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Key Points:

- Processing of organic matter through a peatland preferentially removes carbohydrates and retains lignin
- Dissolved organic matter (DOM) from peatlands is derived from processing of lignin and not carbohydrates
- The atmosphere above the peatland experiences an oxidative ratio (OR) less than 1 and not 1.1 as assumed globally

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The flux of organic matter through a peatland ecosystem: The role of cellulose, lignin, and their control of the ecosystem oxidation state

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Abstract This study used thermogravimetric analysis (TGA) to study the transit of organic C through a peatland ecosystem. The biomass, litter, peat soil profile, particulate organic matter (POM), and dissolved organic matter (DOM) fluxes were sampled from the Moor House National Nature Reserve, a peat-covered catchment in northern England where both the dry matter and carbon budget for the catchment were known. The study showed that although TGA traces showed distinct differences between organic matter reservoirs and fluxes, the traces could not readily be associated with particular functionalities or elemental properties. The TGA trace shows that polysaccharides are preferentially removed by humification and degradation with residual peat being dominated by lignin compositions. The DOM is derived from the degradation of lignin while the POM is derived from erosion of the peat profile. The carbon lost as gases (CO_2 and CH_4) was estimated to be composed of 92 to 95% polysaccharide carbon. The composition of the organic matter lost from the peat ecosystem means that the oxidative ratio (OR) of the ecosystem experienced by the atmosphere was between 0.96 and 0.99: currently, the Intergovernmental Panel on Climate Change uses an OR value of 1.1 for all ecosystems.

1. Introduction

Within the terrestrial biosphere, the northern peatlands are the most important terrestrial carbon (C) store. Despite only covering ~3% of Earth's total land area [*Rydin and Jeglum*, 2013], peatlands store large quantities of carbon. Though estimates vary depending on methods used (see reviews of *Yu* [2012] and *Loisel et al.* [2017] for further discussion), it is estimated that 500 ± 100 GtC is stored in northern peatlands [*Gorham*, 1991; *Yu et al.*, 2014; *Loisel et al.*, 2014], which is approximately equivalent to the total terrestrial vegetation [*(IPCC)*, 2013], or the cumulative anthropogenic CO_2 emissions from fossil fuels, industry, and land use change activities for the period of 1870–2015 [*Le Quere et al.*, 2016].

Many areas of northern peatlands have been subjected to a range of historical and current environmental and anthropogenic pressures, such as climate change, drainage, fire, peat extraction, and land use change. These drivers of change may lead to changes in carbon cycling processes potentially leading to positive feedback mechanisms in turn leading to enhances in atmospheric radiative forcing [e.g., *Petrescu et al.*, 2015].

The very existence of peatlands depends upon the fate of organic matter, and the estimation of C budgets of peatlands 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]. However, this approach must assume accumulation and cannot account for short periods of net loss, nor can it estimate the species of carbon. It is vital to know the species of carbon that are being lost, because carbon from a peatland can be lost to the atmosphere as carbon dioxide (CO_2) or as the yet more powerful greenhouse gas, methane (CH_4) [*Houghton et al.*, 1995]. Furthermore, carbon from peatlands can be released into water as dissolved or particulate forms: dissolved organic carbon (DOC) and particulate organic carbon (POC). As an alternative approach, it is possible to consider the carbon budget as the sum of measurements of the ongoing fluxes of all carbon species in and out of the peat ecosystem, and complete contemporary carbon budgets of peatlands are now common [e.g., *Worrall et al.*, 2003; *Billett et al.*, 2004; *Roulet et al.*, 2007; *Nilsson et al.*, 2008]. If carbon is accumulating in peat soils, then the other elements in organic matter must also be accumulating. Contemporary elemental budgets have been extended to include nitrogen (N) [e.g., *Hemond*; 1983; *Worrall et al.*, 2012]. Similarly, *Worrall et al.* [2016a] considered the transition of organic oxygen (O) through a peat soil ecosystem and showed a peatland to be accumulating oxygen in deep peat soil at a rate of between 16 and 73 t O km^{-2} yr^{-1}. Long-term accumulation of phosphorus (P) has been measured as 0.69 and 2.04 t P/km^2/yr for Chinese peatlands [*Wang et al.*, 2012], between 0.2 and 0.5 t P/km^2/yr for a Michigan fen [*Richardson and Marshall*, 1986], and an average of 1.6 t P/km^2/yr for Canadian peatlands since the last glaciation [*Wang et al.*, 2015], and *Schillereff et al.* [2016] have estimated the P accumulation rate for five UK peat bogs and found an average of 18 ± 4 kg P/km^2/yr. *Worrall et al.* [2016b] found the contemporary P budget of a northern English peat bog to be +29.4 kg P/km^2/yr.

The approaches based on contemporary fluxes do consider the species of the carbon, nitrogen, or oxygen entering or leaving peat ecosystems, and although this can consider the individual gaseous forms (e.g., N_2O, CO_2, or CH_4), 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 consider different types of peatland with different dominant vegetation types, and as such, different substrates. Alternatively, physical and land management controls on carbon biogeochemistry have been considered, for example, the impact on the carbon budget due to drainage [e.g., *Rowson et al.*, 2010]. The impact of land use management and land use change often reflect an influence of water table on the decomposition processes in the peat profile [e.g., *Clay et al.*, 2010]. However, even these detailed studies deal in lumped compositions. For example, primary productivity is viewed as sequestering CO_2 from the atmosphere but, of course, it sequesters it to glucose which is then transformed through metabolic cycles and combined with nutrients to build the components of plants—lignin, carbohydrates (cellulose and hemicellulose), proteins, and lipids [*McDermitt and Loomis*, 1981]. It is this organic matter that is transformed back to CO_2 through root respiration, falls as litter, or is released as plant exudates into the soil pores. It is the litter or exudates that then transform to soil organic matter, and this transformation may result in CO_2, CH_4, DOC, or POC. Contemporary carbon budgets have advanced our understanding of processes and drivers and quantified gas, particulate, and dissolved fluxes. The purpose of this paper is to consider the molecular changes occurring as organic matter moves through the peatland ecosystem.

The composition of organic macromolecules that would be present in peatland ecosystems (e.g., lignin) has been considered by a number of approaches: colorimetric methods from UV/vis spectroscopy [e.g., *Blackford and Chambers*, 1993], coal petrology techniques such as rock-eval [e.g., *Carrie et al.*, 2012], elemental ratios (e.g., C/N [*Kuhry and Vitt*, 1996]), stable isotopes [e.g., *Jones et al.*, 2010], Fourier transform infrared spectroscopy [e.g., *Artz et al.*, 2008], and pyrolysis gas chromatography-mass spectrometry [e.g., *Buurman et al.*, 2006]. These approaches have commonly be focused upon characterization of peat profiles for the purpose of understanding humification [e.g., *Zaccone et al.*, 2008] or palaeohistoric reconstructions [e.g., *McClymont et al.*, 2011]. None of the above techniques have been used to understand the carbon budget of a peatland.

