the successive
237 measurements (Neff and Hooper, 2002), expressed as mg CO_2-C g C^{-1}.
238
239 *2.4.2. Dissolved organic carbon*
240 DOC analysis was performed on the cumulative leachate collected at the end of the
241 simulation period. Samples were filtered through a GF/F filter (Whatman, UK) with a nominal
242 pore size of 0.7 µm, acidified to ~pH 2 with HCl and stored at 4°C prior to analysis. Organic
243 carbon content was measured as non-purgeable organic carbon (NPOC) using a total organic
244 carbon analyser (Shimadzu TOC-V, Japan). Calibration and quality control checks were run
245 daily from freshly prepared standards and samples were analysed within one week of the end
246 of the simulation. Organic carbon concentration (mg L^{-1}) was converted to DOC leached (mg)
247 based on the volume of leachate collected. As temperature and rainfall treatment affected
248 the volume of sample collected, this was then reported as mg DOC–C g C^{-1}, based on the
249 starting dry mass and initial C content of each sample.
250
251 *2.4.3. Mass loss*
252 At the end of the two-month incubation period, samples were removed from the
253 incubators, dried at 70 °C for 48 h and weighed. C loss was estimated based on the starting
254 mass and starting C content, as well as the end mass and end C content. This was expressed
255 as mgC g C^{-1}.
256

257 *2.5. Litter quality analysis*

258 The oven-dry subsamples from the beginning, and all samples from the end of the
259 experiment were ground using a laboratory disc mill with an agate barrel (Tema Machinery
260 Ltd, UK) and analysed for total C and N (Thermo FLASH 2000 elemental analyser). The handling
261 and analysis of samples were undertaken together with reference material (Pahokee Peat,
262 International Humic Substances Society) in order to verify the calibration and quality of the
263 results. Subsamples from the start of the experiment were also analysed for C character using
264 nuclear magnetic resonance (NMR) analysis. Cross polarisation-magic angle spinning (CP-
265 MAS) ^{13}C NMR analysis was undertaken at the University of Reading chemical analysis facility
266 (CAF) on a Bruker AV500 instrument based on the method of Wong et al. (2002). This
267 technique is used widely in environmental studies and is good for looking at relative changes
268 in carbon distribution across a series of samples (Simpson et al., 2011). For the vegetation
269 samples 1024 transients (executions of the pulse sequence) were taken, however due to the
270 presence of paramagnetic material in the peat soil transients were increased to 4096 to
271 improve the signal to noise ratio. Magic angle spinning (MAS) spin rate was set at 10 kHz to
272 shift spinning side bands out of the region of interest and all signals were externally referenced
273 to adamant. The aromatic peak between 110-140 ppm was integrated and its percentage of
274 the total signal calculated to give an indication of the differences between relative aromaticity
275 between samples (Peuravuori et al., 2003), which can be used as an alternative qualitative
276 measure of the recalcitrance of the litter (see Table 1). For further reading on using NMR
277 analysis for environmental research, see Simpson et al. (2011).
278

279 *2.6. Statistical analysis*

280 All statistical analyses were carried out using R version 3.0.2 (R Core Team, 2015) and
281 plots were generated using the ggplot2 package (Wickham, 2009). The experiment involved a
282 three-way analysis of variance (ANOVA) design where temperature, rainfall and substrate
283 were the experimental factors. The effect of these factors, and their interaction, on response
284 variables of CO_2 flux, mass loss, DOC leached and CO_2:DOC ratio production was analysed
285 (Table 2). A Fligner-Killeen test was performed to determine that there was equal variance
286 between groups, and residuals were checked for normality. Carbon dioxide flux, DOC flux and
287 CO_2:DOC ratio were all square-root transformed prior to inclusion, in order to meet the
288 assumption of normally distributed residuals. A critical value of $P = 0.05$ was used for statistical
289 significance. For multiple comparisons, the Tukey honest significant differences (HSD) test was
290 used. The variance explained by each factor was estimated using omega-squared (ω^2), a test
291 which is suitable for estimating effect size from small sample sizes (Keselman, 1975).
292
293 3. Results
294 *3.1. Variability of decomposition rates between different substrates*

295 Decomposition was greatest for the *Molinia* samples and slowest for the peat samples
296 (Fig. 1). The same substrate rankings were evident in terms of the following: the estimated
297 cumulative CO_2 flux (means ranged from 942.87 mgC gC^{-1} for *Molinia* to 41.26 mgC gC^{-1} for
298 peat; Fig. 1); the DOC flux (means ranged from 20.95 mgC gC^{-1} for *Molinia* to 1.07 mgC gC^{-1}
299 for peat; Fig. 1); and the overall total measured mass loss (means ranged from 511.21 mgC
300 gC^{-1} for *Molinia* to 27.43 mgC gC^{-1} for peat; Fig. 2). Substrate was a significant explanatory
301 factor in the ANOVA for all of these response variables ($P < 0.001$; Table 2). Post-hoc tests

302 suggested significant differences in the order *Molina* > *Sphagnum* = Mixed litter > *Calluna* >
303 peat for CO_2 flux; *Molinia* > *Calluna* = Mixed litter > *Sphagnum* > peat for DOC flux; and *Molinia*
304 > *Calluna* > *Sphagnum* = Mixed litter > peat for mass loss.

305 There was a steady decrease in CO_2 release over the entire incubation period, for all
306 substrates and treatments. The decrease in CO_2 flux was greatest for the *Molinia* samples,
307 with a reduction in estimated flux between the first (day 1 to 30) and second half (day 31 to
308 60) of the experiment of 64.27%, compared to peat where the difference was 25.13% – the
309 lowest decline recorded.

