Key Points:
- Thermodynamic consideration of elemental analysis allows the prediction of the fate of carbon fixed as primary production
- Change in the Gibbs free energy of formation of the naturally occurring organic matter (ΔG_f^{OM}) shows that changes in the peat profile must be balanced by production of CO_2, CH_4, or DOM
- Organic matter accumulates in peatlands because further reaction becomes thermodynamically inhibited with depth in the peat profile

Thermodynamic Control of the Carbon Budget of a Peatland

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

1. Introduction

Peatlands are the most important terrestrial carbon (C) store within the terrestrial biosphere. While they occupy only a small percentage of the total land area (~3%, Rydin & Jeglum, 2013), peatlands store a disproportionately large amount of carbon. It is estimated that 500 ± 100 GtC is stored in northern peatlands (Gorham, 1991; Loisel et al., 2014; Yu et al., 2014), which is approximately equivalent to the total terrestrial vegetation (Intergovernmental Panel on Climate Change, 2013).

The very existence of peatlands relies on the fate of organic matter, further that at least at some stage in the past there has been a positive balance of carbon with respect to loss to atmosphere or the fluvial network, which means organic matter has accumulated. Hence, the understanding of a peatland's carbon budget is a statement of the ecosystem's very existence and future. The estimation of C budgets has been a common research target. Initial approaches to C budgeting for peatlands were to measure the long-term accumulation rate by dating the depth profile (e.g., Turetsky et al., 2004). Subsequent approaches then developed the balance of the contemporaneous gaseous fluxes—the net exchange of CO_2 and the efflux of CH_4 (e.g., Fleischer et al., 2016, for earlier studies see compilation by Limpens et al., 2008) and then extended to include the fluvial losses of dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved carbon gases such that complete contemporary carbon budgets of peatlands are now common (e.g., Billett et al., 2004; Nilsson et al., 2008; Roulet et al., 2007; Worrall et al., 2003).

Approaches based on contemporary fluxes do consider the species of the carbon, nitrogen or oxygen entering or leaving peat ecosystems and, although this can include the individual gaseous forms (e.g., N_2O, CO_2, or CH_4), it still means that certain carbon fluxes are not considered in any more detail than the lumped terms such as DOC or POC without further characterization. The contemporary budgets that do exist consider different types of peatland with different dominant vegetation types, different substrates (e.g., Leroy et al., 2017),

and the impact of different physical and land management controls across a range of countries (e.g., United Kingdom, Rowson et al., 2010; Germany, Tiemeyer et al., 2016; Sweden, Von Arnold et al., 2005; and Canada, Nwaishi et al., 2016). However, even these detailed studies have dealt in lumped compositions (e.g., DOC or DOM) or lumped controls, for example, change in water table or change in air temperature, but have not considered the actual molecules transitioning into and through peatland, for example, CO_2 is fixed as glucose through photosynthesis, which is transformed into carbohydrates, lignin, etc.

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

Penning de Vries et al. (1974) proposed that, on the basis of a study of biochemical pathways, it was possible to understand and predict the energetic cost of biomass development from proximate analysis of the composition of that biomass, for example, given the proportion of macromolecules and biopolymers in a plant, it would be possible to estimate the cost of production. Although the purpose of the approach proposed by Penning de Vries et al. (1974) was to predict production values of biomass, it also meant that the amount of CO_2 produced during plant growth from, for example, root respiration, could be predicted. Proximate analysis requires a detailed compositional analysis of biomass and so McDermitt and Loomis (1981) provided an alternative approach based upon elemental analysis of biomass. Williams et al. (1987) suggested that the elemental analysis of McDermitt and Loomis (1981) was too costly or too difficult and proposed an approximation based upon the C/N ratio and the heat of combustion of the biomass. Subsequent advances in technology mean that accurate characterization of the elemental composition of organic matter is now readily available (e.g., Masiello et al., 2008). The proximate and elemental analytical approaches were only ever applied to understand the development of biomass, but the stoichiometric and energetic constraints invoked in these approaches apply to any biochemically mediated transition of organic matter. However, the energetic constraint applied in these approaches have only considered enthalpy and not entropy.

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

2. Approach and Methodology

The approach taken in this study was to consider the change in Gibbs free energy with the fixation, transformation, and loss of carbon through a peatland. Beer and Blodau (2007), and later Boye et al. (2017), relied on measuring the concentration of small organic acids in soil pore water and for these small organic acids (e.g., aminosugar) and the ΔG_f of these small molecules calculated using standard results and the application of the methods of LaRowe and Van Cappellen (2011). The approach of this study is to provide an alternative approach by considering the solid phase, biomacromolecular components (e.g., plant organic matter) and
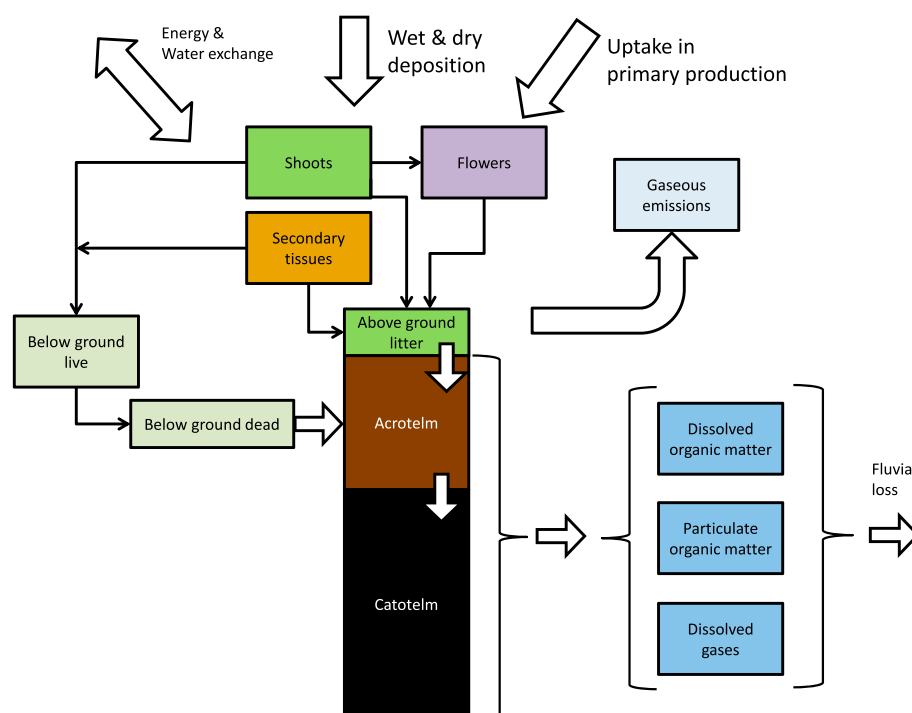
Figure 1. Schematic diagram of organic matter pools and fluxes considered by this study, adapted from Worrall et al. (2016b).

