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1 Thermodynamic control of the carbon budget of a peatland

2

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15

16 Key points

17 • Thermodynamic consideration of elemental analysis allows the prediction of the fate
18 of carbon fixed as primary production.

19 • Change in the Gibbs free energy of formation of the naturally-occurring organic
20 matter (ΔG_f^{OM}) shows that changes in the peat profile must be balanced by production
21 of CO₂, CH₄ or DOM..

22 • Organic matter accumulates in peatlands because further reaction becomes
23 thermodynamically inhibited with depth in the peat profile.

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24

25 **Abstract**

26 The transformations and transitions of organic matter into, through, and out of an ecosystem
27 must obey the second law of thermodynamics. This study considered the transition in the
28 solid components of the organic matter flux through an entire ecosystem. Organic matter
29 samples were taken from each organic matter reservoir and fluvial transfer pathway in a
30 100% peat-covered catchment (Moor House National Nature Reserve, North Pennines, UK)
31 and were analysed by elemental analysis and bomb calorimetry. The samples analysed were:
32 bulk above- and below-ground biomass; individual plant functional types (heather, mosses,
33 sedges); plant litter layer; peat soil; and samples of particulate and dissolved organic matter
34 (POM and DOM). Samples were compared to standards of lignin, cellulose, and plant
35 protein. It was possible to calculate: enthalpy of formation (ΔH_f^{OM}); entropy of formation
36 (ΔS_f^{OM}); and Gibbs free energy of formation (ΔG_f^{OM}) for each of the samples and standards.
37 The increase (decreasing negative values) in ΔG_f^{OM} through the ecosystem mean that for all
38 but litter production the transformations through the system must be balanced by production
39 of low (large negative values) ΔG_f^{OM} products, not only CO_2 or CH_4 , but also DOM. The
40 change in ΔG_f^{OM} down the peat profile shows that reaction of the soil organic matter
41 decreases or even ceases at depth and the majority of the reaction has occurred above 40 cm
42 below the surface. This approach represents a new objective way to test and trace organic
43 matter transformations in and through an ecosystem.

44

45 **1. Introduction**

46 Peatlands are the most important terrestrial carbon (C) store within the terrestrial biosphere.
47 Whilst they occupy only a small percentage of the total land area (~3%, Rydin and Jeghum,

48 2013), peatlands store a disproportionately large amount of carbon. It is estimated that 500
49 ± 100 GtC is stored in northern peatlands (Gorham, 1991; Yu et al, 2014; Loisel et al., 2014),
50 which is approximately equivalent to the total terrestrial vegetation (IPCC, 2013).

51 The very existence of peatlands relies on the fate of organic matter, further that at
52 least at some stage in the past there has been a positive balance of carbon with respect to loss
53 to atmosphere or the fluvial network which means organic matter has accumulated. Hence the
54 understanding of a peatland's carbon budget is a statement of the ecosystem's very existence
55 and future. The estimation of C budgets has been a common research target. Initial
56 approaches to C budgeting for peatlands were to measure the long-term accumulation rate by
57 dating the depth profile (e.g. Turetsky et al., 2004). Subsequent approaches then developed
58 the balance of the contemporaneous gaseous fluxes – the net exchange of CO₂ and the efflux
59 of CH₄ (eg. Fleischer et al., 2016 – for earlier studies see compilation by Limpens et al.,
60 2008) and then extended to include the fluvial losses of dissolved organic carbon (DOC),
61 particulate organic carbon (POC), and dissolved carbon gases such that complete
62 contemporary carbon budgets of peatlands are now common (e.g. Worrall et al., 2003, Billett
63 et al., 2004, Roulet et al., 2007, Nilsson et al., 2008).

64 Approaches based on contemporary fluxes do consider the species of the carbon,
65 nitrogen, or oxygen entering or leaving peat ecosystems and, although this can include the
66 individual gaseous forms (e.g. N₂O, CO₂ or CH₄), it still means that certain carbon fluxes are
67 not considered in any more detail than the lumped terms such as DOC or POC without further
68 characterisation. The contemporary budgets that do exist consider different types of peatland
69 with different dominant vegetation types, different substrates (e.g. Leroy et al., 2017) and the
70 impact of different physical and land management controls across a range of countries (e.g.
71 UK - Rowson et al., 2010; Germany – Tiemeyer et al., 2016; Sweden – Von Arnold et al.,
72 2005; and Canada –Naiwashi et al., 2016). However, even these detailed studies have dealt in

73 lumped compositions (e.g. DOC or DOM) or lumped controls, e.g. change in water table or
74 change in air temperature, but have not considered the actual molecules transitioning in to
75 and through peatland, e.g. CO₂ is fixed as glucose through photosynthesis which is
76 transformed into carbohydrates, lignin, etc.

77 The composition of organic macromolecules that would be present in peatland
78 ecosystems (e.g. lignin) has been considered by a number of approaches: coal petrology
79 techniques such as rock-eval (e.g. Carrie et al., 2012); colorimetric methods from UV/vis
80 spectroscopy (e.g. Blackford and Chambers, 1993); stable isotopes (e.g. Jones et al., 2010);
81 elemental ratios (e.g. C/N – Kuhry and Vitt, 1996); Fourier transform infra-red spectroscopy
82 (FTIR, e.g. Artz et al., 2008); and, pyrolysis gas chromatography mass spectrometry (Py GC-
83 MS, e.g. Buurman et al., 2006). These approaches have commonly focused upon
84 characterisation of peat profiles for the purpose of understanding humification (e.g. Zacoone
85 et al., 2008) or palaeohistoric reconstructions (e.g. McClymont et al., 2011), but these studies
86 were not used to understand the contemporary carbon budget of a peatland. More recently,
87 Moody et al. (2018) have used solid-state ¹³C-NMR to give a molecular budget for a peatland
88 and so show that alkyl functional groups were selectively retained

89 Penning de Vries et al. (1974) proposed that, on the basis of a study of biochemical
90 pathways, it was possible to understand and predict the energetic cost of biomass
91 development from proximate analysis of the composition of that biomass, e.g. given the
92 proportion of macromolecules and biopolymers in a plant, it would be possible to estimate
93 the cost of production. Although the purpose of the approach proposed by Penning de Vries
94 et al. (1974) was to predict production values of biomass, it also meant that the amount of
95 CO₂ produced during plant growth from, for example root respiration, could be predicted.
96 Proximate analysis requires a detailed compositional analysis of biomass and so McDermitt
97 and Loomis (1981) provided an alternative approach based upon elemental analysis of

98 biomass. Williams et al. (1987) suggested that the elemental analysis of McDermitt and
99 Loomis (1981) was too costly or too difficult and proposed an approximation based upon the
100 C/N ratio and the heat of combustion of the biomass. Subsequent advances in technology
101 mean that accurate characterisation of the elemental composition of organic matter is now
102 readily available (e.g. Masiello et al., 2008). The proximate and elemental analytical
103 approaches were only ever applied to understand the development of biomass, but the
104 stoichiometric and energetic constraints invoked in these approaches apply to any
105 biochemically-mediated transition of organic matter. However, the energetic constraint
106 applied in these approaches have only considered enthalpy and not entropy.

107 Lovley and Goodwin (1988) used the calculation of Gibbs free energy (G) to
108 constrain respiration pathways in aquatic sediments. Beer and Blodau (2007) constrained the
109 organic matter turnover in the catotelm of a peat profile by considering the Gibbs free energy
110 change (ΔG) of each possible anaerobic fermentation and methanogenic reaction given the
111 pore water conditions. Similarly, Boye et al. (2017) used the composition of the soil pore
112 water in floodplains to show that the system had become thermodynamically inhibited. The
113 approach of Beer and Blodau (2007), nor that of Boye et al. (2017), did not consider the
114 stoichiometric limits on any reaction and could work only because the catotelm was
115 considered as a closed system with respect to its pore water, which meant that the aqueous
116 equilibria could be considered. However, changes in the solid components (e.g. soil organic
117 matter), changes in the aerobic zone of peat, or changes through the whole peat ecosystem
118 were not considered, eg. the transfer of C from plant biomass through litter to soil organic
119 matter. Therefore, the aim of this study was to consider the change in Gibbs free energy of
120 formation (ΔG_f) and of reaction (ΔG_r), with the transfer of organic matter into and through a
121 peatland, so as to understand the controls on organic matter accumulation.