310 In terms of total mass balance, the overall loss of C measured directly through mass
311 loss of the substrate and by the total fluxes (DOC + CO_2) were not equal. Whilst DOC fluxes
312 were less than the total mass loss, the cumulative CO_2 flux estimated by integration across the
313 experimental period (*sensu* Neff and Hooper, 2002) was greater than the total mass loss.
314

315 *3.2. Carbon dioxide to DOC partitioning*

316 The cumulative flux of CO_2 was greater than DOC for all of the samples (Fig. 1). Mean
317 CO_2:DOC quotients ranged from 31.56 for *Molinia* to 68.67 for *Sphagnum* (all climate
318 treatments pooled), indicating that proportionally more carbon was lost as DOC from *Molinia*
319 than *Sphagnum*. Substrate was again the strongest factor explaining the variation in
320 partitioning between gaseous and aquatic fluxes ($P < 0.001$). There was a significant
321 relationship between total CO_2 flux and DOC leached between groups when all data were
322 pooled, indicating that DOC leaching increases with CO_2 flux. However, this relationship was
323 not observed within substrate groups.

324 The general trend was for an increase in the CO_2:DOC quotient under UKCP09 future
325 climate scenarios (Fig. 1). There was a statistically significant interaction between rainfall and

substrate ($P < 0.001$), with the proportion of C lost as CO_2 generally increasing under the UKCP09 (drier) rainfall scenario. Post-hoc tests revealed that drier conditions were only significant in changing the partitioning between gas and aquatic carbon fluxes for the peat ($P < 0.001$) and *Sphagnum* ($P < 0.001$) samples, the mean of which increased from 24.91 (±5.74) to 78.64 (±13.85) and from 47.34 (±2.41) to 101.78 (±16.25) when comparing the baseline temperature and rainfall to the UKCP09 temperature and rainfall treatments. Partitioning between CO_2 and DOC in other substrates, *Molinia*, *Calluna* and mixed litter, was unaffected by temperature and rainfall treatments ($P > 0.05$).

3.3. Relative importance and interaction between temperature and rainfall in controlling decomposition

Increasing temperature had a significant effect on decreasing DOC flux ($P < 0.001$) and increasing mass loss ($P < 0.001$). In addition, significant interactions between temperature and substrate ($P < 0.001$) and rainfall and substrate ($P = 0.001$) were seen for DOC flux and for mass loss ($P = 0.007$ and $P = 0.035$, respectively), indicating that the effect of simulated climate change depended on substrate type. For DOC, post hoc tests suggested that the interaction was only significant between temperature and *Calluna*, whereas for rainfall, there was a significant interaction between rainfall treatment and *Calluna* and rainfall treatment and *Sphagnum*. This interaction between rainfall and substrate was not unidirectional, however, with the drier rainfall treatment increasing DOC in *Calluna* samples, but decreasing it in *Sphagnum*. With mass loss, only *Sphagnum* was close to being significant on its own. Differences in cumulative CO_2 flux between climate treatments (both temperature and rainfall) were non-significant ($P > 0.05$), though rainfall was close to the critical threshold ($P =$

349 0.075). No significant interaction between temperature and rainfall for any of the measures
350 of decomposition was observed (CO_2 flux, DOC flux or mass loss).
351
352 4. Discussion
353 *4.1. Carbon fluxes and decomposition rates between different substrates*
354 The fluxes of CO_2 and DOC, and the mass loss, were lowest from the peat samples
355 compared to litter sources, consistent with previous work (Moore and Dalva, 2001; Tang et
356 al., 2013). Decomposition in peatland ecosystems progresses along a continuum from freshly
357 senesced plant litter to peat. Part of the reason that peat decomposes more slowly than fresh
358 litter is because more labile compounds are preferentially utilised by decomposers (Wieder
359 and Lang, 1982). This results in older peat being composed of progressively more recalcitrant
360 materials (Broder et al., 2012). In the field, these differences are likely to be even greater as
361 decomposition of peat is further inhibited by anoxic and acidic conditions which prevail for
362 longer at greater depths. Here, we used measures of C:N ratio and aromaticity to characterise
363 the quality of the substrates. A high C:N ratio usually suggests recalcitrant litter, as N is limiting
364 for microbes and can also stimulate the activity of certain enzymes (Bragazza et al., 2012).
365 Here peat had the lowest C:N ratio, which could be due to retention of N containing
366 compounds during the decomposition process (Kalbitz and Geyer, 2002). Aromaticity is
367 another potential measure of decay resistance as aromatic polymers are characterised by
368 structural and chemical recalcitrance. In this instance, peat had the highest estimated
369 proportion of aromatic compounds (Table 1), which could in part explain its low
370 decomposition rate relative to the other substrates.

In terms of specific fluxes, *Sphagnum* produced the least DOC in line with previous observations of high retention of carbon in this species (Fenner et al., 2004). *Sphagnum* also produced slightly more CO_2 than *Calluna*, which was unexpected given the well documented recalcitrance of *Sphagnum* litter which has been shown to decompose much more slowly than other peat forming vegetation (van Breemen, 1995). This could have been a result of environmental conditions, specifically water content, as the poor water holding capacity of *Calluna* litter meant that lack of water supply could have limited its decomposition during laboratory simulation experiments (Blok et al., 2015; Toberman et al., 2008).

The estimates of cumulative CO_2 flux were approximately double the amount estimated from C mass loss, suggesting an overestimation of cumulative CO_2 flux by integrating point measurements recorded here. This could partly be due to the measurement of some autotrophic respiration from peat roots in the earlier stages of the experiment, or an inadequate representation of night-time respiration rates. However, given that all samples were treated in the same way, and were well mixed to begin with, it is reasonable to assume that the observed differences between groups are robust.

4.2. Relative importance of gaseous and fluvial fluxes

The release of DOC during organic matter decomposition to surface waters is an important component of the peatland carbon budget (Billett et al., 2010). Little is known about partitioning between CO_2 and DOC fluxes in peatlands (Bonnett et al., 2006). Herein, it was shown that *Molinia* produced the most DOC as a proportion of its starting mass, and peat produced the least. However, in terms of the ratio of CO_2 to DOC, *Calluna* and mixed litter had the lowest ratios, signalling that a higher proportion of mass is lost as DOC than CO_2 for these substrates, when compared with the others. Again, absolute values for CO_2:DOC may not be

395 accurate due to overestimation of measured CO_2 fluxes, but comparisons between groups
396 should still be robust.