assessing change between these components. The change in Gibbs free energy was considered by analyzing the composition of the organic matter in a series of carbon pools and fluxes within the context of a known carbon budget (Figure 1). The change in the Gibbs free energy was considered by the differences in the Gibbs free energy of formation of each of the organic matters in reservoirs and fluxes in Figure 1. The Gibbs free energy of formation (ΔG_f^{OM}) can be readily calculated from the difference between the enthalpy and entropy of formation of the same organic matter:

$$\Delta G_f^{OM} = \Delta H_f^{OM} - T\Delta S_f^{OM} \tag{1}$$

where: ΔG_f^{OM} = the Gibbs free energy of formation of organic matter (kJ/mol); ΔH_f^{OM} = the standard enthalpy of formation of organic matter (kJ/mol); ΔS_f^{OM} = the standard entropy of formation of organic matter (kJ/K/mol); and T = absolute temperature of the reaction (K). In this study elemental analysis of carbon, hydrogen, nitrogen, and oxygen of each pathway and flux in Figure 1 was used to calculate the entropy of formation of the organic matter (ΔS_f^{OM}). Bomb calorimetry was used to calculate the enthalpy of formation of the organic matter (ΔH_f^{OM}) in each of the pathways and fluxes shown in Figure 1. The Gibbs free energy of formation was then calculated using equation (1). The context for these thermodynamic parameters was then provided by the carbon budget as measured by previous studies within the study catchment.

2.1. Study Site

The peatland ecosystem chosen for this study was the Trout Beck catchment, which is within the Moor House National Nature Reserve, a terrestrial and freshwater site monitored as part of the UK Environmental Change Network. The catchment has been well studied so this study could draw upon existing budgets for dry matter (Forrest, 1971), carbon (Worrall et al., 2003, 2009), nitrogen (Worrall et al., 2012), phosphorus (Worrall et al., 2016a), and energy (Worrall et al., 2015). The catchment is an 11.4 km^2 blanket peat catchment in the headwater of the River Tees (N54°41′18″ W2°22′45″; Figure 2). The recent climate of the site has been summarized by Holden and Rose (2011): between 1991 and 2006 the mean annual temperature was 5.8°C; air frosts were recorded on 99 days in a year; the mean number of days with snow cover was 41, and the mean annual precipitation was 2,012 mm. The vegetation is dominated by *Eriophorum* sp. (cotton grass), *Calluna vulgaris*
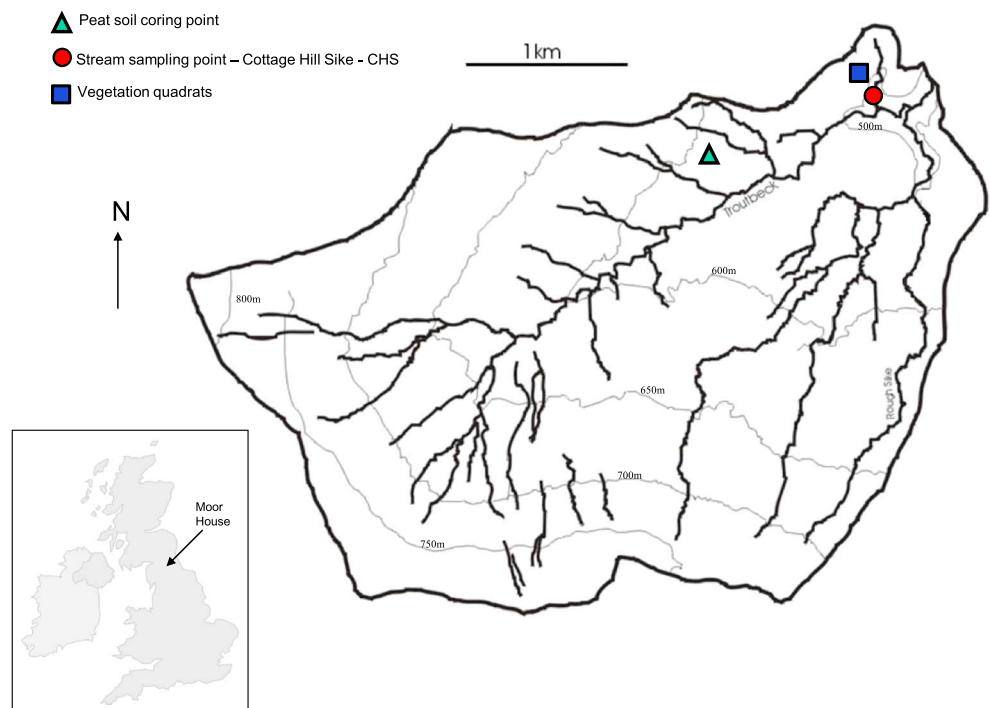
Figure 2. Location of the study site used in this study.