122

123 2. Approach and Methodology

124 The approach taken in this study was to consider the change in Gibbs free energy with the
125 fixation, transformation, and loss of carbon through a peatland. Beer and Blodau (2007), and
126 later Boye et al. (2017), relied on measuring the concentration of small organic acids in soil
127 pore water and for these small organic acids (eg. aminosugar) and the ΔG_f of these small
128 molecules calculated using standard results and the application of the methods of LaRowe
129 and van Cappellan (2011). The approach of this study is to provide an alternative approach by
130 considering the solid phase, biomacromolecular components (eg. plant organic matter) and
131 assessing change between these components. The change in Gibbs free energy was
132 considered by analysing the composition of the organic matter in a series of carbon pools and
133 fluxes within the context of a known carbon budget (Figure 1). The change in the Gibbs free
134 energy was considered by the differences in the Gibbs free energy of formation of each of the
135 organic matters in reservoirs and fluxes in Figure 1. The Gibbs free energy of formation
136 (ΔG_f^{OM}) can be readily calculated from the difference between the enthalpy and entropy of
137 formation of the same organic matter:

138

$$139 \Delta G_f^{OM} = \Delta H_f^{OM} - T\Delta S_f^{OM} \quad (i)$$

140

141 where: ΔG_f^{OM} =the Gibbs free energy of formation of organic matter (kJ/mol); ΔH_f^{OM} = the
142 standard enthalpy of formation of organic matter (kJ/mol); ΔS_f^{OM} = the standard entropy of
143 formation of organic matter (kJ/K/mol); and T = absolute temperature of the reaction (K). In
144 this study elemental analysis of carbon, hydrogen, nitrogen and oxygen (CHNO) of each
145 pathway and flux in Figure 1 was used to calculate the entropy of formation of the organic
146 matter (ΔS_f^{OM}). Bomb calorimetry was used to calculate the the enthalpy of formation of the

147 organic matter (ΔH_f^{OM}) in each of the pathways and fluxes shown in Figure 1. The Gibbs free
148 energy of formation was then calculated using Equation (i). The context for these
149 thermodynamic parameters was then provided by the carbon budget as measured by previous
150 studies within the study catchment.

151

152 **2.1. Study site**

153 The peatland ecosystem chosen for this study was the Trout Beck catchment, which is within
154 the Moor House National Nature Reserve, a terrestrial and freshwater site monitored as part
155 of the UK Environmental Change Network (ECN). The catchment has been well studied so
156 this study could draw upon existing budgets for dry matter (Forrest, 1971); carbon (Worrall et
157 al., 2003, 2009); nitrogen (Worrall et al., 2012), phosphorus (Worrall et al., 2016a) and
158 energy (Worrall et al., 2015). The catchment is an 11.4 km² blanket peat catchment in the
159 headwater of the River Tees (N 54°41'18" W 2°22'45"; Figure 2). The recent climate of the
160 site has been summarised by Holden and Rose (2011): between 1991 and 2006 the mean
161 annual temperature was 5.8 °C; air frosts were recorded on 99 days in a year; and the mean
162 number of days with snow cover was 41, and the mean annual precipitation was 2012 mm.
163 The vegetation is dominated by *Eriophorum sp.* (cotton grass), *Calluna vulgaris* (heather)
164 and *Sphagnum sp.* (moss). This study considered the boundary of the processes and budgets
165 to be exported to the atmosphere and streams from the soils and biomass of the study
166 catchment. For example, DOM or POM export from the soil profile was included but not the
167 further processing of that organic matter within the receiving stream.

168

169 **2.2. Sampling**

170 Given the range of carbon pools and fluxes identified in Figure 1, the following sampling was
171 carried out. The peat profile was sampled at two locations roughly 10 m apart in active, deep

172 peat within the Cottage Hill Sike catchment; a peat core was taken to 1 m depth with a gouge
173 auger at each location – this depth was chosen to cover the entire depth of the acrotelm and in
174 to the catotelm at this site (Worrall et al., 2012). The collected peat cores were sampled in 2
175 cm depth increments from 0 to 20 cm depth from the peat surface, then 5 cm depth
176 increments from 20 cm depth to 50 cm and then one sample taken between 95 and 100 cm
177 depth. Peat core samples were dried at 105°C overnight and checked for no further mass loss,
178 and their bulk density measured prior to further processing.

179 Vegetation samples were chosen to cover the three main plant functional groups -
180 shrubs (dominantly *Calluna vulgaris*, henceforward referred to as Calluna); grasses and
181 sedges (dominantly *Eriophorum spp.*, henceforward referred to as grass/sedge); and mosses
182 (including *Sphagnum spp.*, henceforward referred to as mosses). The vegetation was collected
183 from six quadrats (0.25 m², 0.5 x 0.5 m) located in the Cottage Hill Sike catchment. In three
184 of the quadrats, the entire above-ground biomass was quantitatively recovered. For the three
185 other quadrats, the total above-ground biomass was collected but separated by functional
186 group. From within these quadrats, samples of litter and below-ground biomass were
187 recovered but not quantitatively. To confirm the dry matter budget reported by Forrest
188 (1971), quantitative biomass samples were dried to 105°C and weighed so that an estimate of
189 total above-ground biomass, and the contribution from the dominant functional plant groups,
190 could be estimated. Samples of the litter and below-ground biomass were not recovered
191 quantitatively and were dried to 105°C. The dried samples were then homogenised and
192 powdered as described below. In this way we were able to consider bulk measures of the
193 vegetation carbon pool (above- and below-ground biomass) and assess the contribution of its
194 components (plant functional types – Calluna, grasses/sedge; and mosses). It would be
195 expected that the above-ground biomass would be a weighted average of its components.

196 For dissolved organic matter (DOM) large-volume water samples (at least 25 litres)
197 were collected monthly from the Cottage Hill Sike from October 2011 to December 2014 -
198 except for months where winter conditions precluded taking flowing water samples; 35
199 samples were collected over 38 months. On return to the laboratory, the samples were
200 allowed to settle with water tapped off from above the sediment layer and evaporated to
201 dryness to estimate the total dissolved solids concentration. By using settling as means of
202 separation, no arbitrary filtration cut-off was applied; rather this study defined DOM as being
203 that component which was either colloidal or truly dissolved.

204 From June 2013 to December 2014 the settled sediment from the same large volume
205 samples used for extraction of DOM samples was recovered as a sample of the particulate
206 organic matter (POM). The sediment was dried to 105°C (overnight and checked for no
207 further mass loss) and retained for subsequent analysis.

208 Four standard materials were included in the analysis: lignin (Aldrich, CAS 8068-05-
209 1), humic acid (Alfa-Aesar, CAS 1415-93-6), cellulose (Whatman, CAS 9004-36-4) and
210 protein (Sigma, CAS 100684-25-1). The lignin, cellulose (taken as representative of
211 polysaccharides, including hemicellulose) and protein comprise the three largest components
212 of plants found in a peatland system (McDermitt and Loomis, 1981).

213 The ash content of the samples was analysed. A sub-sample of the biomass, litter,
214 peat, DOM and POM collected was ashed at 550 °C and the residual mass recorded. All
215 subsequent analysis of peat, DOM and POM were corrected so that all elemental analysis are
216 quoted on an ash-free basis.

217

218 ***2.3. The enthalpy of formation (ΔH_f^{OM})***

219 The enthalpy of formation was calculated from the measured heat of combustion using
220 Hess's Law which states:

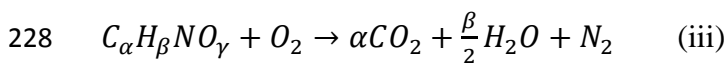
221

$$222 \quad \Delta H_f^{OM} = \Delta H_f^{CO_2} + \Delta H_f^{H_2O} - \Delta H_c^{OM} \quad (\text{ii})$$

223

224 where: ΔH_y^x = the standard enthalpy of y for compound x with y as either f for formation or c
225 for combustion and with x as OM for the organic matter and CO_2 for carbon dioxide and H_2O
226 for water. Equation (ii) follows given the combustion reaction:

227



229

230 where: α , β , and γ are stoichiometric constants given the formula for organic matter (OM) has
231 been normalised to the N content. The $\Delta H_f^{CO_2} = -393.5$ kJ/mol and $\Delta H_f^{H_2O} = -285.8$ kJ/mol,
232 while ΔH_f of O_2 and $N_2 = 0$ kJ/mol (NIST, 2017).

233 The ΔH_c^{OM} was measured on the collected samples and standards using bomb
234 calorimetry and the stoichiometry in Equation (iii) was derived from the elemental analysis of
235 the collected samples. Alternative approaches (Battley 1999) were considered based upon
236 Thornton's rule (Thornton, 1917) which is a simple correlation between ΔH_f^{OM} and ΔH_c^{OM}
237 based upon correlations from simple organic compounds. However, Thornton's rule was only
238 developed because elemental analysis of naturally-occurring organic macromolecules, such
239 as those of concern to this study, was not possible at the time.