Thermogravimetric analysis (TGA) has a number of advantages over other techniques for analyzing organic matter composition. First, unlike, for example, biomarkers (e.g., sphagnum acid [*Rudolph and Samlund*, 1985]), the TGA trace is a measure of the whole sample composition and is not selective; nor does it require extraction or treatment prior to analysis. Second, it is now possible to run the analysis on samples of up to 400 mg which partly avoids issues of heterogeneity of organic matter. Thermogravimetric analysis has been used to characterize soil organic matter (SOM) [e.g., *Lopez-Capel et al.*, 2005; *Plante et al.*, 2009], and it can be viewed as the more generic version of rock-eval [*Gregorich et al.*, 2015]. These studies have generally considered soil organic matter and have focused on the issue of whether thermal stability, as measured by thermogravimetric techniques, can be related to biological stability of SOM in the environment [e.g., *Plante et al.*, 2011], but the technique has not been used to analyze flows of organic matter through an environment. Therefore, the purpose of this study was to use TGA to trace organic matter compositional changes from a site where the carbon budget is already well constrained.

2. Approach and Methodology

The approach taken here was to analyze the composition of the organic matter in a series of carbon pools within the context of a known carbon budget (Figure 1). The composition was analyzed using thermogravimetry, elemental analysis (for C, H, N, and O), and ^{13}C solid state nuclear magnetic resonance (NMR). The

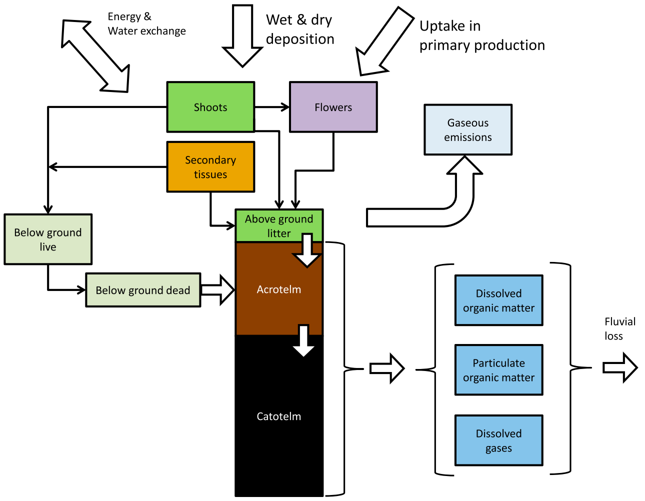

Figure 1. Schematic diagram of organic matter pools and fluxes considered by this study.

combination of methods made it possible to consider what the TGA traces represented in terms of elemental and biochemical compositions of the organic matter.

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 (ECN). 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 ECN collects various chemical and hydrological data from the Trout Beck catchment relevant to this study [*Sykes and Lane*, 1996]. The Trout Beck catchment lies largely above 500 m asl (above sea level); the highest point is the summit of Great Dun Fell at 848 m asl. The underlying geology is a succession of Carboniferous limestones, sands, and shales with intrusions of the doleritic Whin Sill [*Johnson and Dunham*, 1963]. This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat during the Holocene. Blanket peat covers 90% of Trout Beck catchment [*Evans et al.*, 1999]. 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, and the mean number of days with snow cover was 41 while for the same period the mean annual precipitation was 2012 mm. The vegetation is dominated by *Eriophorum* sp. (cotton grass), *Calluna vulgaris* (heather), and *Sphagnum* sp. (moss).

2.2. Sampling

Given the range of carbon pools and fluxes identified in Figure 1, the following sampling was carried out. First, the peat profile was sampled. A location in active, deep peat within the Cottage Hill Sike catchment was selected and a core taken to 1 m depth with a gouge auger. The depth was selected to ensure coverage of both the acrotelm and catotelm [*Worrall et al.*, 2012]. The peat core was sampled in 2 cm depth increments

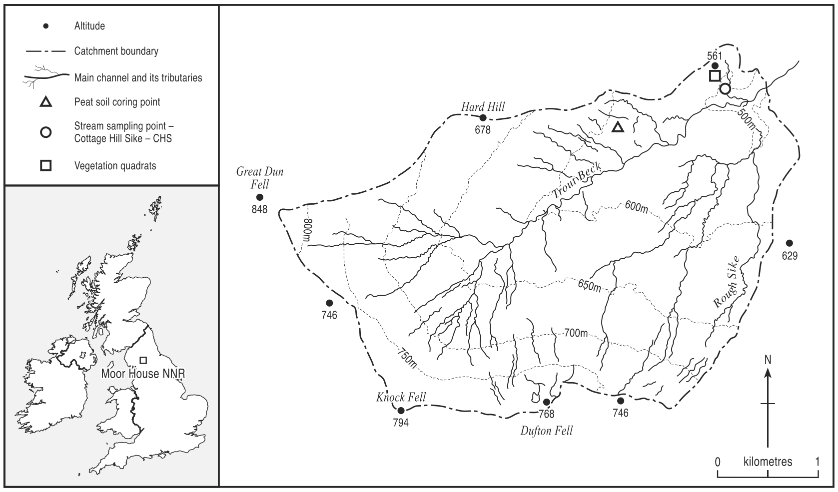

Figure 2. Location of the study site used in this study.

from 0 to 20 cm depth from the peat surface, then 5 cm depth increments from 20 cm depth to 50 cm, and finally 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 collected from six quadrats. The six quadrats (0.25 m^2, 0.5 × 0.5 m) were located in the Cottage Hill Sike catchment and chosen to cover the three main plant functional groups—shrubs (dominantly *Calluna 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). 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. 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. This estimate was then used to confirm the dry matter budget reported by *Forrest* [1971]. *Forrest* [1971] found total aboveground biomass to be 1996 g/m^2 (as dry matter) composing of 78% *Calluna vulgaris*, 17% *Eriophorum* spp., and 5% *Sphagnum* spp. The belowground biomass was 133 g/m^2, and the litter was 590 g/m^2. 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 weighted average of its components.

Dissolved organic matter (DOM) samples were taken from Cottage Hill Sike. Large-volume water samples (at least 25 L) were collected monthly from October 2011 to December 2014, except for months where winter conditions precluded taking flowing water samples (35 samples taken in total). On return of these samples to the laboratory, the samples were allowed to settle, and the next day the water tapped off from above the sediment layer and evaporated to dryness (between 60 and 80°C) to collect the total dissolved solids. By using settling as means of separation, no filtration cutoff was being applied; rather this study was defining DOM as being that component which was either colloidal or truly dissolved.

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

Finally, 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 present the three largest components of plants found in a peatland system [*McDermitt and Loomis*, 1981].

The considerable advantage of considering peatland ecosystems is that soil, total dissolved solids, and suspended sediment would be expected to be predominantly organic matter, but nevertheless 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 was recorded. All subsequent analyses of peat, DOM, and POM were corrected so that all elemental analyses are quoted on an ash-free basis.

2.3. 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 then milled to a submillimeter powder using a Spex 6770 Freezer Mill. For the samples of DOM and POM cyromilling 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, i.e., three times on the CHN setup and a further three times on O setup, and a mean was calculated for C, H, N, and O. All samples were corrected for their measured ash content.

Table 1. The Ranges of Chemical Shifts for ^{13}C NMR, From *Chadwick et al.* [2004]

Chemical Shift (ppm)	Types of Carbon
0–45	C-alkyl
45–65	N-alkyl/methoxyl-C
65–95	O-alkyl
95–110	O_2-alkyl/acetal C
110–145	aromatic/unsaturated-C
145–160	phenolic-C
160–190	amide/carboxyl-C
190–220	aldehyde/ketone-C

The elemental analysis results were converted to molar percentage and considered as elemental ratios but also as measures of oxidation state (C_{ox} and OR [*Masiello et al.*, 2008]) and the degree of unsaturation (Ω [*McMurray*, 2004]).