(heather), and *Sphagnum* sp. (moss). This study considered the boundary of the processes and budgets to be exported to the atmosphere and streams from the soils and biomass of the study catchment. For example, DOM or POM export from the soil profile was included but not the further processing of that organic matter within the receiving stream.

2.2. Sampling

Given the range of carbon pools and fluxes identified in Figure 1, the following sampling was carried out. The peat profile was sampled at two locations roughly 10 m apart in active, deep peat within the Cottage Hill Sike catchment; a peat core was taken to 1 m depth with a gouge auger at each location—this depth was chosen to cover the entire depth of the acrotelm and into the catotelm at this site (Worrall et al., 2012). The collected peat cores were sampled in 2-cm depth increments from 0 to 20-cm depth from the peat surface, then 5-cm depth increments from 20-cm depth to 50 cm and then one sample taken between 95 and 100-cm depth. Peat core samples were dried at 105°C overnight and checked for no further mass loss, and their bulk density measured prior to further processing.

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

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

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

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

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

2.3. The Enthalpy of Formation $\left(\Delta H_f^{OM}\right)$

The enthalpy of formation was calculated from the measured heat of combustion using Hess's law which states

$$\Delta H_f^{OM} = \Delta H_f^{CO2} + \Delta H_f^{H2O} - \Delta H_c^{OM} \tag{2}$$

where ΔH_y^x = the standard enthalpy of y for compound x with y as either f for formation or c for combustion and with x as OM for the organic matter and CO_2 for carbon dioxide and H_2O for water. Equation (2) follows given the combustion reaction:

$$C_\alpha H_\beta NO_\gamma + O_2 \rightarrow \alpha CO_2 + \frac{\beta}{2} H_2O + N_2 \tag{3}$$
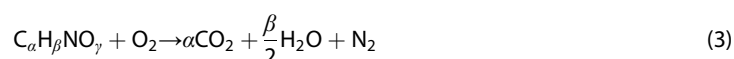
where: α, β, and γ are stoichiometric constants given the formula for organic matter (OM) has been normalized to the N content. The $\Delta H_f^{CO2} = -393.5$ kJ/mol and $\Delta H_f^{H2O} = -285.8$ kJ/mol, while ΔH_f of O_2 and $N_2 = 0$ kJ/mol (National Institute of Standards and Technology (NIST), 2017).

The ΔH_c^{OM} was measured on the collected samples and standards using bomb calorimetry and the stoichiometry in equation (3) was derived from the elemental analysis of the collected samples. Alternative approaches (Battley, 1999) were considered based upon Thornton's rule (Thornton, 1917), which is a simple correlation between ΔH_f^{OM} and ΔH_c^{OM} based upon correlations from simple organic compounds. However, Thornton's rule was only developed because elemental analysis of naturally occurring organic macromolecules, such as those of concern to this study, was not possible at the time.

2.3.1. Bomb Calorimetry

The gross heat value of the sampled organic matter was measured on a Parr 6200 bomb calorimeter. A subsample of known mass, typically 1 g, had its moisture content raised back to approximately 4% by weight before being combusted in the bomb calorimeter. The 4% moisture does not detract from the calorific value but does aid the combustion process in the bomb and helps prevent sputtering of the sample during the ignition process. The bomb calorimeter was calibrated and standardized on each run of samples using benzoic acid. For the samples of DOM for which less than 0.5 g of sample was available, the sample was doped with a known amount of the benzoic acid standard so that a complete combustion was achieved. For both soil and vegetation samples the calorific value was measured in at least triplicate and adjustment made for the measured ash content of the organic matter sample; in this manner the gross heat value as measured by the bomb calorimeter is equal to the heat of combustion of the substance (ΔH_c^{OM}).

2.3.2. Elemental Analysis

Triplicate samples of all the collected samples (aboveground and belowground vegetation, litter, peat soil, DOM, and POM), once dried to 105°C, were milled to a submillimeter powder using a Spex 6770 Freezer

Mill. For the samples of DOM and POM, cryomilling was not necessary. The ground samples were then subject to carbon, hydrogen, nitrogen (CHN), and separately to oxygen (O) analysis on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler. Computer software used was EAS Clarity (DataApex Ltd, Prague, Czech Republic). For both CHN setup and the separate O setup, calibration curves of $r^2 > 0.999$ were created using acetanilide as the standard. Samples of acetanilide were included within each run as unknown samples to act as internal quality control checks. Each sample was analyzed in triplicate, that is, 3 times for CHN and a further 3 times for O, and a mean calculated for C, H, N, and O. All samples were corrected for their measured ash content. The stoichiometry of the organic matter was expressed as molar fraction relative to N as this was always the least abundant element.

2.4. The Entropy of Formation $\left(\Delta S_f^{OM}\right)$

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

$$\Delta S_f^{OM} = S_{OM}^{\phi} - \sum_{i1}^{i} S_i^{\phi} \tag{4}$$

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

$$S_{OM}^{\phi} = 1.03 + 0.039\left(7 + \Delta S_f^{OM}\right) \tag{5}$$

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

$$S_{OM}^{\phi} = 1.1 C_{OM}^{\phi} \tag{6}$$

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

$$C_{OM}^{\phi} = \sum_{i1}^{i} C_i^{\phi} n_i \tag{7}$$

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

Equations (4) and (7) were solved iteratively with initial estimate of S_{OM}^{ϕ} found from equation (6) based on equation (7) and the initial value of ΔS_f^{OM} calculated from equation (4). Then estimates of S_{OM}^{ϕ} and ΔS_f^{OM} were then improved with the iterative application of equations (4) and (5). Equations (4) and (5) required typically three iterations before the value of ΔS_f^{OM} agreed within two decimal places.

