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Sensitivity of peatland litter decomposition to changes in temperature and rainfall

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2 # temperature and rainfall

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23

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

1. Introduction

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

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

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),

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

214 the area of the funnel.

215

216 *2.4. Measurements*

217 *2.4.1. Carbon dioxide evolution*

218 At eight points during the experiment (on days 2, 7, 10, 17, 31, 45, 50, and 60 after the

219 start of the incubation) samples were analysed for CO_2 efflux. Samples were taken out of the

220 incubators individually and the top part of the Buchner funnel, containing the sample, was

221 removed and placed into an airtight container (Lock&Lock, South Korea) which was connected

222 to an infra-red gas analyser, IRGA (8100A, LI-COR, USA). Samples were removed for

223 measurement in a random order to avoid the introduction of systematic measurement error.

224 Observations with the IRGA lasted for 2 minutes during which time the concentration of CO_2

225 in the chamber (water vapour compensated) was measured every second, and the samples

226 were out of the incubators for a maximum of 5 minutes. The rate of change in CO_2

227 concentration in the headspace during the 2-minute measurement period was used to

228 calculate the instantaneous flux by applying a linear regression. The IRGA system was allowed

229 to purge for a minute between samples, and a 30 second deadband (a period where the IRGA

230 is running without the measurements being used in the flux estimate) was introduced at the

231 beginning of each measurement to allow for adequate mixing of air in the headspace. The CO_2

232 time series for each sample was analysed separately, and the deadband was adjusted where

233 necessary. All flux estimates were derived from a minimum of 60 consecutive CO_2

234 concentration measurements (i.e. 60 seconds). Individual flux estimates were converted to

235 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

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

14

326   substrate ($P < 0.001$), with the proportion of C lost as CO_2 generally increasing under the

327   UKCP09 (drier) rainfall scenario. Post-hoc tests revealed that drier conditions were only

328   significant in changing the partitioning between gas and aquatic carbon fluxes for the peat (P

329   < 0.001) and *Sphagnum* ($P < 0.001$) samples, the mean of which increased from 24.91 (±5.74)

330   to 78.64 (±13.85) and from 47.34 (±2.41) to 101.78 (±16.25) when comparing the baseline

331   temperature and rainfall to the UKCP09 temperature and rainfall treatments. Partitioning

332   between CO_2 and DOC in other substrates, *Molinia*, *Calluna* and mixed litter, was unaffected

333   by temperature and rainfall treatments ($P > 0.05$).

334

335   *3.3.   Relative importance and interaction between temperature and rainfall in controlling*

336   *decomposition*

337   Increasing temperature had a significant effect on decreasing DOC flux ($P < 0.001$) and

338   increasing mass loss ($P < 0.001$). In addition, significant interactions between temperature and

339   substrate ($P < 0.001$) and rainfall and substrate ($P = 0.001$) were seen for DOC flux and for

340   mass loss ($P = 0.007$ and $P = 0.035$, respectively), indicating that the effect of simulated climate

341   change depended on substrate type. For DOC, post hoc tests suggested that the interaction

342   was only significant between temperature and *Calluna*, whereas for rainfall, there was a

343   significant interaction between rainfall treatment and *Calluna* and rainfall treatment and

344   *Sphagnum*. This interaction between rainfall and substrate was not unidirectional, however,

345   with the drier rainfall treatment increasing DOC in *Calluna* samples, but decreasing it in

346   *Sphagnum*. With mass loss, only *Sphagnum* was close to being significant on its own.

347   Differences in cumulative CO_2 flux between climate treatments (both temperature and

348   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.

371 In terms of specific fluxes, *Sphagnum* produced the least DOC in line with previous

372 observations of high retention of carbon in this species (Fenner et al., 2004). *Sphagnum* also

373 produced slightly more CO_2 than *Calluna*, which was unexpected given the well documented

374 recalcitrance of *Sphagnum* litter which has been shown to decompose much more slowly than

375 other peat forming vegetation (van Breemen, 1995). This could have been a result of

376 environmental conditions, specifically water content, as the poor water holding capacity of

377 *Calluna* litter meant that lack of water supply could have limited its decomposition during

378 laboratory simulation experiments (Blok et al., 2015; Toberman et al., 2008).