240

241 *Bomb calorimetry*

242 The gross heat value of the sampled organic matter was measured on a Parr 6200 bomb
243 calorimeter. A sub-sample of known mass, typically 1g, had its moisture content raised back
244 to approximately 4% by weight before being combusted in the bomb calorimeter. The 4%

245 moisture does not detract from the calorific value but does aid the combustion process in the
246 bomb and helps prevent sputtering of the sample during the ignition process. The bomb
247 calorimeter was calibrated and standardised on each run of samples using benzoic acid. For
248 the samples of DOM for which less than 0.5 g of sample was available, the sample was doped
249 with a known amount of the benzoic acid standard so that a complete combustion was
250 achieved. For both soil and vegetation samples the calorific value was measured in at least
251 triplicate and adjustment made for the measured ash content of the organic matter sample; in
252 this manner the gross heat value as measured by the bomb calorimeter is equal to the heat of
253 combustion of the substance (ΔH_c^{OM}).

254

255 *Elemental analysis*

256 Triplicate samples of all the collected samples (above-ground and below-ground vegetation,
257 litter, peat soil, DOM and POM), once dried to 105 °C, were milled to a sub-mm powder
258 using a Spex 6770 Freezer Mill. For the samples of DOM and POM, cryomilling was not
259 necessary. The ground samples were then subject to carbon, hydrogen, nitrogen (CHN) and
260 separately to oxygen (O) analysis on a Costech ECS 4010 Elemental combustion system with
261 pneumatic autosampler. Computer software used was EAS Clarity (DataApex Ltd, Prague,
262 Czech Republic). For both CHN set up and the separate O set up, calibration curves of $r^2 >$
263 0.999 were created using acetanilide as the standard. Samples of acetanilide were included
264 within each run as unknown samples to act as internal quality control checks. Each sample
265 was analysed in triplicate i.e. three times for CHN and a further three times for O, and a mean
266 calculated for C, H, N and O. All samples were corrected for their measured ash content. The
267 stoichiometry of the organic matter was expressed as molar fraction relative to N as this was
268 always the least abundant element.

269

270 **2.4. The entropy of formation (ΔS_f^{OM})**

271 The values ΔS_f^{OM} were calculated based upon measured elemental compositions. The
272 approach of Vodyanitskii (2000) uses the elemental composition of the organic matter to
273 estimate ΔS_f^{OM} :

274

$$275 \Delta S_f^{OM} = S_{OM}^{\phi} - \sum_{i1}^i S_i^{\phi} \quad (\text{iv})$$

276

277 where: S_y^{ϕ} = absolute entropy of y with y as the OM or element i (J/K/mol). The absolute
278 entropy of the elements are 5.5, 130.5, 205, and 191.5 J/K/mol for C, H, O, and N
279 respectively (NIST, 2017). The standard absolute entropy of the organic matter (S_{OM}^{ϕ}) was
280 estimated, still based on Vodyanitskii (2000), as:

281

$$282 S_{OM}^{\phi} = 1.03 + 0.039(7 + \Delta S_f^{OM}) \quad (\text{v})$$

283

284 Further that an estimate of the absolute entropy can be estimated from the heat capacity
285 (C_{OM}^{ϕ}):

286

$$287 S_{OM}^{\phi} = 1.1C_{OM}^{\phi} \quad (\text{vi})$$

288

289 In turn the absolute heat capacity of OM (C_{OM}^{ϕ}) can be calculated as:

290

$$291 C_{OM}^{\phi} = \sum_{i1}^i C_i^{\phi} n_i \quad (\text{vii})$$

292

293 where: C_i^ϕ = the atomic heat capacity; and n_i = number of atoms of element i in the
294 stoichiometric formula of OM. The atomic heat capacity (C_i^ϕ) of C, H, N and O are: 7.53,
295 9.62, 11.3 and 16.74 J/K/mol respectively (NIST, 2017). The stoichiometry was derived from
296 elemental analysis.

297 Equations (iv) and (vii) were solved iteratively with initial estimate of S_{OM}^ϕ found
298 from Equation (vi) based on Equation (vii) and the initial value of ΔS_f^{OM} calculated from
299 Equation (iv). Then estimates of S_{OM}^ϕ and ΔS_f^{OM} were then improved with the iterative
300 application of Equations (iv) and (v). Equations (iv) and (v) required typically three iterations
301 before the value of ΔS_f^{OM} agreed within two decimal places.

302 The elemental analysis as described above was used to derive the elemental
303 composition of each the standards and collected samples

304

305 ***2.5. The Gibbs free energy of formation (ΔG_f^{OM})***

306 Given the estimates of ΔH_f^{OM} and ΔS_f^{OM} above then ΔG_f^{OM} can be readily calculated from
307 Equation (i). The ΔG_f^{OM} is then calculated for each of the sampled organic matter pools and
308 the average absolute temperature of the study site. Any pressure dependency was assumed to
309 be negligible in common with approach of Beer and Blodau (2007) based upon Benjamin
310 (2002).

311 It follows from Hess' Law that:

312

$$313 \Delta G_r^{OM} = \sum_1^i \Delta G_i^{OM} - \sum_1^j \Delta G_j^{OM} \quad (\text{viii})$$

314

315 where: $\sum_1^i \Delta G_i^{OM}$ = the sum of the ΔG_f^{OM} of the products; and $\sum_1^j \Delta G_j^{OM}$ = the sum of the
316 ΔG_f^{OM} of the reactants. It is then possible to consider the ΔG_r^{OM} for each transformation and
317 pathway (Equation (viii)). All the transformations considered in Figure 1 are known to occur
318 in peatlands and therefore $\Delta G_r^{OM} < 0$; this means that the transformations may need to include
319 the release of other components to meet the requirement that $\Delta G_r^{OM} < 0$ for that
320 transformation.

321 LaRowe and Van Cappellen (2011) have suggested a different approach to the
322 estimation of the Gibbs free energy of reaction by correlating ΔG for the half reactions of the
323 oxidation of well known, but naturally-occurring organic compounds (e.g. amino acids) with
324 their nominal oxidation state of carbon (NOSC, equivalent to C_{ox} – Masiello et al 2008,
325 Worrall et al., 2013). The correlation between the known ΔG and NOSC was extrapolated to
326 more complex macromolecules such as cell membranes. The value of NOSC (or C_{ox}) can be
327 estimated from elemental analysis. It should be noted that this approach considers only half
328 reactions and would have to be combined with data from the half reaction of an appropriate
329 terminal electron acceptor (TEA, e.g. sulphate). Further, it is important to note that this
330 approach was to study the change in the soil organic matter and not the changes in aqueous
331 solution of the peat porewater: Beer and Blodau (2007) considered the thermodynamic
332 limitations in the porewater solution. In effect our approach reconstructs the ΔG_f^{OM} through
333 and into a peat profile in order to understand the amount of energy that is available or must be
334 transferred to explain the accumulation.

335

336 3. Results

337 The results of the analysis are detailed in Table 1. Equation (ii) implies that there would be a
338 negative correlation between ΔH_f^{OM} and the ΔH_c^{OM} (Figure 3), and ΔH_c^{OM} has been negatively

339 correlated with the carbon oxidation state (C_{ox}) of naturally occurring organic matter
340 (Masiello et al., 2008), i.e. it would be expected that higher, less negative ΔH_f^{OM} would be
341 estimated for more reduced organic matter.