$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} \tag{1}$$

where [X] indicates molar concentration of C, H, N, or O. The OR value is then calculated as

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]} \tag{2}$$

and the degree of unsaturation (Ω) is defined as

$$\Omega = [C] - \frac{[H]}{2} + \frac{[N]}{2} + 1 \tag{3}$$

The value of C_{ox} can be related to the nominal oxidation of the carbon as developed by *LaRowe and Van Cappellan* [2011]. As noted by *Gallagher et al.* [2014], OR is not only a property of organic matter (e.g., peat soil) but can also be a property of an ecosystem and its biosphere-atmosphere exchanges. The OR is defined as the ratio of moles of oxygen (O_2) produced per mole carbon dioxide (CO_2) sequestered by the terrestrial biosphere, and the OR has been used to refine estimates of terrestrial and oceanic carbon sinks of fossil fuel emissions [*Keeling et al.*, 1996; *Prentice et al.*, 2001]. The OR and C_{ox} are linearly related [*Masiello et al.*, 2008].

2.4. ^{13}C Solid-State Nuclear Magnetic Resonance (^{13}C-NMR)

The ^{13}C solid-state NMR data were obtained at the EPSRC UK National Solid-state NMR Service at Durham University. Solid-state ^{13}C spectra were recorded at 100.56 MHz using a Varian VNMRS spectrometer and a 4 mm magic-angle spinning probe. They were obtained using cross polarization with a 0.5 s recycle delay, 1 ms contact time, at ambient probe temperature (~25°C) and at a sample spin-rate of 14 kHz. Between 50,000 and 100,000 repetitions were accumulated. The pulse sequence is a Durham-modified version of a generic provided by the manufacturer. The pulse sequence was a direct excitation one with "DEPTH" background suppression and high-power spinal-64 proton decoupling. Radiofrequency fields equivalent to 75 kHz were used on both channels. The free induction decay was zero filled to 16k data points and transformed with 200 Hz of exponential line broadening. The phased spectrum was baseline corrected using the Bruker "abs" correction with a polynomial of degree 5. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Between 50 and 60 mg of each sample was used. The chemical shift ranges used were adapted from *Chadwick et al.* [2004] and are shown in Table 1. The maximum peak height in each range was divided by the molar carbon concentration of the sample (from the elemental analysis) to get a relative peak height for each type of carbon observed. All collected samples were analyzed by NMR, and no subset was used.

2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric traces were recorded on an SGA I TGH 1200. This analyzer has the advantage that it is a high mass analyzer, and between 300 and 400 mg of organic matter and standard samples could be analyzed at a time. The samples were run from ambient to 1000°C at a ramp rate of 10 K min^{-1} within a stream of N_2.

The thermogravimetric trace were adjusted to be on a common temperature scale and trimmed to the range 150 to 700°C so that any influence from inorganic carbon or absorbed water was excluded. Traces were then normalized to the mass loss between 150 and 700°C so that all traces were then on the same scale, i.e., percentage of organic mass loss per K, given the assumption that it is only organic matter lost between 150 and 700°C. There have been many indices given for TGA traces of soil organic matter with most focused on defining exothermic peaks, but as *Plante et al.* [2009] have shown, these definitions vary considerably between studies. More importantly with respect to this study, previous studies have focused on a single type of natural organic matter, i.e., soil organic matter, but this study considers across the range of natural organic matter in a single environment. Alternatively, this study used the approach of *Dell'Abte et al.* [2002] who interpreted their results as percentage mass losses summed into 50 K ranges (150 to 200°C, 200 to 250°C, and so on to 650 to 700°C), and in this manner a single trace of 550 data points is summarized into 10 variables. In addition, the temperature of maximum mass loss was recorded for each trace.

2.6. Statistical Analysis

When summarized into 50 K ranges the data set can be treated as a multivariate data set. Principal component analysis (PCA) was used to assess the differences between organic matter pools and fluxes on the basis of thermal decomposition. Included in this analysis were traces for standards. In the analysis, the components with an eigenvalue >1 were considered for further examination, as these components are those which represent more of the data set variance than any of the original variables [*Chatfield and Collins*, 1980].

The PCA helped assess what compositions were most likely correlated with mass loss within which ranges in the TGA trace, but to test this further stepwise multiple regression was used. The percentage mass loss in each of the ten 50 K range was compared to (1) parameters derived from the elemental analysis and (2) the proportions of the functionalities as derived from ^{13}C NMR. The stepwise multiple regression was performed using both forward and backward selection with a probability of not being zero <0.05 for inclusion.

2.7. Carbon and Dry Matter Budget

This study considers organic matter in the ecosystem as transferring through a series of carbon pools and fluxes (Figure 1). The fluxes of gases (N_2O, CO_2, and CH_4) have fixed and known molecular composition and as such were not analyzed as part of this study.

The dry matter budget of the catchment was first recorded by *Forrest* [1971] who studied the productive ecology of the dominant species present in the catchment. *Forrest* [1971] did include biomass production (both aboveground and belowground production) and divided production estimates between the dominant functional plants types within the catchment (*Calluna*, grass/sedge, and mosses). *Forrest* [1971] did include litter production rates but not their subsequent decay and peat formation rates nor the loss of production via fluvial pathways. Therefore, this study will combine the study of dry matter production with a carbon budget. This study used the most up-to-date and longest carbon budget information for the site based upon the approach of *Worrall et al.* [2009, 2012], which summarized the median carbon budget after 13 years of budget information as

$$100C_{pp} \Rightarrow 35C_R + 26C_{DOC} + 4C_{CH4} + 4C_{dissco2} + 9C_{POC} + 22C_{RES} \tag{4}$$

where C_x indicates the carbon from the following uptake or release pathways, where x representing pp as primary productivity, R as net ecosystem respiration, DOC as dissolved organic carbon, CH4 as methane, dissco2 as dissolved CO_2, POC as particulate organic carbon, and RES as residual carbon stored in the soil.

The total carbon budget of this ecosystem varied between -20 and -91 t C km^{-2} yr^{-1}; i.e., the ecosystem was accumulating carbon from the atmosphere. Equation (4) gives the carbon budget normalized for 100 C atoms taken up by net primary productivity—average net primary productivity across the study period was -176 t C km^{-2} yr^{-1}. The budget status is assessed relative to the atmosphere and thus a sink into the soil is negative. The TGA traces were weighted according to the carbon budget (equation (4)); e.g., the TGA trace of the average biomass was weighted by a factor of 1 (the proportion of primary productivity C in equation (4)) as it represents the primary production and the TGA trace for DOM, weighted by a factor of 0.26 (the proportion of DOM c IN equation (4)), was subtracted from it and this was then performed for each of the carbon species in the budget as presented by equation (4) for which a TGA trace could be measured. The average biomass was calculated as the mix of the TGA traces of the vegetation samples in the above and belowground biomass mixed in the appropriate ratios as defined by *Forrest* [1971]: this then gives a TGA trace of the primary productivity. The two species of carbon for which there was no trace were the CO_2 ($C_R + C_{dissCO2}$; equation (4)) and CH_4; therefore, the trace of the primary production once all other species have been subtracted from it represents the TGA trace of the organic matter that is transformed to and lost in the gaseous form. In this way it was possible to assess the changes between the organic matter compositions as the organic matter transfers through the ecosystem and so identify what composition has been lost in the process of humification to deep peat soil, degradation to gases, and the creation of fluvial organic matter.