397 Previous studies have reported DOC fluxes equivalent to over 20% of net ecosystem
398 exchange (NEE) (e.g. Dinsmore et al., 2010; Koehler et al., 2011). In some instances, DOC
399 exported to streams has been estimated to exceed NEE (Billett et al., 2004), highlighting the
400 importance of including this flux when estimating source/sink status of a peatland. Strong
401 correlations have been found between gross primary productivity (GPP) and DOC
402 concentrations in peatland catchments (Dinsmore et al., 2013; Harrison et al., 2008),
403 suggesting a large amount of DOC is produced directly by living plants, indirectly by
404 rhizosphere priming or by the decay of fresh plant litter. The difference in the amount of DOC
405 released from the peat and litter samples in this study during decomposition supports the
406 theory that the decay of fresh litter is a substantive DOC source (Evans et al., 2007; Palmer et
407 al., 2001). In the field, a lot will depend on the regulating effect of water table depth on
408 decomposition, flow pathways of runoff (Wallage and Holden, 2011), as well as substrate.

409 We observed a lower DOC flux but no significant change in CO_2 flux under the UKCP09
410 (warmer) temperature scenario. Combined with the lower DOC flux under UKCP09 (drier)
411 rainfall scenario for some of the substrates (*Sphagnum*), this resulted in an increase in the
412 partitioning coefficient between CO_2 and DOC flux for some of the substrates (*Sphagnum* and
413 peat), which is in accordance with the findings of Neff and Hooper (2002) in their arctic soil
414 samples. This implies that a greater proportion of C released from *Sphagnum* and peat would
415 be lost in the form of CO_2 than DOC under warmer and drier conditions, with the effect of
416 rainfall being slightly stronger than temperature. The strength of the rainfall effect suggests
417 that it is due more to the decreased flux of DOC than due to a reduction in total
418 decomposition. The total DOC measured in this study was in effect net DOC production; a

function of release and transport, as well as its mineralisation. The decreased DOC flux could be explained by a suppression of DOC mobility by drought-induced acidification (Clark et al., 2006; Clark et al., 2012). DOC production could be affected by both microbial enzymatic activity and physical leaching. It could be that DOC was produced, but lack of water supply limited physical leaching and so it was subsequently consumed by microbes present in the samples (Moore and Dalva, 2001). The findings presented here, that CO_2:DOC partitioning from *Sphagnum* and peat could be affected by climate change, but that the partitioning from other substrates was not affected, will be of interest to those modelling the response of peatland C balance as it indicates that DOC flux cannot be estimated from ecosystem respiration alone. It is also useful information for water treatment engineers who are trying to plan future climate-proof investments in treatment works, as these results imply that DOC could increase or decrease in the future, depending on the proportion of different plant species in the catchments, and the pattern of rainfall.

4.3. Effects and interactions between temperature and rainfall

Results indicate that simulated temperature changes have a greater effect on the loss of DOC (generally decreasing the flux) and on mass loss (generally increasing the flux) than on the production of CO_2. The effect varied between substrates, for example, drier conditions increased the DOC flux from *Calluna*, but decreased it from *Sphagnum*. When looking at the main drivers of increased decomposition in peatlands, other laboratory based studies have also found mixed results. Higher temperatures led to increased mass loss (between 5, 10 and 15 °C) in a one year incubation of Scots pine needles below a living moss layer (Domisch et al., 2006), supporting the results found here. Neff and Hooper (2002) also found that temperature controlled the CO_2 flux from their incubated soil samples, but the response depended largely

443 on vegetation community. However, in their study on DOC production across a range of spatial
444 scales, Preston et al. (2011) found that temperature had no effect on DOC production in their
445 peat microcosm experiment, regardless of moisture treatment. This contrasts with Clark et al.
446 (2006) who found increased DOC release at 20 °C relative to 10 °C in another laboratory study
447 incubating peat mesocosms.

448 Whilst measured mass loss did increase positively with temperature, measured CO_2
449 fluxes did not. Investigations at lower temperatures than those used here have suggested
450 *Sphagnum* becomes more productive, growing faster, with increases in temperature from a
451 low base (Breeuwer et al., 2008), but that the opposite can occur for warmer temperatures
452 (17.5 and 21.7 °C) (Breeuwer et al., 2009). Results herein indicate that decomposition,
453 measured through mass loss, increased with temperature, suggesting that the strength of the
454 peatland C sink could be reduced during summer months.

455 Rainfall treatment was just above the $P = 0.05$ critical threshold for cumulative CO_2 (P
456 = 0.075) and DOC flux ($P = 0.070$), with lower values seen under the UKCP09 (lower rainfall)
457 conditions. For DOC in peat, this agrees with the findings of Tang et al. (2013) who found that
458 DOC export was greater in the wetter treatments, and declined in the drought treatments.
459 Observed responses of DOC export to drought or experimentally lowered water tables have
460 been varied, with suggestions that DOC export could increase due to drought (Worrall et al.,
461 2006). However, there are mechanisms which could explain the decrease in DOC observed
462 here. Decreased DOC during droughts could be due to a suppression of DOC transport by
463 drought-induced decrease in DOC solubility (Clark et al., 2012, 2006), or an increase in
464 hydrophobicity (Worrall et al., 2008) rather than a change in the production of DOC through
465 organic matter decomposition. A difference here is that this study simulated rainfall whereas

466 those examining the mechanisms have tended to focus on water table effects, either through
467 manipulations in the laboratory or event-based analysis in the field.
468
469 *4.4. Limitations of the study*
470 The data presented here are a useful indication of the relative importance of different
471 substrates as sources of DOC and CO_2 fluxes, decomposition and the potential for changes in
472 partitioning between CO_2 and DOC under future climate conditions. However, these are
473 laboratory based simulation experiments and are subject to constraints that must be taken
474 into account when interpreting the results. Samples may have been exposed to more extreme
475 drying conditions than under field conditions as moisture levels were not regulated by living
476 vegetation and/or underlying water table, and the lack of a peat substrate beneath the
477 samples from the vegetation groups could also have increased the loss of water and so
478 negated any rainfall treatment effect. Ritson et al. (2017) found that any exposure to oxygen
479 (during laboratory experiments) increased DOC from peat and changed the quality of the C.
480 The differences with the results presented here suggest a high sensitivity to the amount and
481 frequency of the rainfall treatments. The findings of these laboratory experiments now need
482 to be tested under field conditions.
483
484 *4.5. Wider implications for our understanding of peatland carbon balances*
485 While predictions about future rainfall patterns are variable, with both increases and
486 decreases projected for northern latitudes (IPCC, 2014), models are in strong agreement that
487 temperatures at mid-to-high latitudes will increase due to climate change (Murphy et al.,
488 2009), and that drought events are likely to become more frequent (Meehl and Tebaldi, 2004).