342

$$343 \quad \Delta H_f^{OM} = -18.3 - 0.64\Delta H_c^{OM} \quad n = 79, r^2 = 0.74, p < 0.05 \quad (ix)$$

$$344 \quad (0.7) \quad (0.04)$$

345

346 The values in the brackets refer to the standard error in the regression coefficient or constant
347 term. The values of ΔH_f^{OM} for the combined above-ground biomass was consistent with it
348 being a mixture of the functional groups of vegetation sampled (above-ground biomass was
349 composed of 78% Calluna, 17% Grasses and sedges; and 5% Mosses) (Table 1, Figure 4a).
350 The values for litter are within those for the vegetation but the top of the soil profile does
351 have some values of ΔH_f^{OM} that are lower (i.e. more negative) than those observed for either
352 the vegetation or the litter. Similarly, the range of ΔH_f^{OM} for the DOM and POM extended to
353 lower, more negative values than observed for any other of the sampled organic matter
354 (ΔH_f^{OM} for DOM between -7.3 and -17.5 kJ/g organic matter, for POM between -5.6 and -
355 19.1 kJ/g of organic matter – Figure 4a). The DOM from this study catchment has been
356 shown to have a statistically significantly higher oxidation state than other the other types of
357 organic matter also included in this study (Worrall et al., 2016b) unlike the study of Boye et
358 al. (2017) which proposed that the DOM was more reduced, however, this study considered
359 DOM samples from first-order peat hosted streams and not the soil pore water itself. In the
360 same study POM was shown to have a composition and oxidation state compatible with it
361 being an admixture of litter and peat soil but did not have a distinct oxidation state from

362 either. Although the lower, more negative values of ΔH_f^{OM} for POM (Figure 4a) are
363 consistent with erosion from the peat profile (eg. via bank erosion of the catchment streams),
364 the median and upper values are not, and it is possible that the POM samples for this study
365 included material very similar to the DOM. The ΔH_f^{OM} of the peat organic matter increases
366 with depth through the soil profile (Figure 4a). Vodyanitskii (2000) gave values for extracted
367 humic and fulvic acids from Russian soils of between 3.15 and 8.72 kJ/g. Battley (1998,
368 1999) used Thornton's rule to assess the ΔH_f of the dry matter of a whole cell of
369 *Saccharomyces cerevisiae* as 11.1 kJ/mol. Schaul et al. (1997) based on measured properties
370 of amino acids gave values of measured values of ΔH_f of between 4.3 kJ/mol for microflora
371 to 19.35 kJ/mol for humin – note that it is not always possible to compare reported values as
372 molecular masses are not given.

373 The values of ΔH_f^{OM} can be compared to the C_{ox} values for the same samples
374 (Figure 4b). The DOM are the most oxic samples and distinct from the rest of the samples
375 examined. The vegetation, peat and below-ground biomass samples are reduced relative to
376 DOM and reduced relative to glucose fixed in photosynthesis ($C_{ox}(\text{glucose}) = 0$). The C_{ox} for
377 this site has been examined by Worrall et al. (2016b) and there is no significant change in C_{ox}
378 down the peat profile.

379 The values of ΔS_f^{OM} follow the pattern as seen for ΔH_f^{OM} although there was no
380 significant link between the two sets of values (Figure 4b). Vodyanitskii (2000) gave values
381 for extracted humic and fulvic acids from Russian soils of between 3.36 and 6.12 J/g. Battley
382 (1999) used Thornton's rule to calculate ΔS_f^{OM} of the dry matter of a whole cell of
383 *Saccharomyces cerevisiae* and found ΔS_f^{OM} as 15.5 J/mol.

384 The values of ΔG_f^{OM} do show some differences from the patterns observed for ΔH_f^{OM}
385 and ΔS_f^{OM} (Figure 4c). Tardy et al. (1997) estimate ΔG_f^{OM} by analogy with estimation methods

386 developed for clay minerals and give values of ΔG_f^{OM} as -3.24 kJ/mol (microflora); -7.42
387 kJ/mol (humic acid); -12.14 kJ/mol (fulvic acid); -14.31 kJ/mol (plant biomass); and -27.37
388 kJ/mol (humins). LaRowe and Van Cappellen (2011) provide values for the half reactions of
389 oxidation and ΔG values were expressed per electron transfer, hence their values are not
390 directly comparable with those of this study. The litter samples have values of ΔG_f^{OM} lower,
391 i.e. more negative, than that of the vegetation samples which was not the case for either
392 ΔH_f^{OM} or ΔS_f^{OM} . The ΔG_f^{OM} of the surface peats are very close in value to those of the litter
393 samples suggesting a very similar composition and supports the obvious idea that peat soil
394 forms in the continuum from fresh litter. The peat soils samples show an increase ΔG_f^{OM} with
395 depth down the profile, i.e. values of ΔG_f^{OM} become less negative. The values ΔG_f^{OM} of DOM
396 and POM spread across a considerable range from very similar to the peat and litter samples
397 to considerably lower, i.e. more negative, values of ΔG_f^{OM} . The peat soil samples when
398 plotted against depth in the profile showed a significant increase (probability of being
399 different from zero of 95%) in the ΔG_f^{OM} with depth:

400

$$401 \quad \Delta G_f^{OM} = -4.22z^{-0.279} \quad n=20, r^2 = 0.32 \quad (x)$$

$$402 \quad (1.42) \quad (0.096)$$

403 where z = depth in to the peat profile (cm – with more positive values indicating deeper
404 depths). The values in the brackets are the standard error in the coefficients.

405 Coupled with the proposed diagram of flows within this ecosystem (Figure 1) and
406 Equation (viii), it is possible to argue that we would expect the spontaneous production of
407 litter from vegetation, and the spontaneous production of DOM from all other organic matter.
408 However, for other transitions, the change in ΔG_f^{OM} implies that the transition would have to

409 be accompanied by emission of low ΔG_f^{OM} compounds (i.e. CO₂, CH₄, or DOM which have
410 more negative values of ΔG_f^{OM} than the solid organic matter types considered).

411 Differentiating Equation (x) gives the profile of the change in ΔG_f^{OM} , or the ΔG_r^{OM}
412 that would have to be balanced by the production of CO₂, DOM or CH₄. Given the fit of the
413 Equation (x), the differentiation was performed numerically within 95% confidence interval
414 defined by fit of Equation (xvi) and the best fit equation was:

415

$$416 \quad \frac{d\Delta G_f^{om}}{dz} = 1.18z^{-1.279} \quad n=16, r^2=0.98, p < 0.05 \text{ (xi)}$$

417 (0.75) (0.032)

418

419 The values in brackets are the standard error in the coefficient and exponent. Although the
420 form of the best-fit equation (Equation (xi) – Figure 5) cannot by mathematical definition
421 equal zero. An one-way analysis of variance (ANOVA) of the values ΔG_r^{OM} (Equation (viii))
422 of the peat soil samples judged across each of the measured depth ranges, using the depth
423 range as the one factor, showed that there was a significant change in the change in ΔG_r^{OM} .
424 *Post hoc* testing, using the Tukey test, ΔG_r^{OM} was not significantly different from zero after
425 the sample in the depth range 40 to 45 cm depth in the soil profile. The fact that ΔG_r^{OM} is
426 close to zero implies very little (if any) reaction of peat at depth.

427 The variation in the ΔG_f^{DOM} could imply that there is a variation in the maturity of the
428 DOM and as such DOM might itself react to release of CO₂. Taking the highest value of
429 ΔG_f^{DOM} (i.e. least negative value -3.3 KJ/gC - Figure 4c) as the most reacted or mature DOM,
430 and that other measured DOM composition would react to that composition and that the

431 reaction is balanced by the loss of CO₂. The assumption that the DOM with the highest value
432 of ΔG_f^{DOM} is the most reacted or mature matches the pattern assumed for the peat soils that
433 the most reacted peat soil has the highest values of ΔG_f^{OM} . Given this assumption then it is
434 possible to estimate the amount of CO₂ released from processing of DOM – based upon
435 Equation (iii). The proportion of CO₂ that would have to be released per 1g of C as DOM for
436 each of the measured DOM compositions to transform it to the DOM composition with the
437 highest ΔG_f^{DOM} varied from 0.0 to 0.57 with an arithmetic mean of 0.30. The value of 0.0
438 represents the sample assumed to be the most mature and the arithmetic means represents a
439 30% of DOM is turned over to CO₂ prior to loss to the stream network. Moody and Worrall
440 (2016) measured an average DOC loss rate in the light of 64% over a 70 hour period but
441 found an average of 6% DOC loss over 70 hours when the sample was kept in the dark.