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

2.5. The Gibbs Free Energy of Formation $\left(\Delta G_f^{OM}\right)$

Given the estimates of ΔH_f^{OM} and ΔS_f^{OM} above, then ΔG_f^{OM} can be readily calculated from equation (1). The ΔG_f^{OM} is then calculated for each of the sampled organic matter pools and the average absolute temperature of the study site. Any pressure dependency was assumed to be negligible in common with the approach of Beer and Blodau (2007) based upon Benjamin (2002).

It follows from Hess's law that

$$\Delta G_r^{OM} = \sum_{1}^{i} \Delta G_i^{OM} - \sum_{1}^{j} \Delta G_j^{OM} \tag{8}$$

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 ΔG_f^{OM} of the reactants.

It is then possible to consider the ΔG_r^{OM} for each transformation and pathway [equation (8)]. All the

Table 1
The Median Composition of the Carbon Pools Considered by the Study

		M_r	ΔH_f	ΔG_f	ΔS_f	ΔH_f	ΔG_f	ΔS_f	ΔH_f	ΔG_f	ΔS_f
			(kJ/mol)		(J/K/mol)	(kJ/g OM)		(J/K/g OM)	(kJ/g C)		(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
Aboveground 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
Belowground 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 and 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

Note. Median stoichiometry is expressed relative to N content except for cellulose which is expressed relative to C. M_r = the relative molecular mass of the given molecular formula.

transformations considered in Figure 1 are known to occur in peatlands and therefore $\Delta G_r^{OM} < 0$; this means that the transformations may need to include the release of other components to meet the requirement that $\Delta G_r^{OM} < 0$ for that transformation.

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

3. Results

The results of the analysis are detailed in Table 1. Equation (2) implies that there would be a negative correlation between ΔH_f^{OM} and the ΔH_c^{OM} (Figure 3), and ΔH_c^{OM} has been negatively correlated with the carbon oxidation state (C_{ox}) of naturally occurring organic matter (Masiello et al., 2008), that is, it would be expected that higher, less negative ΔH_f^{OM} would be estimated for more reduced organic matter.

$$\Delta H_f^{OM} = -18.3 - 0.64 \Delta H_c^{OM} \quad n = 79, r2 = 0.74, p < 0.05 \ (0.7)(0.04) \tag{9}$$

The values in the brackets refer to the standard error in the regression coefficient or constant term. The values of ΔH_f^{OM} for the combined aboveground biomass was consistent with it being a mixture of the functional groups of vegetation sampled (aboveground biomass was composed of 78% Calluna, 17% grasses and sedges, and 5% mosses) (Table 1, Figure 4a). The values for litter are within those for the vegetation, but the top of the soil profile does have some values of ΔH_f^{OM} that are lower (i.e., more negative) than those observed for either the vegetation or the litter. Similarly, the range of ΔH_f^{OM} for the DOM and POM extended to lower, more negative values than observed for any other of the sampled organic matter (ΔH_f^{OM} for DOM between −7.3 and −17.5 kJ/g organic matter, for POM between −5.6 and −19.1 kJ/g of organic matter, Figure 4a). The DOM from this study catchment has been shown to have a statistically significantly higher oxidation state than the other types of organic matter also included in this study (Worrall et al., 2016b) unlike the
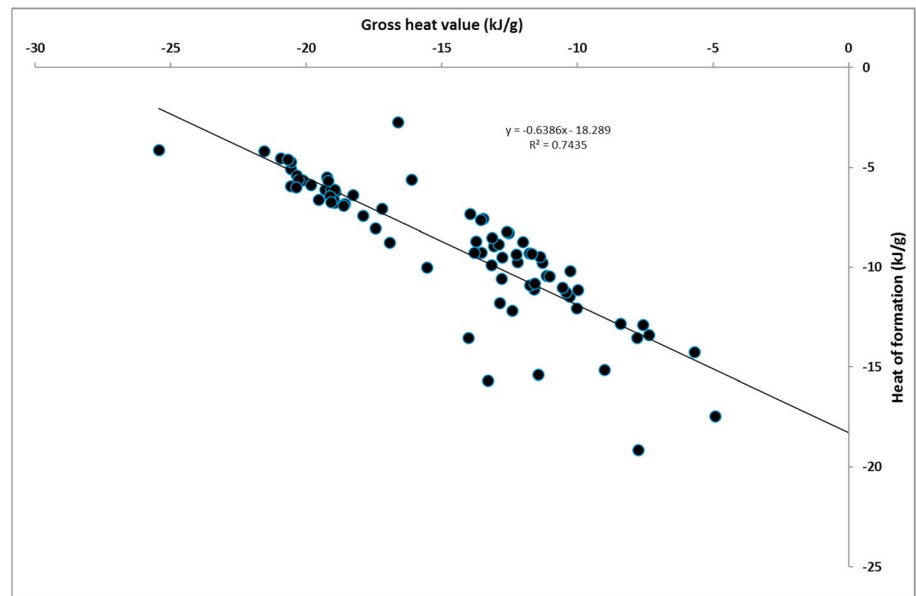
Figure 3. Comparison of ΔH_f^{OM} and the ΔH_c^{OM} for the all the samples measured in the study.
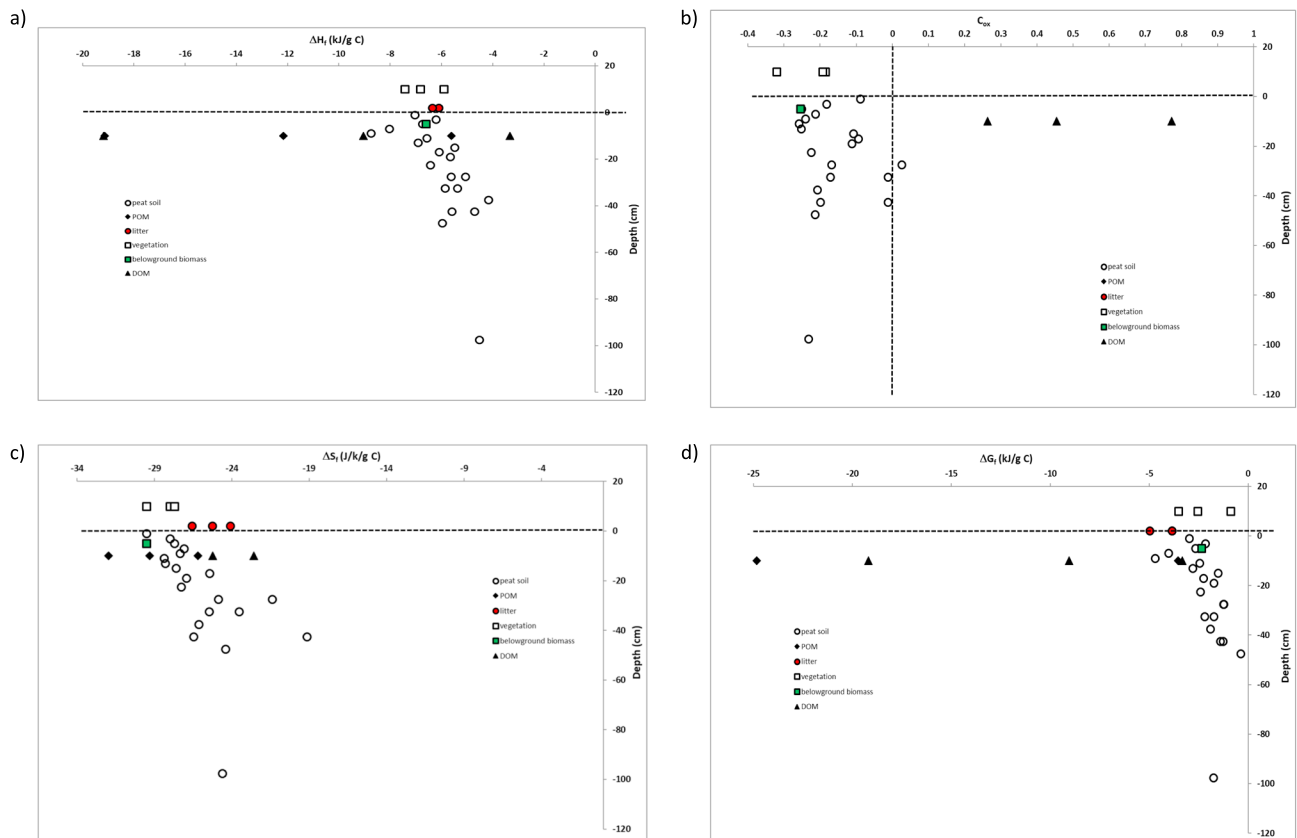