3. Results

The TGA trace for the standards shows that cellulose has two sharp peaks with mass loss focused into these peaks without much mass loss before 270°C or after 400°C (Figure 3a). In comparison, loss for lignin is more distributed across a wider range of temperatures with peak mass loss higher than that for the cellulose. In contrast, the maximum loss for protein is below that of both cellulose and lignin, but with a considerable proportion of mass loss above 470°C which we consider to be combustion of the product of the re-arrangement from the lower temperature mass loss. Humic acid was included but proved to be an erratic trace perhaps reflecting the specific origin of the standard and that it was a mixture of a smaller number of quite distinct molecular compositions as opposed to a more continuous range of compositions.

Both the biomass and litter samples show three peaks (Figure 3b). The low-temperature peak is at 288°C in litter and 316°C in the biomass which is closest to the position of protein (Figure 3a). Depending upon which study is used for indices, this peak could be exotherm 1 [e.g., *Dell'Abte et al.*, 2003] or exotherm 2 [*Kristensen*, 1990; *Plante et al.*, 2005]. The second peak with rising temperature and the highest peak for each material are at 348°C and 358°C for litter and biomass, respectively, and is closest to the cellulose standard; again, this could be compared with exotherms 1 or 2 depending upon the study used for comparison [e.g., *Lopez-Capel et al.*, 2006]. There is a third peak present in both litter and biomass between 421°C and 525°C which is not apparent in the standards but would be in the region of exotherm 3 [*Lopez-Capel et al.*, 2006]. Comparing the TGA for the aboveground biomass to that of the individual plant functional groups shows that the best fit (by least squares errors) gave an aboveground biomass composition of 74% Calluna, 16% grass/sedge, and 9% mosses with a mean average percentage error of 0.6% of mass loss/K—within the 95% confidence interval of values quoted by *Forrest* [1971].

The peat samples are dominated by a peak at 301°C and then a shoulder between 380 and 420°C (Figure 3c). Examining the change with depth in the peat profile shows that the maximum change between surface and the depth in the peat profile occurred at 356°C which is close to peak loss in both cellulose and lignin (Figure 3a). Taking the change at 356°C with depth (Figure 4) shows that any change in the peak at 356°C is not monotonic but that the change appears to be greatest at 20 cm depth before decreasing and stabilizing and becoming near-constant after 40 cm depth, although no samples were taken between 50 and 95 cm depths. It is possible to consider these changes to relate to position of the water table and the acrotelm-catotelm boundary. *Worrall et al.* [2012] suggested, on the basis of the C/N ratio, that the acrotelm-catotelm boundary was at 42 cm depth; however, there was no such evidence in the oxidation state of the organic matter [*Worrall et al.*, 2016a]. The oxidation state instead could be reflecting changes in inputs to the peat profile as vegetation and climate shifts on timescales of hundreds of years.

The TGA traces from the POM shows a high degree of commonality with both the peat soil samples and vegetation or litter (Figure 5), but contrasts with the results for the traces for DOM. The TGA traces for DOM show maximum losses at temperatures lower than observed for the other types of organic matter considered (Figure 6).

3.1. Multiple Regression Analysis

The median composition of sampled organic matter pools is given in Table 2. Although this study found a number of significant relationships between mass loss and the other compositional measures (Table 3), there were a number of temperature ranges for which no significant relationship with other compositional measures was found including 250 to 300°C and between 500 and 600°C. Equally, there was no significant relationship found between any of the 50 K ranges and C-alkyl functionality (Table 3). Mass loss in the low-temperature regions (150 to 200°C and 200 to 250°C) correlates well with measures of oxidation and oxygen content of the organic matter (C_{ox}, aldehyde and carbonyl), and indeed increased mass loss in region of 200 to 250°C is also correlated with decreasing H/C (Table 3). Most of the significant regressions are in the temperature ranges between 300 and 500°C which makes it difficult in distinguishing contributions relative to other composition measures—it is this region (i.e., 300 to 500°C) in which the most variation was observed in the TGA traces.

3.2. Principal Component Analysis

The analysis of the data set based only on changes in mass in the 50 K ranges found four components with an eigenvalue >1 and together these explain 79% of the original variance. The first principal component has high negative loadings for mass loss between 300–350°C and 350–400°C with negative loadings for ranges between