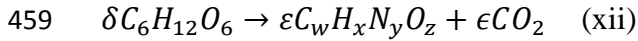
442

443 **4. Discussion**

444 Given that this study could calculate the ΔG_f^{OM} for each of the substances and reservoir as
445 illustrated in Figure 1 it was then possible to at least consider the ΔG_r^{OM} for each
446 transformation and pathway and thus we have shown which can occur spontaneously and
447 which transformations require the production of low (i.e. more negative) ΔG_f^{OM} products such
448 as CH₄, CO₂ or indeed, given the results of this study, DOM. For the release of CO₂, in the
449 sense of LaRowe and Van Cappellen (2011), oxygen is acting as the terminal electron
450 acceptor and the other half reaction. For the formations of plant components (lignin, cellulose
451 and protein) and the biomass (above- and below-ground biomass as well as the plant
452 functional types), the reactant was taken as glucose ($\Delta G_f^{glucose} = -910$ kJ/mol – NIST, 2017)
453 produced directly from photosynthesis. The transformations of glucose to plant components,
454 the plant components to litter, and litter to the surface peat are all assumed to have occurred

455 in oxic conditions and will react to release CO₂. The $\Delta G_f^{CO_2} = -394$ kJ/mol (NIST, 2017) and
456 the amount of CO₂ can be used to balance out the transformation, e.g. the transformation
457 from glucose:

458



460

461 In Equation (xii), although δ , ε and ϵ are stoichiometric constants ϵ represents the amount of
462 a carbon that has to be lost (eg. emitted to the atmosphere as CO₂) while ε represents the
463 amount of carbon passed through into the peatland. If the values in Equation (xii) are
464 expressed per mole of C and then per unit mass of carbon, the stoichiometry of Equation (xii)
465 is simplified and each of reactions can be considered as the fate of 1 g of C of reactant
466 organic matter (i.e. $\delta = 1$). Then only the following equations need to be satisfied:

467

$$468 \quad 1 = \varepsilon + \epsilon \quad (\text{xiii})$$

$$469 \quad \Delta G_r^{OM} = \sum_1^i \Delta G_i^{OM} - \sum_1^j \Delta G_j^{OM} < 0 \quad (\text{xiv})$$

470

471 Equations (xiii) and (xiv) can be solved iteratively for the transformation. Even
472 though a reaction will occur in favour of products when $\Delta G_r^{OM} < 0$ kJ/mol, or to completion
473 with $\Delta G_r^{OM} < -60$ kJ/mol, there is a thermodynamic threshold after which it has been
474 observed that biological systems cannot effectively obtain sufficient free energy for the
475 reaction to occur, i.e. $\Delta G_r^{OM} < 0$ kJ/mol is not the effective limit of spontaneous reaction in
476 biological systems. Schink (1997) propose a theoretical value of the thermodynamic
477 threshold for biological systems as $\Delta G_r^{OM} < -20$ kJ/mol, but other studies have suggested
478 values for this thermodynamic threshold as high as -15 kJ/mol. This thermodynamic threshold

479 for biological systems has been equated to the energy required to produce one quarter mole of
480 ATP.

481 Furthermore, it is not possible to transfer 100% of the energy content of any substrate
482 even after the threshold described above has been accounted for, and it matters by which
483 biochemical pathway the oxidation and energy transfer occurs. Lafitte and Loomis (1988)
484 showed that the efficiency in plant processes varied between 0.84 and 0.89. That range was
485 used here and as such ε and ϵ were recalculated using an effective value of ΔG_f for CO₂:

486

$$487 \quad {}^{eff}\Delta G_f^{CO_2} = \varphi \Delta G_f^{CO_2} \quad (xv)$$

488

489 Where: ${}^{eff}\Delta G_f^{CO_2}$ = the effective value of ΔG_f for CO₂ after allowing for the efficiency of
490 energy transfer (Kj/mol); φ = the energy transfer efficiency, taken as between 0.84 and 0.89.
491 The energy transfer efficiency can be considered as equivalent to a thermodynamic efficiency
492 factor as used by Hoehler (2004).

493 It was assumed that no other elements (e.g. N) in Equation (xii) were limiting and so
494 Equation (xii) was balanced only with respect to C. Further, it was assumed that the
495 contribution of the ΔG_f^{OM} of other components required to balance Equations (xii), e.g.
496 nitrate, was minimal because their stoichiometric fraction was small. Equally, we admit that
497 naturally-occurring organic matter in a peatland will contain elements not included in
498 Equation (xii) such as S and P, but we would argue that they are present in quantities even
499 less than that of N. Worrall et al. (2016a) showed that the lowest value of C:P in this
500 ecosystem was 769 for the *Calluna vulgaris* biomass. It is possible to solve Equations (xiii)
501 and (xiv) then 1g of C fixed as glucose by photosynthesis would result in 0.68 g C as biomass
502 and 0.32 g C as CO₂.

503 For the transformation in to and through the peat profile it is less likely that oxygen
504 can be the terminal electron acceptor and the transformation to CO₂ is only one possible
505 option and this study has shown that other low (high negative) ΔG_f^{OM} species could act to
506 balance increases in ΔG_f^{OM} in the soil profile. The production of dissolved organic matter
507 (DOM) or methane (CH₄) would be possible act as other electron accepters but other terminal
508 electron acceptors may be available. Perhaps the most important would be the role of
509 sulphate at depth in the peat. Several studies have shown that the utilisation of sulphate and
510 methanogenesis cannot account for the rate of anaerobic CO₂ production in ombrotrophic
511 peatlands (e.g. Vile et al., 2003); this is even the case with the recycling of sulphate (e.g.
512 Weider et al., 1990). Long term monitoring of shallow (10 cm depth) and deep (50 cm) soil
513 water by the ECN monitoring at the site can be summarised (Table 2) to show that nitrate is
514 absent from the soil porewater. Furthermore, the long term monitoring of the soil water at the
515 site also shows that there was little sulphate present and the change in sulphate concentration
516 is small in comparison to concentration and change in DOC. Lovley et al. (1996) have shown
517 that DOM can act as a terminal electron acceptor and divert energy from methanogenesis.
518 Furthermore, Minderlein and Blodau (2010) suggested that there was a toxic effect of
519 intensely humified DOM on both methanogenesis and sulphate-reducing bacteria but not on
520 fermenting microbes. Bauer et al. (2007) showed that DOM could act as redox buffer as its
521 polyfunctionality means that it has groups that act across redox potentials from -0.9 to 1.0 V,
522 and indeed that is shown to be possible in this study by consideration of the ΔG_f^{OM} that DOM
523 could be a TEA. Equally, microenvironments can always exist which could give redox
524 environments distinct from the bulk environment of the peat soil (Wachinger et al. 2000).
525 Keiluweit et al (2016) have shown that for the free energy available from terminal electron
526 acceptors other than O₂ not only follows a succession of decreasing available ΔG but also the
527 available ΔG decreases with the decreasing oxidation state (C_{ox}) of the organic matter

528 substrate with which the particular electron acceptor is reacting. However, for the study site
529 Worrall et al. (2016b) have shown there is no significant change in C_{ox} with depth in to the
530 peat profile and indeed for 8 peatlands across the UK, not including this study site, Clay and
531 Worrall (2015) found a mixture of significant increases, significant decreases, and lack of
532 significant change in C_{ox} down peat profiles.

533 The study has taken this approach without reference to the stoichiometry of the
534 reactions. This study has made a series of simplifying assumptions: that there is steady-state
535 production (i.e. that inter-annual variation can be ignored on the timescales of the peat profile
536 accumulation); that all other elements, in whatever the appropriate form, were available; and
537 that their requirement was insufficient to alter the Gibbs free energy balance. An alternative
538 approach would be to consider the stoichiometry: Penning de Vries et al. (1974) considered
539 such an approach to calculate the amount of glucose that would be required to produce
540 biomass and as a consequence the amount of CO_2 produced and sequestered by biomass
541 production. McDermitt and Loomis (1981) provided an alternative approach based upon
542 elemental analysis of biomass and the energy constraints of the redox processes involved.
543 Both approaches only considered the development of biomass and not its subsequent
544 degradation or storage of organic matter as would be the case in a peat ecosystem such as
545 studied here. Therefore, a stoichiometric approach that considers all the available elements
546 and goes beyond just the production of biomass but also considers the transfer of litter into
547 the soil with the production of deep humified peat including losses of DOM and POM. Such
548 an approach could be and is based upon balancing elemental composition and redox state to
549 understand and constrain organic matter processing and carbon release from ecosystems,
550 especially in organic matter-dominated environments such as peatlands.

551 This present study would suggest that peat humic matter accumulates because the
552 available Gibbs free energy (ΔG_r^{OM}) from soil is no longer sufficient for reaction to occur.

553 Beer and Blodau (2007) suggested that organic matter turnover in deep peat profiles is
554 limited because the pore water becomes a closed system and so reaches an equilibrium. The
555 argument of Beer and Blodau (2007) is important for this study for two reasons. Firstly, this
556 study would suggest that indeed reactions at depth in peat are thermodynamically limited, but
557 in the case of this study it is the solid component and not the dissolved components that
558 cannot react. Secondly, this study has not considered the dissolved component, and therefore
559 ongoing reaction at depth could be reaction of the dissolved and not the solid component.
560 Production of CO₂ and CH₄ at depth could be due to the supply of labile DOM from surface
561 peat layers. Unfortunately, this study did not examine the composition of DOM from the pore
562 water but rather sampled fresh DOM from a first-order stream assuming it was a reasonable
563 approximation to the pore water DOM - based upon studies of the source of mixing and water
564 in this catchment (Worrall et al., 2006), but the potential for turnover to CO₂ within profile
565 was estimated by comparison between the most and least evolved DOM (as assessed by their
566 comparative ΔG_f^{OM}). The indication here that reaction has ceased at depth is only based upon
567 the compositional change within the substrate but this does not mean that there is not
568 continuing reaction in the pore water. Chaser et al. (2000) showed that the radiocarbon age of
569 DOC at depth in peat soil pore water in a peat profile was younger than the surrounding peat
570 soil organic matter, eg. at 80 cm depth the age of the peat soil organic matter was 800 years
571 BP while that of the CH₄ was 135 years BP and the DOC age was 123 years BP. Similar,
572 Charman et al. (1994) dated CO₂ and CH₄ samples collected from depth show that both gases
573 were between 500 and 2000 years younger than the adjacent peat.