While there are differences in both magnitude and direction of change between the substrates, the data here suggest that warmer summer temperatures and decreased rainfall could increase overall decomposition, reduce the flux of DOC, and subsequently alter the partitioning of carbon released during decomposition from DOC to CO_2.

Other studies have suggested that the effect of climate change will be more through indirect effects on the composition of vegetation, with graminoids and dwarf shrubs being favoured over *Sphagnum* mosses in warmer, drier conditions (Kapfer et al., 2011; Weltzin et al., 2003). Given the greater lability of the litter produced by these plant functional types, seen here in the greater decomposition of the *Molinia* samples, this could be a concern for climate change mitigation. However, in SW England, where these samples were collected, graminoids (*Molinia*) are already highly prevalent (Chambers et al., 1999) and so the effect may not be as severe, as climate-induced vegetation change may already have occurred. The shallow peat in this area suggests the area could have been sequestering C at a lower rate than other blanket peatlands, or even losing C, though further work looking at the entire C balance is needed to verify this.

In the field, it is likely that climate change may increase productivity, and therefore litter production, alongside any increase in decomposition rates. Studies have already provided evidence that warmer temperatures can increase rates of carbon sequestration at some northern latitude peatlands, due in part to longer and warmer growing seasons enhancing plant growth (Loisel and Yu, 2013). Therefore, when interpreting the differences in decomposition rates of the different substrates in the context of *in situ* actual conditions, it is also important to consider their respective litter production rates and substrate supply (Ritson et al., 2016). While *Molinia* showed the fastest decomposition in this experiment, it also tends to produce more litter than *Calluna* (e.g. Aerts, 1989), so is likely to be a more significant

source of C at the catchment scale. Also, while both substrates generally produce less "litter" than *Sphagnum* (Bragazza et al., 2012), this may change in a warmer, drier climate (Breeuwer et al., 2009). Further work is needed to take into account the effect of climate change on productivity and litter production, as well as on decomposition, to assess the likely impacts of climate change on the future carbon balance of peatlands.

5. Conclusions

This study has used short-term laboratory incubations of peat and peat-forming vegetation from a climatically marginal blanket peatland in SW England in order to assess the relative importance of different temperature and rainfall scenarios for the main C fluxes (CO_2 and DOC) and their partitioning during short-term litter decay. The largest variation in C fluxes and total mass loss was seen between substrates, with smaller fluxes (cumulative CO_2 and DOC) and mass lost from *Sphagnum*/peat compared to higher fluxes and mass loss from dwarf shrub/graminoids. The CO_2:DOC ratio was lowest for *Molinia* and highest for *Sphagnum*. Climate factors were important too, but the effect depended largely on the substrate. For example, while the future (drier) rainfall scenario increased the DOC flux from *Calluna*, it had the opposite effect for *Sphagnum*. Therefore, indirect effects on species composition in peatlands could ultimately turn out to be more important than direct effects of climate change from increased temperatures and decreased rainfall.

Upscaling of this work from laboratory to field is needed in order to confirm these laboratory-based findings and improve understanding of the likely impacts of climate change on C fluxes and decomposition in peatlands. Further work across natural climatic gradients is one way of addressing this research need, deploying a space for time substitution to understand future climate change.

Acknowledgements

This research was funded by a studentship received by Michael Bell from the Natural Environment Research Council (grant number 1227376). Jonathan Ritson would like to thank the Grantham Institute: Climate and Environment and Climate-KIC for financial support. Brazier acknowledges the support of the South West Water-funded Mires-on-the-Moors project. The authors would also like to thank South West Water and especially the Mires project staff for access to sites as well as the Exmoor National Park Authoritiy. The help of Dr Radek Kowalczyk of University of Reading for running the NMR experiments and advising on their experimental design is also greatly appreciated.

References

1. Aerts, R., 1989. Aboveground Biomass and Nutrient Dynamics of Calluna vulgaris and Molinia caerulea in a Aboveground biomass and nutrient dynamics of Callnna vulgaris and Molinia caerulea in a dry heathland. OIKOS 56, 31–38.
2. Billett, M., Charman, D., Clark, J., Evans, C., Evans, M., Ostle, N., Worrall, F., Burden, A., Dinsmore, K., Jones, T., McNamara, N., Parry, L., Rowson, J., Rose, R., 2010. Carbon balance of UK peatlands: current state of knowledge and future research challenges. Clim. Res. 45, 13–29. doi:10.3354/cr00903
3. Billett, M.F., Palmer, S.M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K.J., Flechard, C., Fowler, D., 2004. Linking land-atmosphere-stream carbon fluxes in a lowland peatland system. Global Biogeochem. Cycles 18, 1–12. doi:10.1029/2003GB002058
4. Blok, D., Elberling, B., Michelsen, A., 2015. Initial Stages of Tundra Shrub Litter