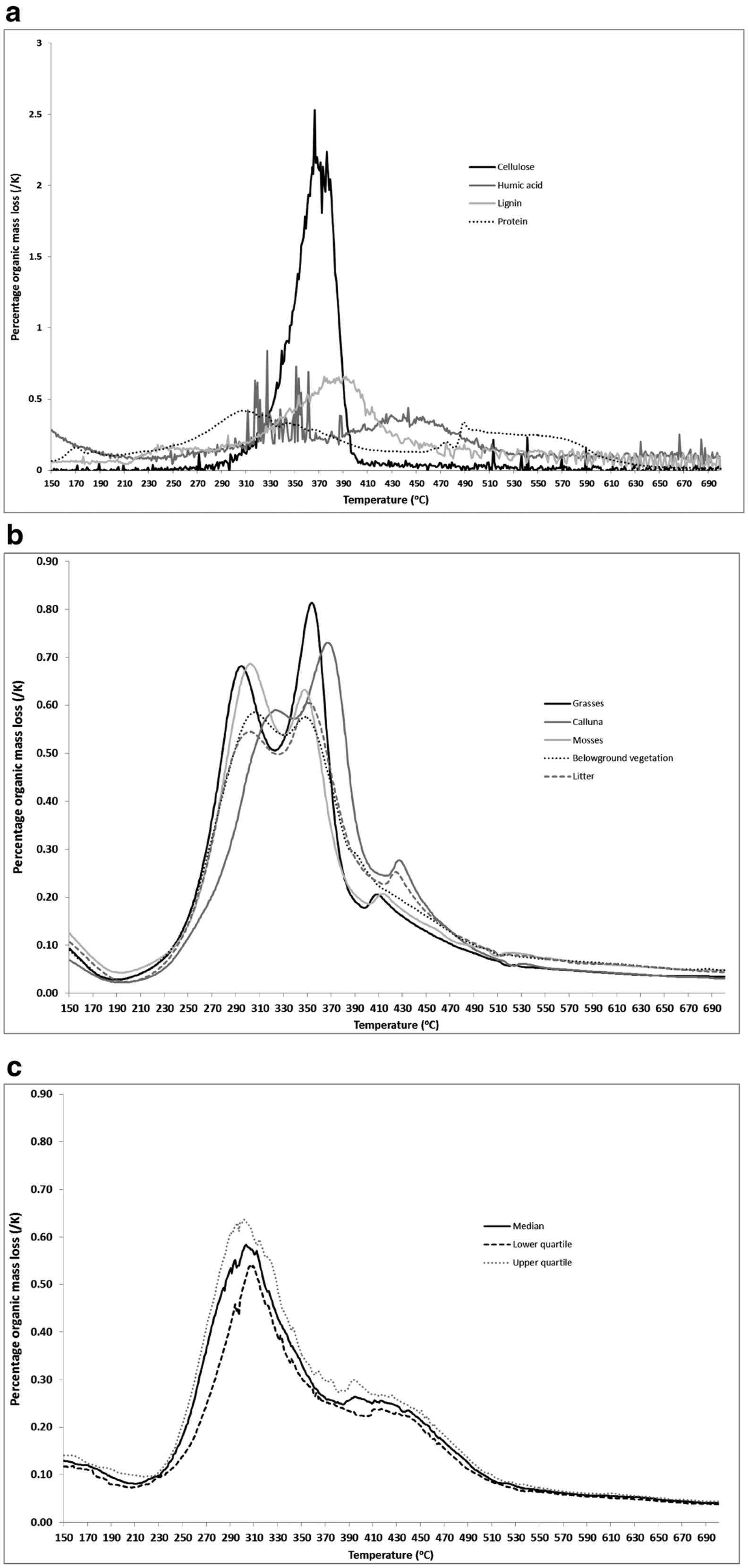

Figure 3. The organic matter normalized TGA trace for (a) standard materials of lignin, cellulose, protein, and humic acid; (b) average biomass and litter; and (c) average peat soil.

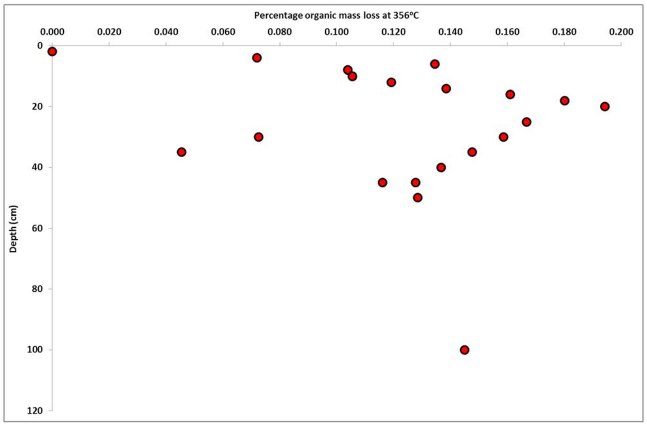

Figure 4. The variation in organic mass loss at 356°C with depth in the peat profile.

450–500°C and 650 to 700°C (Table 4). The second component had high negative loadings peaking for the range 250 to 300°C and a high positive loadings peaking at 400 to 450°C. The third component shows a distinct positive loading for 350 to 400°C. The fourth component has a high negative loading for the temperature of maximum mass loss. When the scores on PC1 were plotted against those on PC2, distinct patterns were observed, and the standards now aid the interpretation (Figure 7).

The standards show that PC1 contrasts cellulose with a DOM sample which implies that cellulose is marked by mass loss peaks in the region 300 to 400°C. The humic acid standard plots at high positive values of PC2 which means that it is distinguished by mass loss in the ranges 300 to 350°C and 450 to 550°C. The plot of the humic acid standard sets it clearly apart and so is not probably representative of soil humic compounds but rather reflects its particular origin or extraction. Lignin is not distinguished by PC1 but has a positive score on PC2, while protein has positive scores on PC1 which correlates with mass loss in the lower temperature ranges (200 to 300°C).

The sample data can be broadly analyzed as plotting in two regions (Figure 7). First, the vegetation, litter, peat, and most of the POM samples plot from between the line joining cellulose and lignin standards and a POM sample (marked A, Figure 7). Peat soil samples plot parallel to the *y* axis suggesting variation only on PC2. When plotted against the depth (in cm) of the sample a clear and significant trend is observed (PC2 = 0.05 + 0.029 depth, $r^2 = 0.39$, $n = 19$, $P < 0.05$) that shows that the shallowest samples plot at the lowest values of PC2 and so are distinguished by mass loss in the 250–300°C range. This increase of PC2 with depth suggests that peat evolves toward more lignin-like compositions with depth which represents a shift from mass loss in the 250–300°C range to mass loss in the 400 to 450°C range. The very shallowest peats soils samples (labeled B) plot very close to some litter samples, while litter and vegetation samples plot between the very shallowest peat soil samples and a line between the cellulose and lignin standards. The vegetation and litter samples can now be interpreted as a mixture of the cellulose, lignin, and protein standards and compared to the composition based upon the elemental analysis (Table 5).

It is possible therefore that POM composition A does not relate to peat, vegetation, and litter samples but instead represents a separate composition. Some POM samples plot with the peat soil samples, and these can be explained as coming from erosion of the deep peat soils where they are exposed in river banks within the catchment. Alternatively, some POM samples plot close to vegetation and litter implying that in some cases particulate flux is from the peat surface. *Worrall et al.* [2016a] showed, on the basis of CHNO composition, that POM in this composition was a mixture of vegetation and peat soil. The POM composition A comes from August 2014 whose TGA trace is distinguished by a peak in the range between 200 and 250°C and another one in the range between 400 and 450°C; this could

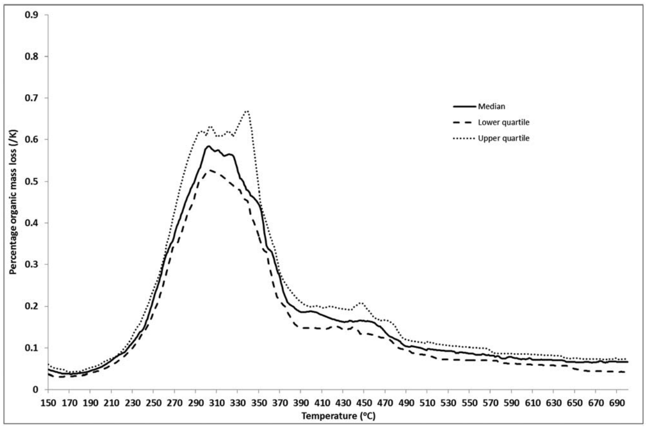

Figure 5. The organic matter normalized TGA trace for average particulate organic matter (POM).

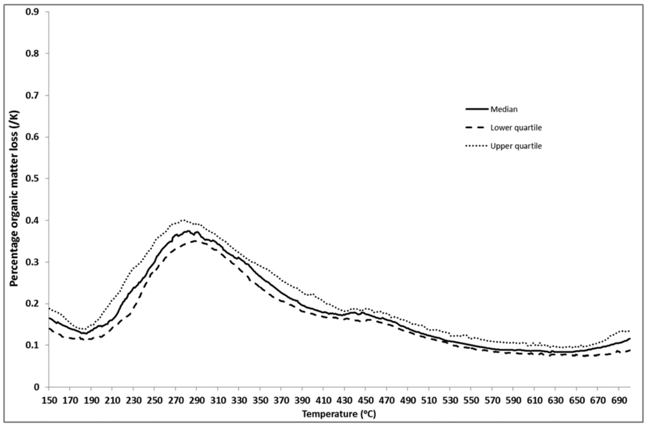

Figure 6. The organic matter normalized TGA trace for average dissolved organic matter (DOM).

be autochthonous POM, i.e., a POM sourced from within the stream itself. Alternatively, POM composition A could be viewed as one end-member of a trend that evolves, with both increasing values of both PC2 and PC1, toward and including the DOM samples. Therefore, the POM of composition A could be a flocculated DOM.