574 It is difficult to know whether the change or lack of change of ΔG_f^{OM} is the cause or
575 the effect of what is constraining the transfer of organic matter into and through a peat profile
576 – as half-reaction it would not happen spontaneously without the other half reaction. This
577 study has suggested why organic matter accumulates in peatlands. The profile as measured

578 shows that the change in ΔG_f^{OM} declines or becomes zero but this cannot provide information
579 as to why this would occur. Freeman et al. (2001) have shown that hydrolase enzymes in peat
580 bogs are inhibited by the presence of phenolic compounds, which can build up in peat
581 because of the activity of phenol oxidase is severely restricted in the absence of oxygen.
582 Therefore, the organic matter can accumulate because of restriction of a key enzyme in the
583 degradation process. If the water table in peat bogs falls, the phenyl oxidase activity increases
584 and oxygen ingress increases, destroying the phenolic compounds that repress the hydrolase
585 activity. A loss of phenolic compounds means that decomposition can continue even after the
586 water table rises again. This process has been referred to as an “enzyme latch” mechanism.
587 This enzyme-latch production does not immediately cease once the water tables have been
588 restored and the additional turnover of organic matter such as DOC production can continue
589 for long periods. The changes in DOC concentration and flux in the runoff from peatlands has
590 been taken as evidence of the enzyme latch process. The deepest water table depth recorded
591 for this site was 42 cm below the surface, i.e. the maximum depth of the oxygen ingress in
592 this catchment closely coincides with the depth of at which decomposition ceases as
593 predicted by this study. The thermodynamic approach of Beer and Blodau (2007) would
594 argue that organic matter accumulates because the pore water components cease to react as
595 the pore water system becomes closed and therefore there ceases to be a thermodynamic
596 driver for the solid organic matter to react further and to release components into solution.
597 Therefore, rather like the “enzymic-latch” mechanism the thermodynamic explanation does
598 not prohibit further reaction of the organic matter if conditions change, eg. if a closed pore
599 system became open again.

600 The study here has shown that processing of organic matter would have a 5% chance
601 of having ceased by 40 to 45 cm depth and this can be considered the depth below which
602 further reaction has been thermodynamically inhibited (LaRowe and Van Capellen, 2011).

603 Note that for pore water reactions Beer and Blodau (2007) suggested that thermodynamic
 604 inhibition did not occur until approximately 2 m depth; although at a very different site from
 605 the one in this study, it therefore illustrates there may be a zone where the solid organic
 606 matter substrate is no longer being processed but that pore water constituents are. However,
 607 in such a zone the pore water components would have to originate in overlying peat layers.
 608 Above a zone of thermodynamic inhibition, the available energy release diminishes rapidly
 609 and the available energy has been related to the kinetics of turnover processes (e.g. Jin and
 610 Berthe, 2002, Dale et al., 2006), where the rate of the redox reaction:

611

$$612 \quad r = \mu_{max} B F_K F_T \quad (\text{xv})$$

613

614 where: μ_{max} = maximum rate for the reaction per unit biomass; B = available biomass; F_K =
 615 kinetic function; and F_T = thermodynamic function. The kinetic function (F_K) and
 616 thermodynamic function (F_T) are defined on the scale 0 to 1 and Jin and Berthe (2005) define
 617 F_T as:

618

$$619 \quad F_T = 1 - \exp\left(\frac{\Delta G_r + m\Delta G_r^{ATP}}{\chi RT}\right) \quad (\text{xvi})$$

620

621 where: ΔG_r^{ATP} = the Gibbs free energy required for synthesis of ATP; m, χ = stoichiometric
 622 constants for the reaction with ATP. Thus, as the ATP threshold is approached, the rate of
 623 reaction will slow. Therefore, we may consider that the rates of processing of organic matter
 624 slow dramatically from the surface to the depth and so Figure 5 can be viewed as an analogue
 625 of the kinetic profile. It should be noted that Figure 5 represents the change in the ΔG_r^{om} and
 626 so it must always be balanced by production of highly negative ΔG_r^{om} products such as CO_2 .
 627 Alternatively, the kinetic limitation in this case may simply be a diffusive one whereby the

628 source of the reactive products is in the upper layers of the peat and there reaction is limited
629 by their diffusion down the peat profile. The approach of Jin and Berthe (2005) (Equations
630 (xv) and (xvi)) is the same approach used by Keiluweit et al. (2016) to explain the
631 preservation of organic matter in soils.

632 The approach outlined here in this study provides a framework by which we can
633 consider the stability of organic matter in soil and in the natural environment more generally.
634 By being able to calculate the ΔG_f^{OM} and then calculate the ΔG_r^{OM} to assess whether reactions
635 could occur and, if so, how fast. Comparing profiles ΔG_f^{OM} in a range of peat profiles could
636 define the stability of peat soils and their resistance to long-term degradation.

637

638 **5. Conclusions**

639 This study has estimated the changes in ΔG_f^{OM} across a peatland and considered the changes
640 which would have to be balanced by production of CO₂, DOM or CH₄. Estimation of ΔG_f^{OM}
641 and the ΔG_r^{OM} profile provides an alternative and objective method of assessing the degree of
642 decomposition in peat. The study has found:

643 i) All the transformations considered, except for the production of litter from biomass, would
644 have to occur through the loss or emissions of the low (i.e. more negative) ΔG_f^{OM} product
645 such as CO₂, DOM or CH₄.

646 ii) Most of the CO₂ lost in the transfer of organic matter was lost in the production of biomass
647 rather than the decay of litter or soil organic matter.

648 iii) The change in ΔG_f^{OM} of the peat soil would suggest that further reaction becomes
649 thermodynamically inhibited after depths of approximately 40 cm. the study shows that
650 organic matter accumulation in peat profiles could be explained by the lack of change in
651 ΔG_f^{OM} and that this could be predicted simply from the elemental composition.

652

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656

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848

Table 1. The median composition of the carbon pools considered by the study. Median stoichiometry is expressed relative to N content except for cellulose which expressed relative to C. M_r = the relative molecular mass of the given molecular formula.

		M_r	ΔH_f kJ/mol	ΔG_f kJ/mol	ΔS_f J/K/mol	ΔH_f kJ/g OM	ΔG_f kJ/g OM	ΔS_f J/K/g OM	ΔH_f kJ/g C	ΔG_f kJ/g C	ΔS_f J/kg C
DOM	$C_{31}H_{38}NO_{24}$	732	-7.24	-6.37	-8.14	-21.69	-19.86	-25.28	-10.43	-9.04	-26.29
POM	$C_{22}H_{35}NO_{14}$	462	-5.63	-8.06	-6.28	-24.94	-50.90	-27.85	-12.35	-24.82	-27.85
Above-ground biomass	$C_{57}H_{86}NO_{35}$	1344	-9.78	-2.78	-17.78	-13.21	-4.07	-25.97	-6.72	-2.07	-13.12
Below-ground biomass	$C_{49}H_{73}NO_{29}$	1140	-7.54	-2.68	-15.03	-12.76	-4.54	-25.14	-6.61	-2.35	-25.43
Grass & sedge	$C_{33}H_{52}NO_{21}$	801	-5.47	-2.87	-10.75	-13.80	-7.14	-27.13	-6.82	-9.05	-27.12
Mosses	$C_{95}H_{145}NO_{56}$	1343	-9.98	-3.44	-17.98	-15.06	-5.19	-27.13	-7.43	-2.55	-27.13
Calluna	$C_{55}H_{86}NO_{46}$	2194	-12.98	-1.92	-29.32	-11.39	-1.70	-25.74	-5.91	-0.88	-25.74
Litter	$C_{25}H_{35}NO_{15}$	587	-7.58	-2.39	-7.58	-8.37	-5.29	-17.67	-6.19	-3.86	-17.68
Peat soil	$C_{43}H_{62}NO_{26}$	1115	-6.60	-2.04	-14.79	-7.91	-2.49	-17.74	-6.04	-1.86	-17.74
Lignin	$C_{87}H_{103}NO_{31}$	1658	-6.83	-0.60	-19.58	-6.51	-0.57	-18.68	-4.12	-0.36	-18.88
Cellulose	CH_2O	146	-0.40	-0.75	-1.70	-6.62	-12.49	-28.35	-2.72	-5.13	-28.35
Protein	C_5H_5NO	101	-0.46	-0.29	-1.46	-9.68	-6.10	-30.42	-4.58	-2.89	-30.42

Table 2. 20 year averages of the concentrations of redox active species in the soil water of the study site.