379 The estimates of cumulative CO_2 flux were approximately double the amount

380 estimated from C mass loss, suggesting an overestimation of cumulative CO_2 flux by

381 integrating point measurements recorded here. This could partly be due to the measurement

382 of some autotrophic respiration from peat roots in the earlier stages of the experiment, or an

383 inadequate representation of night-time respiration rates. However, given that all samples

384 were treated in the same way, and were well mixed to begin with, it is reasonable to assume

385 that the observed differences between groups are robust.

386

387 *4.2. Relative importance of gaseous and fluvial fluxes*

388 The release of DOC during organic matter decomposition to surface waters is an

389 important component of the peatland carbon budget (Billett et al., 2010). Little is known

390 about partitioning between CO_2 and DOC fluxes in peatlands (Bonnett et al., 2006). Herein, it

391 was shown that *Molinia* produced the most DOC as a proportion of its starting mass, and peat

392 produced the least. However, in terms of the ratio of CO_2 to DOC, *Calluna* and mixed litter had

393 the lowest ratios, signalling that a higher proportion of mass is lost as DOC than CO_2 for these

394 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

419 function of release and transport, as well as its mineralisation. The decreased DOC flux could

420 be explained by a suppression of DOC mobility by drought-induced acidification (Clark et al.,

421 2006; Clark et al., 2012). DOC production could be affected by both microbial enzymatic

422 activity and physical leaching. It could be that DOC was produced, but lack of water supply

423 limited physical leaching and so it was subsequently consumed by microbes present in the

424 samples (Moore and Dalva, 2001). The findings presented here, that CO_2:DOC partitioning

425 from *Sphagnum* and peat could be affected by climate change, but that the partitioning from

426 other substrates was not affected, will be of interest to those modelling the response of

427 peatland C balance as it indicates that DOC flux cannot be estimated from ecosystem

428 respiration alone. It is also useful information for water treatment engineers who are trying

429 to plan future climate-proof investments in treatment works, as these results imply that DOC

430 could increase or decrease in the future, depending on the proportion of different plant

431 species in the catchments, and the pattern of rainfall.

432

433 *4.3. Effects and interactions between temperature and rainfall*

434   Results indicate that simulated temperature changes have a greater effect on the loss

435 of DOC (generally decreasing the flux) and on mass loss (generally increasing the flux) than on

436 the production of CO_2. The effect varied between substrates, for example, drier conditions

437 increased the DOC flux from *Calluna*, but decreased it from *Sphagnum*. When looking at the

438 main drivers of increased decomposition in peatlands, other laboratory based studies have

439 also found mixed results. Higher temperatures led to increased mass loss (between 5, 10 and

440 15 °C) in a one year incubation of Scots pine needles below a living moss layer (Domisch et al.,

441 2006), supporting the results found here. Neff and Hooper (2002) also found that temperature

442 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).

489   While there are differences in both magnitude and direction of change between the

490   substrates, the data here suggest that warmer summer temperatures and decreased rainfall

491   could increase overall decomposition, reduce the flux of DOC, and subsequently alter the

492   partitioning of carbon released during decomposition from DOC to CO_2.

493   Other studies have suggested that the effect of climate change will be more through

494   indirect effects on the composition of vegetation, with graminoids and dwarf shrubs being

495   favoured over *Sphagnum* mosses in warmer, drier conditions (Kapfer et al., 2011; Weltzin et

496   al., 2003). Given the greater lability of the litter produced by these plant functional types, seen

497   here in the greater decomposition of the *Molinia* samples, this could be a concern for climate

498   change mitigation. However, in SW England, where these samples were collected, graminoids

499   (*Molinia*) are already highly prevalent (Chambers et al., 1999) and so the effect may not be as

500   severe, as climate-induced vegetation change may already have occurred. The shallow peat in

501   this area suggests the area could have been sequestering C at a lower rate than other blanket

502   peatlands, or even losing C, though further work looking at the entire C balance is needed to

503   verify this.