All the DOM samples are clearly distinguished from all other samples, but there is no apparent substructure to the DOM samples and there were insufficient samples to perform a separate PCA of the DOM samples alone.

3.3. TGA Budget

The TGA traces can now be apportioned through equation (4) given that the organic matter entering the ecosystem is fixed as primary productivity into biomass. The TGA trace of primary productivity is shown in Figure 8. The TGA trace for litter that is produced from this biomass is difficult to distinguish from the curve for biomass (Figure 3b) and so subsequent calculations were performed using the TGA trace for the litter weighted by a factor of 1 (Figure 8). From the produced litter we can subtract the trace of the deepest measured peat (95–100 cm depth—residual peat; Figure 8) weighted by a factor of 0.22 (the proportion of residual C in equation (4)) to give the TGA trace of what has been lost in the processing of the produced litter, except for that this organic matter is also lost as POM and DOM. Therefore, adding the appropriate proportion of POM and DOM (weighted by 0.09 and 0.26, respectively; equation (4)) gives the total organic matter that could be accounted for in the solids that could be sampled from the study site. Therefore, by knowing the trace of the inputs (biomass and litter) and the outputs of the organic matter (residual peat, POM and DOM) then, by subtraction, the trace of the organic matter that has been lost from the ecosystem to the atmosphere can be calculated—henceforward referred to as the "lost composition" (Figure 8). Comparing the traces in Figure 8 with Figure 3 suggest that what has been lost is a combination of protein and cellulose. The calculated traces can now be included in the principal component analysis with the other samples and standards.

Table 2. The Median Composition of the Carbon Pools Considered by the Study[a]

Carbon Pool/Type	C_{ox}	OR	Degree of Unsaturation (Ω)	Median Stoichiometry	C-alkyl	N-alkyl	O-alkyl	O2-alkyl	Aromatic	Phenolic	Aldehyde	Carbonyl
DOM	0.40	0.92	2.42	$C_{31}H_{38}NO_{24}$	14.6	8.8	11.8	10.9	12.4	9.6	7.3	23.1
POM	−0.21	1.09	1.76	$C_{22}H_{35}NO_{14}$	17.0	11.8	37.9	14.6	5.9	4.0	0.5	8.2
Aboveground biomass	−0.26	1.08	1.98	$C_{57}H_{86}NO_{35}$	13.4	8.2	37.5	16.2	8.0	7.6	1.4	7.7
Belowground biomass	−0.25	1.08	2.12	$C_{49}H_{73}NO_{29}$	14.3	11.6	32.8	16.1	8.1	7.7	1.9	7.5
Grass & sedge	−0.19	1.07	1.95	$C_{33}H_{52}NO_{21}$	10.4	14.1	37.8	17.2	5.2	5.7	0.9	8.7
Mosses	−0.19	1.06	1.92	$C_{95}H_{145}NO_{56}$	8.8	11.6	42.0	15.6	8.1	5.9	1.5	6.4
Calluna	−0.32	1.09	2.03	$C_{55}H_{86}NO_{46}$	11.2	14.5	36.2	17.3	5.6	7.3	0.2	7.8
Litter	−0.05	1.05	2.30	$C_{25}H_{35}NO_{15}$	16.2	11.6	30.4	15.3	9.0	7.5	1.7	8.9
Peat soil	−0.15	1.06	2.20	$C_{43}H_{62}NO_{26}$	34.2	11.7	13.7	7.3	9.8	7.2	3.8	10.2
Lignin	−0.43	1.12	3.14	$C_{87}H_{103}NO_{31}$	7.0	28.5	6.2	13.0	19.1	23.7	0.8	1.8
Cellulose	0.05	0.99	1.11	CH_2O	30.2	12.8	40.4	13.6	1.2	0.5	0.8	0.5
Humic acid	0.19	0.97	2.18	$C_{49}H_{60}NO_{33}$	26.0	9.5	3.1	6.8	25.9	10.5	3.0	15.1
Protein	0.18	0.96	3.63	C_5H_5NO	27.5	19.7	10.9	2.4	8.6	2.3	0.9	27.6

[a] Median stoichiometry is expressed relative to nitrogen content except for cellulose which expressed relative to carbon.

Table 3. Coefficients of the Significant Multiple Regressions on the Range of Compositional Parameters Measured Across the Range of Organic Matter Types and Standards Used Within This Study

	Upper End of the Temperature Range (°C)												
Parameter	200	250	300	350	400	450	500	550	600	650	Max (°C)	Const.	R^2
C_{ox}		0.054			0.011					0.11		−0.87	0.72
C/N	2.8			0.7	2.2	2.6						−54	0.54
H/C		−0.038				−0.023						1.9	0.37
C-alkyl													
N-alkyl											0.04	−0.9	0.18
O-alkyl				1.4		−1.7						6	0.64
O_2- alkyl							−0.9					18	0.33
Aromatic				−0.48		1.03						10	0.73
Phenolic				−0.60	−0.10	1.5	−1.7					20	0.74
Aldehyde	0.7											0.4	0.44
Carbonyl	1.0	1.0										3	0.59

When the PCA is performed again but now including the traces calculated for the compositions lost from the ecosystem, it can be seen that the lost composition plots very close to the cellulose composition (Figure 9). The lost composition can be viewed as being largely cellulose but with some component of either lignin or humic acid. If viewed as a mixing between the studied standards, then the lost composition is either 97% cellulose and 3% humic acid or 92% cellulose and 8% lignin or a combination of these two end-member mixtures (e.g., 95% cellulose, 2% humic acid, and 3% lignin).

Alternatively, the PCA could be used to give the cellulose, lignin, and protein composition of the aboveground biomass, litter, deep peat, POM, and DOM. Given the compositions of the primary productivity, POM, DOM, and residual peat, then the lost composition can be calculated using equation (4) (Table 6). In this case the lost composition would be $\mathrm{Cell}_{40}\mathrm{Lig}_{5}\mathrm{Pro}_{0}$ per 100 g C of primary productivity, once again confirming the result found above that cellulose is preferentially lost when organic matter is transferred into and through a peat soil. Furthermore, the analysis in Table 6 shows that POM is predominantly from the residual peat (i.e., peat soil from between 95 and 100 cm depth). The DOM composition is predominantly from lignin and not from cellulose and has compositions similar to protein.

4. Discussion

The comparison of the TGA trace to other measures of the composition shows that the interpretation of the trace in terms of elemental or functional group composition would be difficult because the mass loss for organic matter is concentrated into the region between 300 to 500°C. However, DOM did have a lower thermal stability than other organic matter fractions studied, and the DOM has a more oxidized nature than the other types of organic matter studied. *Plante et al.* [2011] and *Dorodnikov et al.* [2007] have both tried to correlate thermal stability indices derived from TGA with measures of biological turnover of the same soil organic matter. *Dell'Abte et al.* [2002] associated the "first exothermic region" (300–350°C) with the burning of carbohydrates and aliphatic compounds, while the "second exothermic region" (400–450°C) was attributed with the oxidation of aromatic compounds. Table 3 does provide some evidence that losses in region 400 to 450°C were positively correlated with the proportion of aromatic and phenolic groups; for example, approximately 30% of lignin mass was lost in the region 400 to 450°C (Figure 3a), but there was also positive correlation in this region with the C:N ratio. Further, this study