	Mean concentration	
	Shallow (10 cm)	Deep (50 cm)
Sulphate (mg S/l)	0.11	0.02
Nitrate (mg N/l)	0.01	0.01
Ammonium (mg N/l)	0.06	0.42
Iron (mg Fe/l)	0.17	0.21
DOC (mg C/l)	21.3	17.5
Conductivity (μ S/cm)	39.1	31.4
pH	4.3	4.6

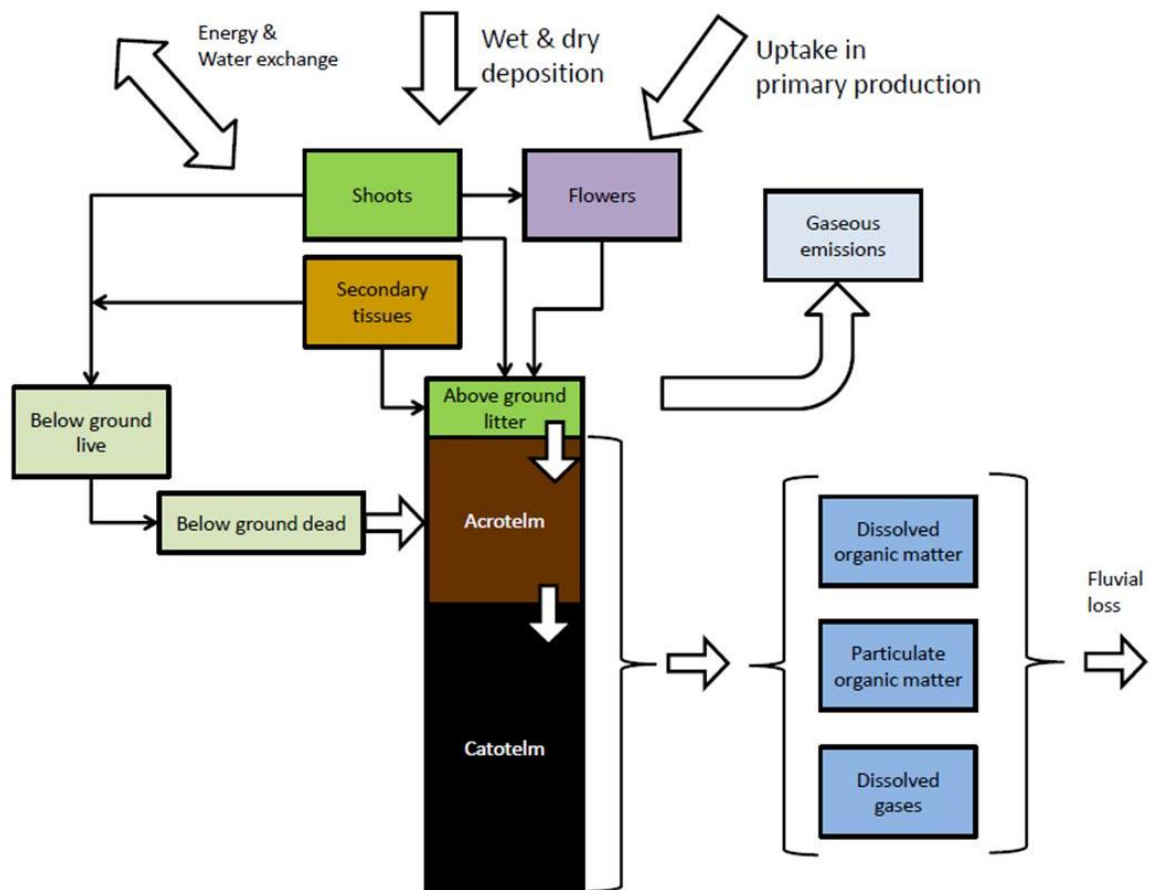


Figure 1. Schematic diagram of organic matter pools and fluxes considered by this study, adapted from Worrall et al. (2016b).

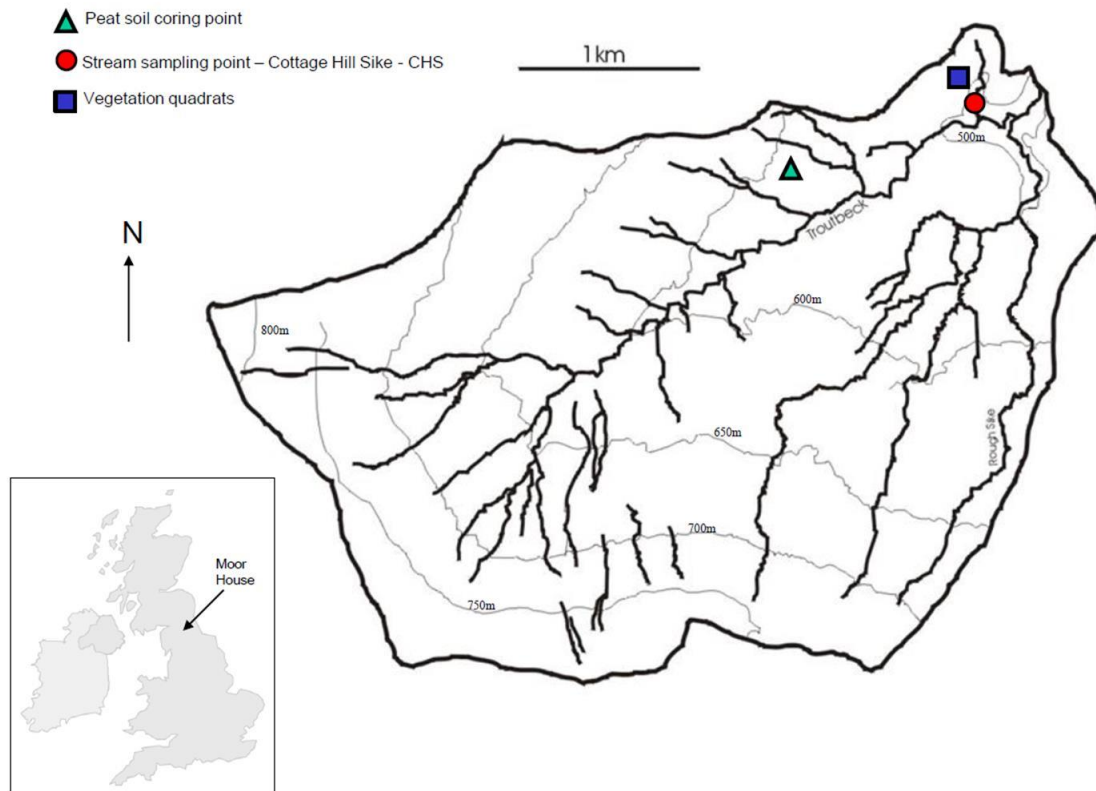


Figure 2. Location of the study site used in this study.