561 Decomposition May Be Accelerated by Deeper Winter Snow But Slowed Down by
562 Spring Warming. Ecosystems 19, 155–169. doi:10.1007/s10021-015-9924-3
563 5. Bonnett, S.A.F., Ostle, N., Freeman, C., 2006. Seasonal variations in decomposition
564 processes in a valley-bottom riparian peatland. Sci. Total Environ., 370, 561–573.
565 6. Bragazza, L., Buttler, A., Habermacher, J., Brancaleoni, L., Gerdol, R., Fritze, H.,
566 Hanajík, P., Laiho, R., Johnson, D., 2012. High nitrogen deposition alters the
567 decomposition of bog plant litter and reduces carbon accumulation. Glob. Chang.
568 Biol. 18, 1163–1172. doi:10.1111/j.1365-2486.2011.02585.x
569 7. Bragazza, L., Buttler, A., Robroek, B.J.M., Albrecht, R., Zaccone, C., Jassey, V.E.J.,
570 Signarbieux, C., 2016. Persistent high temperature and low precipitation reduce peat
571 carbon accumulation. Glob. Chang. Biol. 22, 4114–4123. doi:10.1111/gcb.13319
572 8. Bragazza, L., Buttler, A., Siegenthaler, A., Mitchell, E.A.D., 2009. Plant Litter
573 Decomposition and Nutrient Release in Peatlands, in: Baird, A.J., Belyea, L.R., Comas,
574 X., Reeve, A.S., Slater, L.. (Eds.), Carbon Cycling in Northern Peatlands. American
575 Geophysical Union, pp. 99–110.
576 9. Breeuwer, A., Heijmans, M.M.P.D., Gleichman, M., Robroek, B.J.M., Berendse, F.,
577 2009. Response of Sphagnum species mixtures to increased temperature and
578 nitrogen availability. Plant Ecol. 204, 97–111. doi:10.1007/s11258-009-9571-x
579 10. Breeuwer, A., Heijmans, M.M.P.D., Robroek, B.J.M., Berendse, F., 2008. The effect of
580 temperature on growth and competition between Sphagnum species. Oecologia 156,
581 155–67. doi:10.1007/s00442-008-0963-8
582 11. Broder, T., Blodau, C., Biester, H., Knorr, K.H., 2012. Peat decomposition records in
583 three pristine ombrotrophic bogs in southern Patagonia. Biogeosciences 9, 1479–
584 1491. doi:10.5194/bg-9-1479-2012

585 12. Bubier, J.L., Moore, T.R., Bledzki, L. a., 2007. Effects of nutrient addition on
586 vegetation and carbon cycling in an ombrotrophic bog. Glob. Chang. Biol. 13, 1168–
587 1186. doi:10.1111/j.1365-2486.2007.01346.x
588 13. Buttler, A., Robroek, B.J.M., Laggoun-Défarge, F., Jassey, V.E.J., Pochelon, C., Bernard,
589 G., Delarue, F., Gogo, S., Mariotte, P., Mitchell, E.A.D., Bragazza, L., 2015.
590 Experimental warming interacts with soil moisture to discriminate plant responses in
591 an ombrotrophic peatland. J. Veg. Sci. 26, 964–974. doi:10.1111/jvs.12296
592 14. Chambers, F.M., Mauquoy, D., Todd, P.A., 1999. Recent rise to dominance of Molinia
593 caerulea in environmentally sensitive areas : new perspectives from palaeoecological
594 data. J. Appl. Ecol. 36, 719–733.
595 15. Clark, J., Gallego-Sala, A., Allott, T., Chapman, S., Farewell, T., Freeman, C., House, J.,
596 Orr, H., Prentice, I., Smith, P., 2010. Assessing the vulnerability of blanket peat to
597 climate change using an ensemble of statistical bioclimatic envelope models. Clim.
598 Res. 45, 131–150. doi:10.3354/cr00929
599 16. Clark, J.M., Chapman, P.J., Heathwaite, A.L., Adamson, J.K., 2006. Suppression of
600 Dissolved Organic Carbon by Sulfate Induced Acidification during Simulated Droughts.
601 Environ. Sci. Technol. 40, 1776–1783. doi:10.1021/es051488c
602 17. Clark, J.M., Heinemeyer, A., Martin, P., Bottrell, S.H., 2012. Processes controlling DOC
603 in pore water during simulated drought cycles in six different UK peats.
604 Biogeochemistry 109, 253–270. doi:10.1007/s10533-011-9624-9
605 18. Dieleman, C.M., Branfireun, B.A., McLaughlin, J.W., Lindo, Z., 2015. Climate change
606 drives a shift in peatland ecosystem plant community: Implications for ecosystem
607 function and stability. Glob. Chang. Biol. 21, 388–395. doi:10.1111/gcb.12643
608 19. Dinsmore, K.J., Billett, M.F., Dyson, K.E., 2013. Temperature and precipitation drive

609 temporal variability in aquatic carbon and GHG concentrations and fluxes in a
610 peatland catchment. Glob. Chang. Biol. 19, 2133–48. doi:10.1111/gcb.12209
611 20. Dinsmore, K.J., Billett, M.F., Skiba, U.M., Rees, R.M., Drewer, J., Helfter, C., 2010. Role
612 of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland
613 catchment. Glob. Chang. Biol. 16, 2750–2762. doi:10.1111/j.1365-2486.2009.02119.x
614 21. Domisch, T., Finér, L., Laine, J., Laiho, R., 2006. Decomposition and nitrogen dynamics
615 of litter in peat soils from two climatic regions under different temperature regimes.
616 Eur. J. Soil Biol. 42, 74–81. doi:10.1016/j.ejsobi.2005.09.017
617 22. Evans, C.D., Freeman, C., Cork, L.G., Thomas, D.N., Reynolds, B., Billett, M.F., Garnett,
618 M.H., Norris, D., 2007. Evidence against recent climate-induced destabilisation of soil
619 carbon from 14C analysis of riverine dissolved organic matter. Geophys. Res. Lett. 34,
620 L07407. doi:10.1029/2007GL029431
621 23. Fenner, N., Freeman, C., Ostle, N.J. and Reynolds, B., 2004. Peatland carbon efflux
622 partitioning reveals that sphagnum photosynthate contributes to the DOC pool.
623 Plant and Soil. 259, 345–354.
624 24. Fenner, N., Ostle, N.J., McNamara, N., Sparks, T., Harmens, H., Reynolds, B., Freeman,
625 C., 2007. Elevated CO2 Effects on Peatland Plant Community Carbon Dynamics and
626 DOC Production. Ecosystems 10, 635–647. doi:10.1007/s10021-007-9051-x
627 25. Frolking, S., Roulet, N.T., Tuittila, E., Bubier, J.L., Quillet, A., Talbot, J., Richard, P.J.H.,
628 2010. A new model of Holocene peatland net primary production, decomposition,
629 water balance, and peat accumulation. Earth Syst. Dyn. 1, 1–21. doi:10.5194/esd-1-1-
630 2010
631 26. Freeman, C., Lock, M.A., Reynolds, B., 1993. Fluxes of carbon dioxide, methane and
632 nitrous oxide from a Welsh peatland following simulation of water table draw-down:

633 Potential feedback to climatic change. Biogeochemistry. 19, 51–60.
634 27. Gatis, N., Luscombe, D.J., Grand-Clement, E., Hartley, I.P., Anderson, K., Smith, D.,
635 Brazier, R.E., 2015. The effect of drainage ditches on vegetation diversity and CO2
636 fluxes in a Molinia caerulea-dominated peatland. Ecohydrology n/a-n/a.
637 doi:10.1002/eco.1643
638 28. Gorham, E., 1991. Northern Peatlands: Role in the carbon cycle and probable
639 responses to climatic warming. Ecol. Appl. 1, 182–195.
640 29. Grand-Clement, E., Anderson, K., Smith, D., Luscombe, D., Gatis, N., Ross, M., Brazier,
641 R.E., 2013. Evaluating ecosystem goods and services after restoration of marginal
642 upland peatlands in South-West England. J. Appl. Ecol. n/a-n/a. doi:10.1111/1365-
643 2664.12039
644 30. Grand-Clement, E., Luscombe, D.J., Anderson, K., Gatis, N., Benaud, P., Brazier, R.E.,
645 2014. Antecedent conditions control carbon loss and downstream water quality from
646 shallow, damaged peatlands. Sci. Total Environ. 493, 961–73.
647 doi:10.1016/j.scitotenv.2014.06.091
648 31. Harrison, A.F., Taylor, K., Scott, A., Poskitt, J., Benham, D., Grace, J., Chaplow, J.,
649 Rowland, P., 2008. Potential effects of climate change on DOC release from three
650 different soil types on the Northern Pennines UK: examination using field
651 manipulation experiments. Glob. Chang. Biol. 14, 687–702. doi:10.1111/j.1365-
652 2486.2007.01504.x
653 32. Holden, J., Burt, T.P., 2002. Infiltration, runoff and sediment production in blanket
654 peat catchments: implications of field rainfall simulation experiments. Hydrol.
655 Process. 16, 2537–2557. doi:10.1002/hyp.1014
656 33. Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river

657 water: Fluxes and processes. Environ. Pollut. 84, 301–324.
658 34. IPCC, 2014. IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of
659 Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental
660 Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)].
661 Geneva, Switzerland.
662 35. Johnson, L.C., Damman, A.W.H., 1991. Species Controlled Sphagnum Decay on a
663 South Swedish raised bog Sphagnum decay. Oikos 61, 234–242.
664 36. Kalbitz, K., Geyer, S., 2002. Different effects of peat degradation on dissolved organic
665 carbon and nitrogen. Org. Geochem. 33, 319–326. doi:10.1016/S0146-
666 6380(01)00163-2
667 37. Kapfer, J., Grytnes, J.-A., Gunnarsson, U., Birks, H.J.B., 2011. Fine-scale changes in
668 vegetation composition in a boreal mire over 50 years. J. Ecol. 99, 1179–1189.
669 doi:10.1111/j.1365-2745.2011.01847.x
670 38. Keselman, H.J., 1975. A Monte Carlo investigation of three estimates of treatment
671 magnitude: Epsilon squared, eta squared, and omega squared. Can. Psychol. Rev. 16,
672 44–48.
673 39. Keuskamp, J.A., Dingemans, B.J.J., Lehtinen, T., Sarneel, J.M., Hefting, M.M., 2013.
674 Tea Bag Index: a novel approach to collect uniform decomposition data across
675 ecosystems. Methods Ecol. Evol. 4, 1070–1075. doi:10.1111/2041-210X.12097
676 40. Koehler, A.-K., Sottocornola, M., Kiely, G., 2011. How strong is the current carbon
677 sequestration of an Atlantic blanket bog? Glob. Chang. Biol. 17, 309–319.
678 doi:10.1111/j.1365-2486.2010.02180.x
679 41. Laine, A., Sottocornola, M., Kiely, G., Byrne, K.A., Wilson, D., Tuittila, E.-S., 2006.
680 Estimating net ecosystem exchange in a patterned ecosystem: Example from blanket

681 bog. Agric. For. Meteorol. 138, 231–243.
682 42. Limpens, J., Berendse, F., 2003. How litter quality affects mass loss and N loss from
683 decomposing Sphagnum. Oikos 103, 537–547. doi:10.1034/j.1600-
684 0706.2003.12707.x
685 43. Limpens, J., Berendse, F., Blodau, C., Canadell, J.G., Freeman, C., Holden, J., Roulet,
686 N., Rydin, H., Schaepman-Strub, G., 2008. Peatlands and the carbon cycle: from local
687 processes to global implications - a synthesis. Biogeosciences Discuss. 5, 1379–1419.
688 44. Loisel, J., Yu, Z., 2013. Recent acceleration of carbon accumulation in a boreal
689 peatland, south central Alaska. J. Geophys. Res. Biogeosciences 118, 41–53.
690 doi:10.1029/2012JG001978
691 45. Luscombe, D.J., Anderson, K., Gatis, N., Grand-Clement, E., Brazier, R.E., 2015. Using
692 airborne thermal imaging data to measure near-surface hydrology in upland
693 ecosystems. Hydrol. Process. 29, 1656–1668. doi:10.1002/hyp.10285
694 46. Meehl, G.A., Tebaldi, C., 2004. More intense, more frequent, and longer lasting heat
695 waves in the 21st century. Science 305, 994–7. doi:10.1126/science.1098704
696 47. Moore, T.R., Bubier, J.L., Bledzki, L., 2007. Litter Decomposition in Temperate
697 Peatland Ecosystems: The Effect of Substrate and Site. Ecosystems 10, 949–963.
698 doi:10.1007/s10021-007-9064-5
699 48. Moore, T.R., Dalva, M., 2001. Some controls on the release of dissolved organic
700 carbon by plant tissues and soils. Soil Sci. 166, 38–47.
701 49. Moore, T.R., Paré, D., Boutin, R., 2008. Production of Dissolved Organic Carbon in
702 Canadian Forest Soils. Ecosystems 11, 740–751. doi:10.1007/s10021-008-9156-x
703 50. Murphy, J.M., Sexton, D.M.H., Jenkins, G.J., Booth, B.B.B., Brown, C.C., Clark, R.T.,
704 Collins, M., Harris, G.R., Kendon, E.J., Betts, R.A., Brown, S.J., Humphrey, K.A.,