Table 4. The Loadings on the Principal Components

Variable	PC1	PC2	PC3	PC4
200	0.36	0.10	0.00	0.39
250	0.36	−0.28	0.01	0.32
300	−0.05	−0.51	−0.57	−0.04
350	−0.39	−0.08	−0.19	−0.26
400	−−0.30	0.15	0.57	0.14
450	−0.06	0.58	−0.44	0.21
500	0.29	0.49	−0.26	−0.10
550	0.29	0.08	0.20	−0.42
600	0.38	−0.04	0.09	−0.42
650	0.39	−0.11	0.03	−0.18
Max °C	−0.15	0.18	−0.08	−0.48

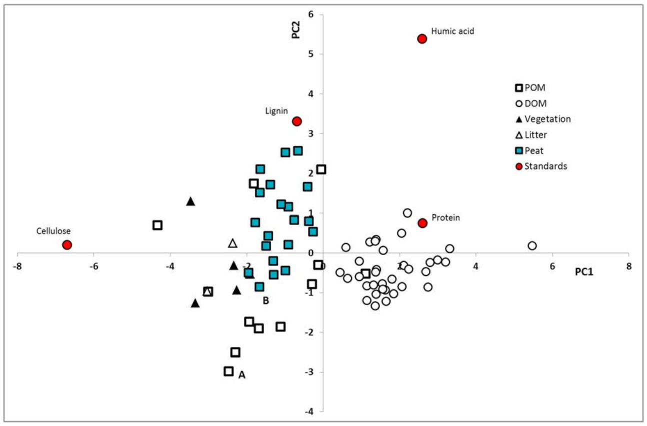

Figure 7. The comparison of PC1 and PC2 for all sample types.

found no correlation between C-alkyl groups or O-alkyl groups in the 300 to 350°C region.

If it is difficult to interpret the TGA trace in terms of elemental or functional composition, it does give clear patterns in terms of whole composition when interpreted using a multivariate PCA approach. The principal component analysis of the TGA data allows a coherent interpretation of the organic matter budget of a peat ecosystem. Primary productivity sequesters CO_2 from the atmosphere which forms biomass as lignin and polysaccharides (here referred to as cellulose). The primary productivity forms litter and exudates which becomes humified into peat soil. The humification process in this ecosystem sees the loss of 78% of the primary productivity, but preferentially this loss is of cellulose with 100% of the C sequestered into the aboveground biomass as cellulose lost by 100 cm depth but only 54% of the C sequestered in the aboveground biomass as lignin has been lost.

The loss of carbon can be as any combination of CO_2, CH_4, DOM, or POM. The POM composition shows that it is dominantly sourced from the erosion of peat soil and wash off of vegetation except for the POM of composition A (Figure 7). The DOM composition shows that it is predominantly derived from the humification (or degradation) of lignin but not cellulose. *Worrall et al.* [2016a] studied the C_{ox} values of DOM in the context of this field site and suggested that DOM was an intermediary in the complete oxidation of organic matter to CO_2. However, this study would separate the process responsible for the majority of the CO_2 production (oxidation of carbohydrates such as cellulose) from the process producing the majority of the DOM (lignin metabolism). A number of studies have also observed the preferential loss of polysaccharides over lignin in peat soils [*Bracewell et al.*, 1980; *Benner et al.*, 1984; *Van der Heijden and Boon*, 1994; *Biester et al.*, 2014]. Equation (4) can now be re-written to account for the changes in polysaccharide, lignin, and protein:

$$\begin{aligned} 100\left[0.50C_{\mathrm{cell}} + 0.46C_{\mathrm{lig}} + 0.04C_{\mathrm{pro}}\right]_{\mathrm{PP}} = {} & 45\left[0.89C_{\mathrm{cell}} + 0.11C_{\mathrm{lig}}\right]_{\mathrm{R+CH4+dissCO2}} \\ & + 26\left[0.19C_{\mathrm{cell}} + 0.81C_{\mathrm{lig}}\right]_{\mathrm{DOC}} + 9\left[0.93C_{\mathrm{lig}} + 0.06C_{\mathrm{pro}}\right]_{\mathrm{POC}} \\ & + 22\left[0.94C_{\mathrm{lig}} + 0.06C_{\mathrm{pro}}\right]_{\mathrm{RES}} \end{aligned} \tag{5}$$

where C_x indicates carbon from biopolymer x, with cell representing as cellulose (polysaccharide), lig as lignin, and pro as protein; with other terms as defined for equation (4). Equation (5) can be represented schematically (Figure 10), and this would imply that protein survives the transition through the peat profile; however, it may simply be that this represents the residual organic N components or that a microbial population is present in the deep peat which has a protein content and that original plant proteins were readily transformed.

Table 5. Composition of Biomass and Litter Components as Calculated TGA Trace

Organic Matter Reservoir	Composition
Calluna	$Cell_{36}Lig_{64}Pro_0$
Sedges/grass	$Cell_{74}Lig_{23}Pro_3$
Mosses	$Cell_{61}Lig_{24}Pro_{15}$
Aboveground biomass	$Cell_{45}Lig_{52}Pro_3$
Belowground biomass	$Cell_{53}Lig_{15}Pro_3$
Litter	$Cell_{54}Lig_{19}Pro_{26}$
Primary productivity	$Cell_{50}Lig_{46}Pro_4$

The lost composition has important implications for the oxidation state of the peatland. As noted above, OR can be more than a property of a carbon flux or reservoir and can be a property of an ecosystem: the oxidation state of ecosystems can be described by C_{ox} which in turn is linearly related to the oxidative ratio of that ecosystem. The value of OR

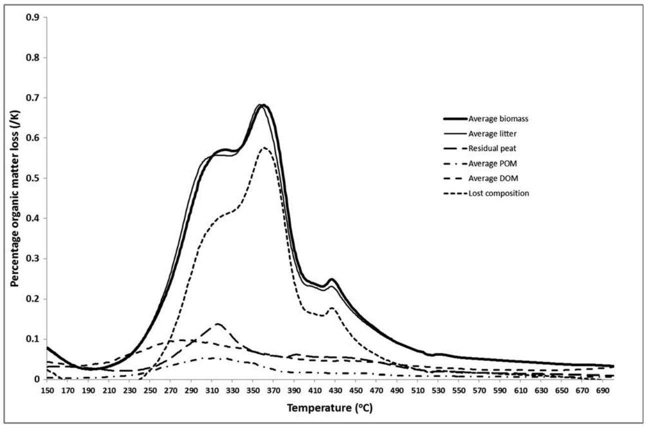

Figure 8. The comparison of the average TGA traces weighted according to their C flux as per equation (1).

has until recently been assumed to be 1.1 [*Keeling et al.*, 1996; *Battle et al.*, 2000; *Prentice et al.*, 2001; *Langenfelds et al.*, 1999; *Steinbach et al.*, 2011; *IPCC*, 2013] although *Keeling and Shertz* [1992] used a lower value of 1.05, and *Keeling and Manning* [2014] have suggested that any attempt to update this value as likely to have only a minimal impact. *IPCC* [2013] do only use one value of OR for the globe and that value was based upon one value from a single study of the Biosphere 2 experiment [*Severinghaus*, 1995] that did not set out to measure an OR value applicable to the global terrestrial biosphere.