Figure 4. The ΔH_f^{OM} (a); Cox (b); ΔS_f^{OM} (c); and ΔG_f^{OM} (d) of the peat soil, DOM, POM, vegetation, and litter samples considered in this study. The samples of DOM and POM are given a nominal depth of 10 cm in the peat profile. The values shown for the peat soil are the average for each sampled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

study of Boye et al. (2017), which proposed that the DOM was more reduced; however, this study considered DOM samples from first-order peat-hosted streams and not the soil pore water itself. In the same study POM was shown to have a composition and oxidation state compatible with it being an admixture of litter and peat soil but did not have a distinct oxidation state from either. Although the lower, more negative values of ΔH_f^{OM} for POM (Figure 4a) are consistent with erosion from the peat profile (e.g., via bank erosion of the catchment streams), the median and upper values are not, and it is possible that the POM samples for this study included material very similar to the DOM. The ΔH_f^{OM} of the peat organic matter increases with depth through the soil profile (Figure 4a). Vodyanitskii (2000) gave values for extracted humic and fulvic acids from Russian soils of between 3.15 and 8.72 kJ/g. Battley (1998, 1999) used Thornton's rule to assess the ΔH_f^{OM} of the dry matter of a whole cell of *Saccharomyces cerevisiae* as 11.1 kJ/mol. Schaul et al. (1997) based on measured properties of amino acids gave values of measured values of ΔH_f^{OM} of between 4.3 kJ/mol for microflora to 19.35 kJ/mol for humin—note that it is not always possible to compare reported values as molecular masses are not given.

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

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

The values of ΔG_f^{OM} do show some differences from the patterns observed for ΔH_f^{OM} and ΔS_f^{OM} (Figure 4c). Tardy et al. (1997) estimate ΔG_f^{OM} by analogy with estimation methods developed for clay minerals and give values of ΔG_f^{OM} as −3.24 kJ/mol (microflora); −7.42 kJ/mol (humic acid); −12.14 kJ/mol (fulvic acid); −14.31 kJ/mol (plant biomass); and −27.37 kJ/mol (humin). LaRowe and Van Cappellen (2011) provide values for the half reactions of oxidation, and ΔG values were expressed per electron transfer, hence their values are not directly comparable with those of this study. The litter samples have values of ΔG_f^{OM} lower, that is, more negative, than that of the vegetation samples which was not the case for either 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 samples suggesting a very similar composition and supports the obvious idea that peat soil forms in the continuum from fresh litter. The peat soils samples show an increase ΔG_f^{OM} with depth down the profile, that is, values of ΔG_f^{OM} become less negative. The values ΔG_f^{OM} of DOM and POM spread across a considerable range from very similar to the peat and litter samples to considerably lower, that is, more negative, values of ΔG_f^{OM}. The peat soil samples when plotted against depth in the profile showed a significant increase (probability of being different from zero of 95%) in the ΔG_f^{OM} with depth:

$$\Delta G_f^{OM} = -4.22z^{-0.279} \quad n = 20, r2 = 0.32 \ (1.42)(0.096) \tag{10}$$

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

Coupled with the proposed diagram of flows within this ecosystem (Figure 1) and equation (8), it is possible to argue that we would expect the spontaneous production of litter from vegetation, and the spontaneous production of DOM from all other organic matter. However, for other transitions, the change in ΔG_f^{OM} implies that the transition would have to be accompanied by emission of low ΔG_f^{OM} compounds (i.e., CO_2, CH_4, or DOM which have more negative values of ΔG_f^{OM} than the solid organic matter types considered).