McCarthy, M.P., McDonald, R.E., Stephens, A., Wallace, C., Warren, R., Wilby, R., Wood, R.A., 2009. UK Climate Projections Science Report: Climate Change Projections.

51. Neff, J.C., Hooper, D.U., 2002. Vegetation and climate controls on potential CO2, DOC and DON production in northern latitude soils. Glob. Chang. Biol. 8, 872–884. doi:10.1046/j.1365-2486.2002.00517.x

52. Palmer, S.M., Hope, D., Billett, M.F., Dawson, J.J.C., Bryant, C.L., 2001. Sources of organic and inorganic carbon in a headwater stream: Evidence from carbon isotope studies. Biogeochemistry 52, 321–338. doi:10.1023/A:1006447706565

53. Parry, L.E., Charman, D.J., 2013. Modelling soil organic carbon distribution in blanket peatlands at a landscape scale. Geoderma 211–212, 75–84. doi:10.1016/J.GEODERMA.2013.07.006

54. Pastor, J., Solin, J., Bridgham, S.D., Updegraff, K., Harth, C., Weishampel, P., Dewey, B., 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. Oikos 100, 380–386. doi:10.1034/j.1600-0706.2003.11774.x

55. Peuravuori, J., Ingman, P. and Pihlaja, K., 2003. Critical comments on accuracy of quantitative determination of natural humic matter by solid state (13)C NMR spectroscopy. Talanta 59(1), 177–89.

56. Preston, M.D., Eimers, M.C., Watmough, S.A., 2011. Effect of moisture and temperature variation on DOC release from a peatland: conflicting results from laboratory, field and historical data analysis. Sci. Total Environ. 409, 1235–42. doi:10.1016/j.scitotenv.2010.12.027

57. R Core Team, 2015. R: A language and environment for statistical computing.

58. Ritson, J.P., Bell, M., Graham, N.J.D., Templeton, M.R., Brazier, R.E., Verhoef, A.,

729 Freeman, C., Clark, J.M., 2014. Simulated climate change impact on summer
730 dissolved organic carbon release from peat and surface vegetation: Implications for
731 drinking water treatment. Water Res. 67, 66–76. doi:10.1016/j.watres.2014.09.015
732 59. Ritson, J.P., Bell, M., Brazier, R.E., Grand-Clement, E., Graham, N.J.D., Freeman, C.,
733 Smith, D., Templeton, M.R., Clark, J.M., 2016. Managing peatland vegetation for
734 drinking water treatment. Scientific Reports. 6, 36751.
735 60. Ritson, J.P., Brazier, R.E., Graham, N.J.D., Freeman, C., Templeton, M.R., Clark, J.M.,
736 2017. The effect of drought on dissolved organic carbon (DOC) release from peatland
737 soil and vegetation sources. Biogeosciences 14, 2891–2902. doi:10.5194/bg-14-2891-
738 2017
739 61. Rodwell, J., 1991. British pant communities, Vol 2: mires and heaths. Cambridge
740 Univeristy Press, Cambridge.
741 62. Simpson, A.J., McNally, D.J., Simpson, M.J., 2011. NMR spectroscopy in
742 environmental research: From molecular interactions to global processes. Prog. Nucl.
743 Magn. Reson. Spectrosc. 58, 97–175. doi:10.1016/j.pnmrs.2010.09.001
744 63. Smith, J., Gottschalk, P., Bellarby, J., Chapman, S., Lilly, A., Towers, W., Bell, J.,
745 Coleman, K., Nayak, D., Richards, M., Hillier, J., Flynn, H., Wattenbach, M.,
746 Aitkenhead, M., Yeluripati, J., Farmer, J., Milne, R., Thomson, A., Evans, C., Whitmore,
747 A., Falloon, P., Smith, P., 2010. Estimating changes in Scottish soil carbon stocks using
748 ECOSSE. I. Model description and uncertainties. Clim. Res. 45, 179–192.
749 doi:10.3354/cr00899
750 64. Straková, P., Penttilä, T., Laine, J., Laiho, R., 2012. Disentangling direct and indirect
751 effects of water table drawdown on above- and belowground plant litter
752 decomposition: consequences for accumulation of organic matter in boreal

753 peatlands. Glob. Chang. Biol. 18, 322–335. doi:10.1111/j.1365-2486.2011.02503.x
754 65. Tang, R., Clark, J.M., Bond, T., Graham, N., Hughes, D., Freeman, C., 2013.
755 Assessment of potential climate change impacts on peatland dissolved organic
756 carbon release and drinking water treatment from laboratory experiments. Environ.
757 Pollut. 173, 270–277.
758 66. Toberman, H., Evans, C.D., Freeman, C., Fenner, N., White, M., Emmett, B.A., Artz,
759 R.R.E., 2008. Summer drought effects upon soil and litter extracellular phenol oxidase
760 activity and soluble carbon release in an upland Calluna heathland. Soil Biology &
761 Biochemistry 40, 1519–1532.
762 67. Turetsky, M.R., 2003. The Role of Bryophytes in Carbon and Nitrogen Cycling.
763 Bryologist 106, 395–409.
764 68. van Breemen, N., 1995. How Sphagnum bogs down other plants. Trends Ecol. Evol.
765 10, 270–275.
766 69. Wallage, Z.E., Holden, J., 2011. Near-surface macropore flow and saturated hydraulic
767 conductivity in drained and restored blanket peatlands. Soil Use Manag. 27, 247–254.
768 doi:10.1111/j.1475-2743.2011.00336.x
769 70. Weltzin, J.F., Bridgham, S.D., Pastor, J., Chen, J., Harth, C., 2003. Potential effects of
770 warming and drying on peatland plant community composition. Glob. Chang. Biol. 9,
771 141–151. doi:10.1046/j.1365-2486.2003.00571.x
772 71. Wickham, H., 2009. ggplot2: elegant graphics for data analysis. Springer, New York.
773 72. Wickland, K.P., Neff, J.C., Aiken, G.R., 2007. Dissolved Organic Carbon in Alaskan
774 Boreal Forest: Sources, Chemical Characteristics, and Biodegradability. Ecosystems
775 10, 1323–1340. doi:10.1007/s10021-007-9101-4
776 73. Wieder, R.K., Lang, G.E., 1982. A Critique of the Analytical Methods Used in