504   In the field, it is likely that climate change may increase productivity, and therefore litter

505   production, alongside any increase in decomposition rates. Studies have already provided

506   evidence that warmer temperatures can increase rates of carbon sequestration at some

507   northern latitude peatlands, due in part to longer and warmer growing seasons enhancing

508   plant growth (Loisel and Yu, 2013). Therefore, when interpreting the differences in

509   decomposition rates of the different substrates in the context of *in situ* actual conditions, it is

510   also important to consider their respective litter production rates and substrate supply (Ritson

511   et al., 2016). While *Molinia* showed the fastest decomposition in this experiment, it also tends

512   to produce more litter than *Calluna* (e.g. Aerts, 1989), so is likely to be a more significant

513   source of C at the catchment scale. Also, while both substrates generally produce less "litter"

514   than *Sphagnum* (Bragazza et al., 2012), this may change in a warmer, drier climate (Breeuwer

515   et al., 2009). Further work is needed to take into account the effect of climate change on

516   productivity and litter production, as well as on decomposition, to assess the likely impacts of

517   climate change on the future carbon balance of peatlands.

518

519   5. Conclusions

520   This study has used short-term laboratory incubations of peat and peat-forming

521   vegetation from a climatically marginal blanket peatland in SW England in order to assess the

522   relative importance of different temperature and rainfall scenarios for the main C fluxes (CO_2

523   and DOC) and their partitioning during short-term litter decay. The largest variation in C fluxes

524   and total mass loss was seen between substrates, with smaller fluxes (cumulative CO_2 and

525   DOC) and mass lost from *Sphagnum*/peat compared to higher fluxes and mass loss from dwarf

526   shrub/graminoids. The CO_2:DOC ratio was lowest for *Molinia* and highest for *Sphagnum*.

527   Climate factors were important too, but the effect depended largely on the substrate. For

528   example, while the future (drier) rainfall scenario increased the DOC flux from *Calluna*, it had

529   the opposite effect for *Sphagnum*. Therefore, indirect effects on species composition in

530   peatlands could ultimately turn out to be more important than direct effects of climate change

531   from increased temperatures and decreased rainfall.

532   Upscaling of this work from laboratory to field is needed in order to confirm these

533   laboratory-based findings and improve understanding of the likely impacts of climate change

534   on C fluxes and decomposition in peatlands. Further work across natural climatic gradients is

535   one way of addressing this research need, deploying a space for time substitution to

536   understand future climate change.

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Table 1. Organic matter properties for peatland vegetation and peat classes used in the experiment. Values are means (*n* = 5) of subsample values, numbers in brackets are the standard error of the mean. Aromaticity is a qualitative measure and was calculated from 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

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Table 2. ANOVA model results, where the model fitted is *response* = Temperature * Rainfall *

Substrate (Cumulative CO_2, DOC and CO_2:DOC ratio are square-root transformed data).

Significant differences ($P < 0.05$) are highlighted in bold and effect sizes (ω^2) are stated in

brackets. "Temp", "Rain" and "Sub" are short for Temperature, Rainfall and Substrate,

respectively).

Variable	Factor	*F*	df	*P* value
Cumulative CO_2	Temperature	1.04	1	0.311
(mgCO$_2$-C gC^{-1})	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	Temperature	20.10	1	**< 0.001** (0.005)
(mgCO$_2$-C gC^{-1})	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	Temperature	18.19	1	**< 0.001** (0.015)
(mgCO$_2$-C gC^{-1})	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**

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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 ($P < 0.05$).

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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 ($P < 0.05$).

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