Differentiating equation (10) gives the profile of the change in ΔG_f^{OM} or the ΔG_r^{OM} that would have to be balanced by the production of CO_2, DOM, or CH_4. Given the fit of equation (10), the differentiation was performed numerically within 95% confidence interval defined by the fit of equation (17) and the best fit equation was
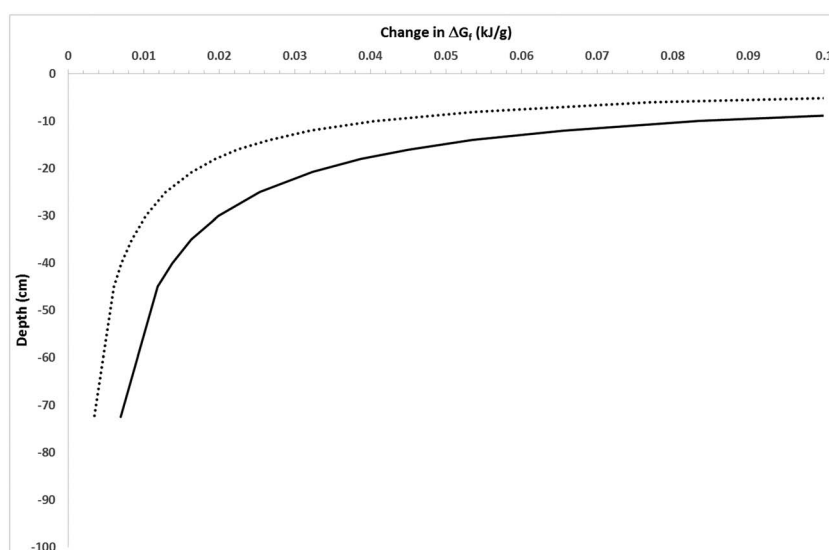
Figure 5. The 95% confidence interval on the change in ΔG_f^{OM} of the peat soil with depth. Depth is expressed in centimeter below the soil surface as negative.

$$\frac{d\Delta G_f^{om}}{dz} = 1.18z^{-1.279} \quad n = 16, r2 = 0.98, p < 0.05 \; (0.75)(0.032) \tag{11}$$

The values in brackets are the standard error in the coefficient and exponent. Although the form of the best fit equation [equation (11), Figure 5] cannot by mathematical definition equal zero. A one-way analysis of variance (ANOVA) of the values ΔG_r^{OM} (equation (8) of the peat soil samples judged across each of the measured depth ranges, using the depth range as the one factor, showed that there was a significant change in the change in ΔG_r^{OM}. Post hoc testing, using the Tukey test, ΔG_r^{OM} was not significantly different from zero after the sample in the depth range 40 to 45 cm depth in the soil profile. The fact that ΔG_r^{OM} is close to zero implies very little (if any) reaction of peat at depth.

The variation in the ΔG_f^{DOM} could imply that there is a variation in the maturity of the DOM and as such DOM might itself react to release of CO_2. Taking the highest value of ΔG_f^{DOM} (i.e., least negative value -3.3 KJ/gC; Figure 4c) as the most reacted or mature DOM and that other measured DOM composition would react to that composition and that the reaction is balanced by the loss of CO_2. The assumption that the DOM with the highest value of ΔG_f^{DOM} is the most reacted or mature matches the pattern assumed for the peat soils that the most reacted peat soil has the highest values of ΔG_f^{OM}. Given this assumption then it is possible to estimate the amount of CO_2 released from processing of DOM—based upon equation (3). The proportion of CO_2 that would have to be released per 1 g of C as DOM for each of the measured DOM compositions to transform it to the DOM composition with the highest ΔG_f^{DOM} varied from 0.0 to 0.57 with an arithmetic mean of 0.30. The value of 0.0 represents the sample assumed to be the most mature and the arithmetic means represents that 30% of DOM is turned over to CO_2 prior to loss to the stream network. Moody and Worrall (2016) measured an average DOC loss rate in the light of 64% over a 70-hr period but found an average of 6% DOC loss over 70 hr when the sample was kept in the dark.

4. Discussion

Given that this study could calculate the ΔG_f^{OM} for each of the substances and reservoir as illustrated in Figure 1, it was then possible to at least consider the ΔG_r^{OM} for each transformation and pathway and thus we have shown which can occur spontaneously and which transformations require the production of low (i.e., more negative) ΔG_f^{OM} products such as CH_4, CO_2, or indeed, given the results of this study, DOM. For the release of CO_2, in the sense of LaRowe and Van Cappellen (2011), oxygen is acting as the terminal electron acceptor and the other half reaction. For the formations of plant components (lignin, cellulose, and protein)

and the biomass (aboveground and belowground biomass as well as the plant functional types), the reactant was taken as glucose ($\Delta G_f^{glucose} = -910$ kJ/mol; NIST, 2017) produced directly from photosynthesis. The transformations of glucose to plant components, the plant components to litter, and litter to the surface peat are all assumed to have occurred in oxic conditions and will react to release CO_2. The $\Delta G_f^{CO2} = -394$ kJ/mol (NIST, 2017) and the amount of CO_2 can be used to balance out the transformation, for example, the transformation from glucose:

$$\Delta C_6 H_{12} O_6 \rightarrow \varepsilon C_w H_x N_y O_z + \epsilon CO_2 \tag{12}$$