Examining Decomposition Data Obtained From Litter Bags. Ecology 63, 1636–1642.

74. Wong, S., Hanna, J. V, King, S., Carroll, T.J., Eldridge, R.J., Dixon, D.R., Bolto, B.A., Hesse, S., Abbt-Braun, G., Frimmel, F.H., 2002. Fractionation of natural organic matter in drinking water and characterization by 13C cross-polarization magic-angle spinning NMR spectroscopy and size exclusion chromatography. Environ. Sci. Technol. 36, 3497–503. doi:10.1021/es010975z

75. Worrall, F., Gibson, H.S., Burt, T.P., 2008. Production vs. solubility in controlling runoff of DOC from peat soils – The use of an event analysis. J. Hydrol. 358, 84–95. doi:10.1016/j.jhydrol.2008.05.037

801 Tables and figure captions

802 **Table 1**. Organic matter properties for peatland vegetation and peat classes used in the
803 experiment. Values are means (*n* = 5) of subsample values, numbers in brackets are the
804 standard error of the mean. Aromaticity is a qualitative measure and was calculated from
805 cross polarization-magic angle spinning nuclear magnetic resonance (CP-MAS NMR).

Class	Dominant substrate	C (%)	N (%)	C:N ratio	Moisture content (g g dry wt^{-1})	Aromaticity (%)
Calluna	*Calluna vulgaris*	49.3 (0.02)	1.35 (0.01)	36.4 (0.22)	1.90 (0.01)	8
Mixed litter	Senesced *Molinia c*	45.9 (0.01)	1.29 (0.01)	35.6 (0.28)	5.38 (0.11)	5
Molinia	*Molinia caerulea*	45.5 (0.02)	2.34 (0.02)	19.5 (0.13)	3.56 (0.05)	5
Peat	Peat	29.1 (0.02)	1.64 (0.01)	17.7 (0.07)	6.06 (0.06)	11
Sphagnum	*Sphagnum* spp.	41.8 (0.03)	1.00 (0.01)	42.1 (0.28)	15.020.15)	7

806
807
808
809
810
811
812
813
814
815
816

817 **Table 2**. ANOVA model results, where the model fitted is *response* = Temperature * Rainfall *
818 Substrate (Cumulative CO_2, DOC and CO_2:DOC ratio are square-root transformed data).
819 Significant differences ($P < 0.05$) are highlighted in bold and effect sizes (ω^2) are stated in
820 brackets. "Temp", "Rain" and "Sub" are short for Temperature, Rainfall and Substrate,
821 respectively).

Variable	Factor	*F*	df	*P* value
Cumulative CO_2 ($mgCO_2$-C gC^{-1})	Temperature	1.04	1	0.311
	Rainfall	3.25	1	0.075
	Substrate	631.08	4	**< 0.001** (0.960)
	Temp:Rain	0.06	1	0.804
	Temp:Sub	1.27	4	0.288
	Rain:Sub	1.68	4	0.164
	Temp:Rain:Sub	1.27	4	0.290
Mass loss ($mgCO_2$-C gC^{-1})	Temperature	20.10	1	**< 0.001** (0.005)
	Rainfall	0.01	1	0.927
	Substrate	946.23	4	**< 0.001** (0.966)
	Temp:Rain	0.01	1	0.915
	Temp:Sub	3.80	4	**0.007** (0.003)
	Rain:Sub	2.72	4	**0.035** (0.002)
	Temp:Rain:Sub	0.56	4	0.690
DOC ($mgCO_2$-C gC^{-1})	Temperature	18.19	1	**< 0.001** (0.015)
	Rainfall	3.38	1	0.070
	Substrate	247.14	4	**< 0.001** (0.838)
	Temp:Rain	0.04	1	0.837
	Temp:Sub	5.12	4	**0.001** (0.014)
	Rain:Sub	11.34	4	**< 0.001** (0.035)
	Temp:Rain:Sub	4.43	4	**0.003** (0.012)
CO_2-C:DOC-C	Temperature	15.57	1	**< 0.001** (0.056)
	Rainfall	26.16	1	**< 0.001** (0.097)
	Substrate	19.96	4	**< 0.001** (0.292)
	Temp:Rain	0.01	1	0.921
	Temp:Sub	3.27	4	**0.015** (0.035)
	Rain:Sub	8.71	4	**< 0.001** (0.119)
	Temp:Rain:Sub	2.24	4	**0.072**

822

823

824 **Figure 1**. Treatment effects on measures of carbon fluxes, and their ratio; (a) Cumulative CO_2
825 flux, (b) DOC flux, (c) Cumulative CO_2 to DOC ratio (Error bars indicate one standard error).
826 Different letters denote statistically significant differences in means between substrates and
827 asterisks denote significant differences between treatments for substrates based on Tukey
828 HSD test ($P < 0.05$).
829
830 **Figure 2**. Treatment effects on C loss estimated from mass and C quotient measurements
831 (Error bars indicate one standard error). Different letters denote statistically significant
832 differences in means between substrates and asterisks denote significant differences
833 between treatments for substrates based on Tukey HSD test ($P < 0.05$).
834
835