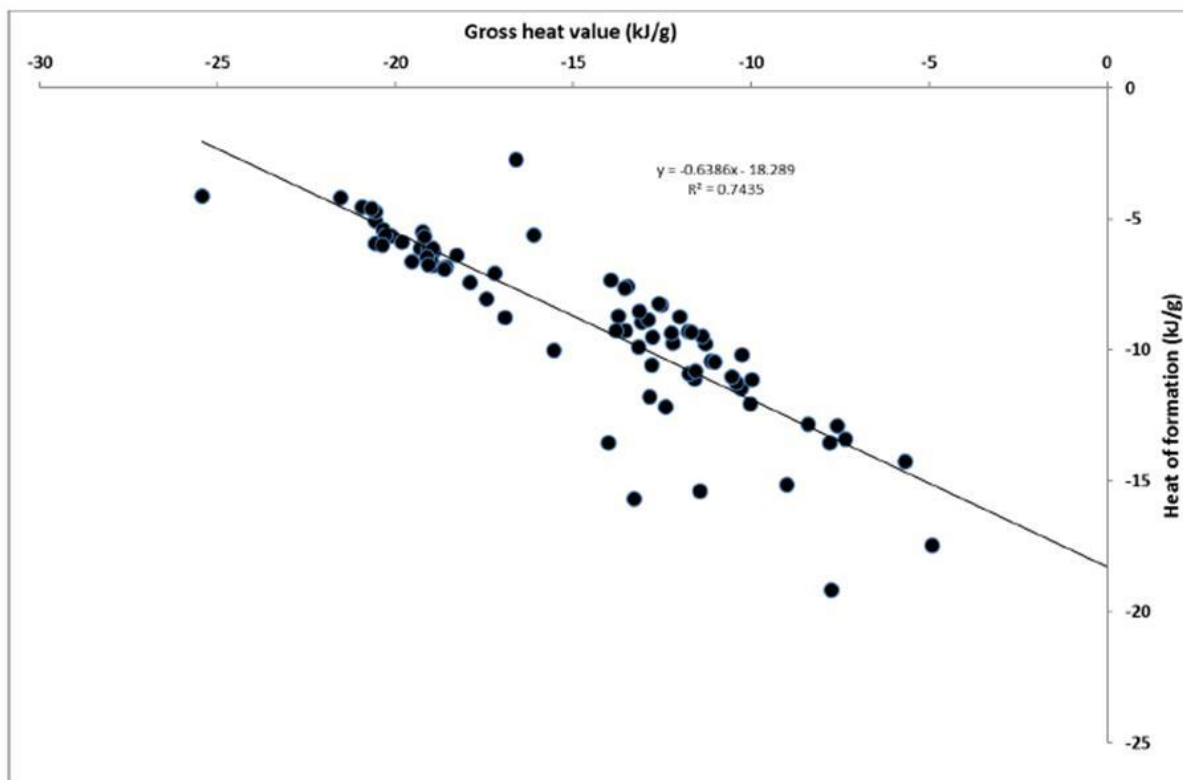


Figure 3. Comparison of ΔH_f^{OM} and the ΔH_c^{OM} for the all the samples measured in the study.

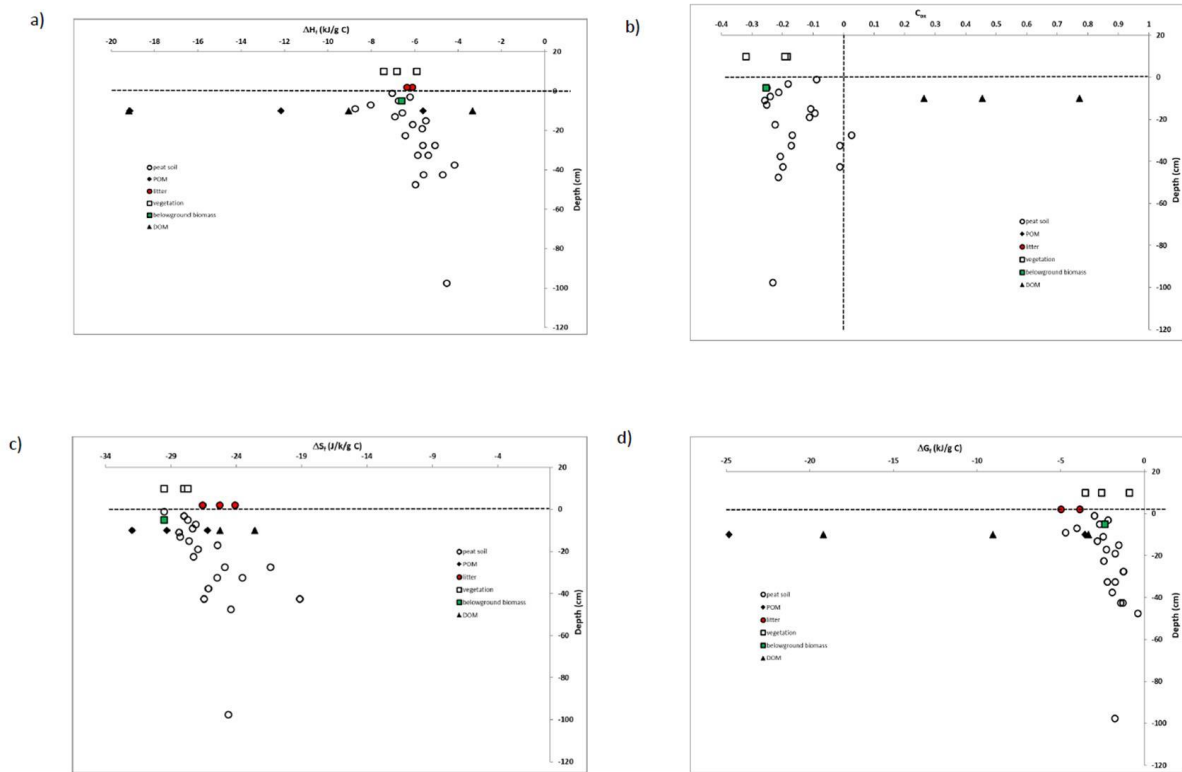


Figure 4. The ΔH_f^{OM} (a); C_{ox} (b); ΔS_f^{OM} (c); and ΔG_f^{OM} (d) of the peat soil, DOM, POM, vegetation and litter samples considered in this study. The samples of DOM and POM are given a nominal depth of 10 cm in the peat profile. The values shown for the peat soil are the average for each sampled depth while for samples of litter, vegetation, POM and DOM the range and median is shown at the nominal depth relative to the surface.

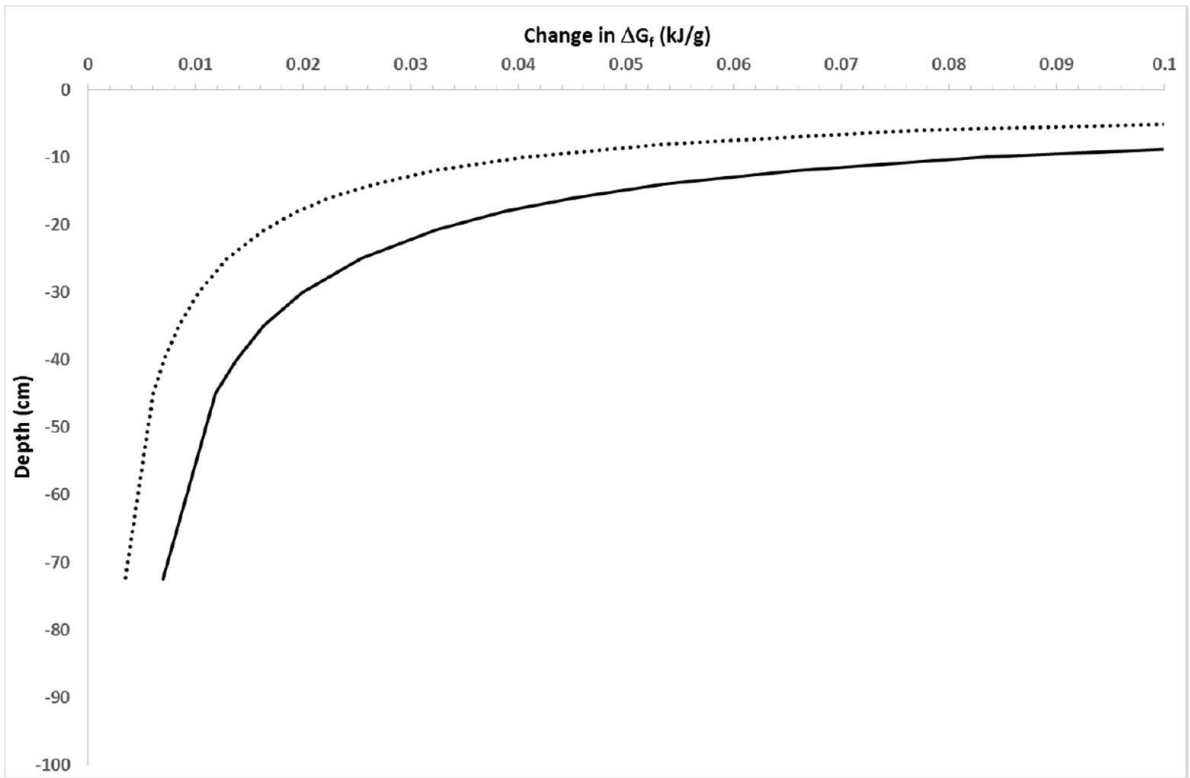


Figure 5. The 95% confidence interval on the change in ΔG_f^{OM} of the peat soil with depth.

Depth is expressed as cm below the soil surface as negative.