In equation (12), although δ, ε, and $\in$ are stoichiometric constants; $\in$ represents the amount of a carbon that has to be lost (e.g., emitted to the atmosphere as CO_2), while ε represents the amount of carbon passed through into the peatland. If the values in equation (12) are expressed per mole of C and then per unit mass of carbon, the stoichiometry of equation (12) is simplified and each of the reactions can be considered as the fate of 1 g of C of reactant organic matter (i.e., $\delta = 1$). Then only the following equations need to be satisfied:

$$1 = \varepsilon + \epsilon \tag{13}$$

$$\Delta G_r^{OM} = \sum_1^i \Delta G_i^{OM} - \sum_1^j \Delta G_j^{OM} < 0 \tag{14}$$

Equations (13) and (14) can be solved iteratively for the transformation. Even though a reaction will occur in favor of products when $\Delta G_r^{OM} < 0$ kJ/mol, or to completion with $\Delta G_r^{OM} < -60$ kJ/mol, there is a thermodynamic threshold after which it has been observed that biological systems cannot effectively obtain sufficient free energy for the reaction to occur, that is, $\Delta G_r^{OM} < 0$ kJ/mol is not the effective limit of spontaneous reaction in biological systems. Schink (1997) propose a theoretical value of the thermodynamic threshold for biological systems as $\Delta G_r^{OM} < -20$ kJ/mol, but other studies have suggested values for this thermodynamic threshold as high as -15 kJ/mol. This thermodynamic threshold for biological systems has been equated to the energy required to produce one quarter mole of ATP.

Furthermore, it is not possible to transfer 100% of the energy content of any substrate even after the threshold described above has been accounted for, and it matters by which biochemical pathway the oxidation and energy transfer occurs. Lafitte and Loomis (1988) showed that the efficiency in plant processes varied between 0.84 and 0.89. That range was used here and as such ε and ϵ were recalculated using an effective value of ΔG_f for CO_2:

$$_{OM}^{eff}\Delta G_f^{co2} = \varphi \Delta G_f^{co2} \tag{15}$$

Where: $_{OM}^{eff}\Delta G_f^{co2} = $ the effective value of ΔG_f for CO_2 after allowing for the efficiency of energy transfer (Kj/mol); $\varphi = $ the energy transfer efficiency, taken as between 0.84 and 0.89. The energy transfer efficiency can be considered as equivalent to a thermodynamic efficiency factor as used by Hoehler (2004).

It was assumed that no other elements (e.g., N) in equation (12) were limiting and so equation (12) was balanced only with respect to C. Further, it was assumed that the contribution of the ΔG_f^{OM} of other components required to balance equation (12), for example, nitrate, was minimal because their stoichiometric fraction was small. Equally, we admit that naturally occurring organic matter in a peatland will contain elements not included in equation (12) such as S and P, but we would argue that they are present in quantities even less than that of N. Worrall et al. (2016a) showed that the lowest value of C:P in this ecosystem was 769 for the *C. vulgaris* biomass. It is possible to solve equations (13) and (14) then 1 g of C fixed as glucose by photosynthesis would result in 0.68 g C as biomass and 0.32 g C as CO_2.

For the transformation into and through the peat profile it is less likely that oxygen can be the terminal electron acceptor and the transformation to CO_2 is only one possible option and this study has shown that other low (high negative) ΔG_f^{OM} species could act to balance increases in ΔG_f^{OM} in the soil profile. The production of dissolved organic matter (DOM) or methane (CH_4) would be possible act as other electron acceptors but other terminal electron acceptors may be available. Perhaps the most important would be the role of sulfate at depth in the peat. Several studies have shown that the utilization of sulfate and methanogenesis cannot account for the rate of anaerobic CO_2 production in ombrotrophic peatlands (e.g., Vile et al., 2003); this is

Table 2
Twenty-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)
Sulfate (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 (μS/cm)	39.1	31.4
pH	4.3	4.6

even the case with the recycling of sulfate (e.g., Weider et al., 1990). Long-term monitoring of shallow (10-cm depth) and deep (50 cm) soil water by the Environmental Change Network monitoring at the site can be summarized (Table 2) to show that nitrate is absent from the soil pore water. Furthermore, the long-term monitoring of the soil water at the site also shows that there was little sulfate present and the change in sulfate concentration is small in comparison to concentration and change in DOC. Lovley et al. (1996) have shown that DOM can act as a terminal electron acceptor and divert energy from methanogenesis. Furthermore, Minderlein and Blodau (2010) suggested that there was a toxic effect of intensely humified DOM on both methanogenesis and sulfate-reducing bacteria but not on fermenting microbes. Bauer et al. (2007) showed that DOM could act as redox buffer as its polyfunctionality means that it has groups that act across redox potentials from -0.9 to 1.0 V, and indeed that is shown to be possible in this study by consideration of the ΔG_f^{OM} that DOM could be a TEA. Equally, micro-environments can always exist which could make redox environments distinct from the bulk environment of the peat soil (Wachinger et al., 2000). Keiluweit et al. (2016) have shown that the free energy available from terminal electron acceptors other than O_2 follows a succession not only of decreasing available ΔG but also the available ΔG decreases with the decreasing oxidation state (C_{ox}) of the organic matter substrate with which the particular electron acceptor is reacting. However, for the study site Worrall et al. (2016b) have shown that there is no significant change in C_{ox} with depth in to the peat profile and indeed for eight peatlands across the United Kingdon, not including this study site, Clay and Worrall (2015) found a mixture of significant increases, significant decreases, and lack of significant change in C_{ox} down peat profiles.

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

This present study would suggest that peat humic matter accumulates because the available Gibbs free energy (ΔG_r^{OM}) from soil is no longer sufficient for reaction to occur. Beer and Blodau (2007) suggested that organic matter turnover in deep peat profiles is limited because the pore water becomes a closed system and so reaches an equilibrium. The argument of Beer and Blodau (2007) is important for this study for two reasons. First, this study would suggest that indeed reactions at depth in peat are thermodynamically limited, but in the case of this study it is the solid component and not the dissolved components that cannot react. Second, this study has not considered the dissolved component, and therefore ongoing reaction at depth could be reaction of the dissolved and not the solid component. Production of CO_2 and CH_4 at depth could be due to the supply of labile DOM from surface peat layers. Unfortunately, this study did not examine the composition of DOM from the pore water but rather sampled fresh DOM from a first-order stream assuming it was a reasonable approximation to the pore water DOM—based upon studies of the source of mixing and water in this catchment (Worrall et al., 2006), but the potential for turnover to CO_2 within the profile was estimated by comparison between the most and least evolved DOM (as assessed by their comparative ΔG_f^{OM}).

The indication here that reaction has ceased at depth is only based upon the compositional change within the substrate, but this does not mean that there is not a continuing reaction in the pore water. Chaser et al. (2000) showed that the radiocarbon age of DOC at depth in peat soil pore water in a peat profile was younger than the surrounding peat soil organic matter, for example, at 80 cm depth the age of the peat soil organic matter was 800 years B.P., while that of the CH_4 was 135 years B.P., and the DOC age was 123 years B.P. Similarly, Charman et al. (1994) dated CO_2 and CH_4 samples collected from depth show that both gases were between 500 and 2000 years younger than the adjacent peat.

It is difficult to know whether the change or lack of change of ΔG_f^{OM} is the cause or the effect of what is constraining the transfer of organic matter into and through a peat profile—as half-reaction it would not happen spontaneously without the other half reaction. This study has suggested why organic matter accumulates in peatlands. The profile as measured shows that the change in ΔG_f^{OM} declines or becomes zero, but this cannot provide information as to why this would occur. Freeman et al. (2001) have shown that hydrolase enzymes in peat bogs are inhibited by the presence of phenolic compounds, which can build up in peat because the activity of phenol oxidase is severely restricted in the absence of oxygen. Therefore, the organic matter can accumulate because of restriction of a key enzyme in the degradation process. If the water table in peat bogs falls, the phenyl oxidase activity increases and oxygen ingress increases, destroying the phenolic compounds that repress the hydrolase activity. A loss of phenolic compounds means that decomposition can continue even after the water table rises again. This process has been referred to as an "enzyme latch" mechanism. This enzyme latch production does not immediately cease once the water tables have been restored, and the additional turnover of organic matter such as DOC production can continue for long periods. The changes in DOC concentration and flux in the runoff from peatlands has been taken as evidence of the enzyme latch process. The deepest water table depth recorded for this site was 42 cm below the surface, that is, the maximum depth of the oxygen ingress in this catchment closely coincides with the depth at which decomposition ceases as predicted by this study. The thermodynamic approach of Beer and Blodau (2007) would argue that organic matter accumulates because the pore water components cease to react as the pore water system becomes closed, and therefore, there ceases to be a thermodynamic driver for the solid organic matter to react further and to release components into solution. Therefore, rather like the "enzymic-latch" mechanism the thermodynamic explanation does not prohibit further reaction of the organic matter if conditions change, for example, if a closed pore system became open again.

The study here has shown that processing of organic matter would have a 5% chance of having ceased by 40 to 45 cm depth, and this can be considered the depth below which further reaction has been thermodynamically inhibited (LaRowe & Van Cappellen, 2011). Note that for pore water reactions Beer and Blodau (2007) suggested that thermodynamic inhibition did not occur until approximately 2-m depth; although at a very different site from the one in this study, it therefore illustrates that there may be a zone where the solid organic matter substrate is no longer being processed but that pore water constituents are. However, in such a zone the pore water components would have to originate in overlying peat layers. Above a zone of thermodynamic inhibition, the available energy release diminishes rapidly and the available energy has been related to the kinetics of turnover processes (e.g., Dale et al., 2006; Jin & Bethke, 2002), where the rate of the redox reaction:

$$r = \mu_{max} B F_K F_T \tag{16}$$

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

$$F_T = 1 - \exp\left(\frac{\Delta G_r + m\Delta G_r^{ATP}}{\chi RT}\right) \tag{17}$$

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

the reactive products is in the upper layers of the peat and the reaction is limited by their diffusion down the peat profile. The approach of Jin and Bethke (2005, equations (15) and (17)) is the same approach used by Keiluweit et al. (2016) to explain the preservation of organic matter in soils.

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

5. Conclusions

This study has estimated the changes in ΔG_f^{OM} across a peatland and considered the changes which would have to be balanced by production of CO_2, DOM, or CH_4. Estimation of ΔG_f^{OM} and the ΔG_r^{OM} profile provides an alternative and objective method of assessing the degree of decomposition in peat. The study has found the following:

1. All the transformations considered, except for the production of litter from biomass, would have to occur through the loss or emissions of the low (i.e., more negative) ΔG_f^{OM} product such as CO_2, DOM, or CH_4.
2. Most of the CO_2 lost in the transfer of organic matter was lost in the production of biomass rather than the decay of litter or soil organic matter.
3. The change in ΔG_f^{OM} of the peat soil would suggest that further reaction becomes thermodynamically inhibited after depths of approximately 40 cm. The study shows that organic matter accumulation in peat profiles could be explained by the lack of change in ΔG_f^{OM} and that this could be predicted simply from the elemental composition.

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