As an alternative to the assumed value of OR as 1.1, *Worrall et al.* [2013] compiled elemental analysis from the literature for whole soil and vegetation data from across the globe to provide a flux-weighted estimate of global OR and found a value of 1.03 ± 0.03 and argued that the present value used by the Intergovernmental Panel on Climate Change (IPCC) represents the 97th percentile of observed values. Indeed, other studies have confirmed that OR should and does vary in time [*Randerson et al.*, 2006] and between environmental reservoirs [*Hockaday et al.*, 2015]. This approach has been updated to consider the different organic matter pools and reservoirs [*Clay and Worrall*, 2015a, 2015b] and the speciation of the fluxes from the ecosystem [*Worrall et al.*, 2016a]. Indeed, *Worrall et al.* [2016a] considered the ecosystem in this study and the flux- and speciation-weighted ecosystem OR was 1.04. However, measurements of OR based upon atmospheric measurements have tended to find even lower values of ecosystem OR than suggested even by *Worrall et al.* [2016a] with *Ishidoya et al.* [2013] suggesting a value of 0.86 and *van der Laan et al.* [2014] a value of 0.89. For terrestrial litter bag experiments (where oxygen would not be limiting) have shown that organic matter remaining after decomposition is more reduced than the initial biomass [*Baldock et al.*, 2004] because carbohydrates and polysaccharides (oxidized biomolecules) are most readily removed in the initial stages of decomposition.

The present studies of OR [e.g., *Clay and Worrall*, 2015a] have been largely based upon measurements of the organic matter left behind after oxidation (e.g., soil organic matter), or in some cases have taken into account the organic matter that is in transition (e.g., DOM) into longer-term carbon stores. It is impossible to directly sample the organic matter that had already reacted and turned over to the atmosphere as this component has been lost from the ecosystem although studies based on atmospheric measurement [*Ishidoya et al.*, 2013; *van der Laan et al.*, 2014] provide an alternative perspective. The carbon-flux-weighted TGA traces demonstrate that the composition that is missing (removed to the atmosphere) is dominated by cellulosic compounds. Since the composition starts as a ligno-cellulose copolymer and is observed to evolve toward a lignin-like composition, then it must be a cellulosic composition that is lost. In this case, however, erosion of particles and flushing of dissolved organic matter mean that some organic matter is lost from the ecosystem not as gases. Therefore, the OR of the ecosystem, the OR

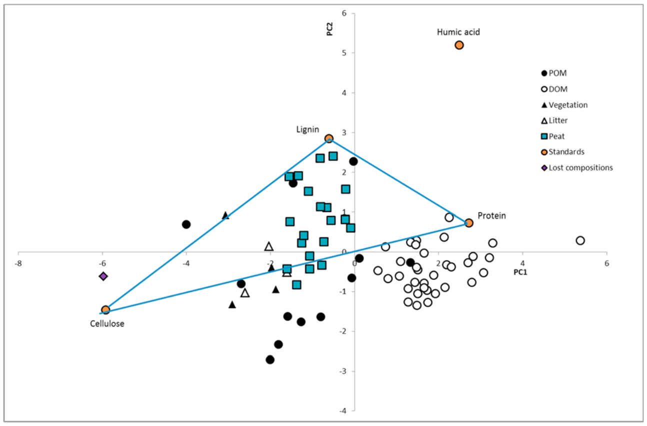

Figure 9. The comparison of PC1 and PC2 for all sample types including the projected lost composition.

Table 6. Composition of the Organic Matter Reservoirs and Fluxes Based Upon TGA Trace and as Weighted via Equation (1)

Organic Matter Reservoir	Proportion	Mass
Primary productivity	$Cell_{50}Lig_{46}Pro_4$	612
Primary productivity/100gC	$Cell_{50}Lig_{46}Pro_4$	100
Reacted composition	$Cell_{41}Lig_{33}Pro_3$	78
Lost composition	$Cell_{40}Lig_5Pro_0$	45
Fluvial flux composition	$Cell_2Lig_{28}Pro_3$	33
POM composition	$Cell_0Lig_8Pro_1$	9
DOM composition	$Cell_2Lig_{21}Pro_3$	26
Residual peat	$Cell_0Lig_{21}Pro_1$	22

experienced by the atmosphere, is the flux-weighted OR of the organic matter being lost through mineralization to gases—the OR of the ecosystem so accounted corresponds to OR_{ba} as defined by *Gallagher et al.* [2014]. Furthermore, the POM and DOM are atmospherically active and the proportion of each that is lost to the atmosphere can be accounted for

$$OR_{ecosystem} = f_{lost}OR_{lost} + \delta_{POM}f_{POM}OR_{POM} + \delta_{DOM}f_{DOM}OR_{DOM} \tag{6}$$

$$1 = f_{lost} + \delta_{POM}f_{POM} + \delta_{DOM}f_{DOM} \tag{7}$$

where OR_x is the oxidative ratio of x (x is lost composition, POM or DOM), f_x is the fraction of the flux from the ecosystem that is x (x is lost composition, POM or DOM), and δ_x is the fraction of the flux of x from the ecosystem that atmospherically active with x as POM or DOM. The OR_{lost} comes from the linear combination of the OR of cellulose, humic acid, or lignin; the OR_{POM} and OR_{DOM} were taken as the average and range of that measured above, 1.08 (0.93 to 1.22) and 0.91 (0.86 to 0.96), respectively. The fractions of the POM and DOM that are lost to atmosphere have been measured in this catchment [*Moody et al.*, 2013] as 0.76 for DOM and between 0.18 and 0.38 for POM. Given these values, the $OR_{ecosystem}$ ranges from 0.96 to 0.99: still higher than measured or observed by *Ishidoya et al.* [2013] and *van der Laan et al.* [2014] but distinctly lower than the value of 1.04 previously proposed for this ecosystem by *Worrall et al.* [2016a].

Battle et al. [2000] have proposed the following equations:

$$f_{land} = -\frac{CS}{OR^{global}_{terra}}f_{fuel} + \frac{1}{k_1k_2OR^{global}_{terra}}\frac{d\left(\frac{O_2}{N_2}\right)}{dt} \tag{8}$$

$$f_{ocean} = -\frac{1}{k_1}\frac{d(CO_2)}{dt} - \frac{1}{k_1k_2OR^{global}_{terra}}\frac{d\left(\frac{O_2}{N_2}\right)}{dt} - \frac{OR^{global}_{terra} - CS}{OR^{global}_{terra}}f_{fuel} - f_{cement} \tag{9}$$

where f_x is the annual flux of CO_2 (Gt C/yr) with x as the land, ocean, fuel, or cement; (O_2/N_2) is the molar ratio of atmospheric O_2 and N_2; CS is the combustion stoichiometry (1.43 [*Battle et al.*, 2000]); OR^{global}_{terra} is the oxidative ratio of the global terrestrial biosphere; and constants k_1 and k_2 are converted ppm in the atmosphere to per meg (which is ppm on a molecular basis for oxygen alone)—the values are 0.471 and 4.776, respectively. Applying the previously used value of OR (OR^{terra}_{global} = 1.1) and leaving all other terms equal in equations (8) and (9) then f_{land} = 1.40 Gt C/yr and f_{ocean} = 2.11 Gt C/yr. Taking the estimate of OR^{terra}_{global} value of 1.04 from *Worrall et al.* [2016a] then f_{land} = 1.47 Gt C/yr and f_{oceans} = 2.0 Gt C/yr. Given the

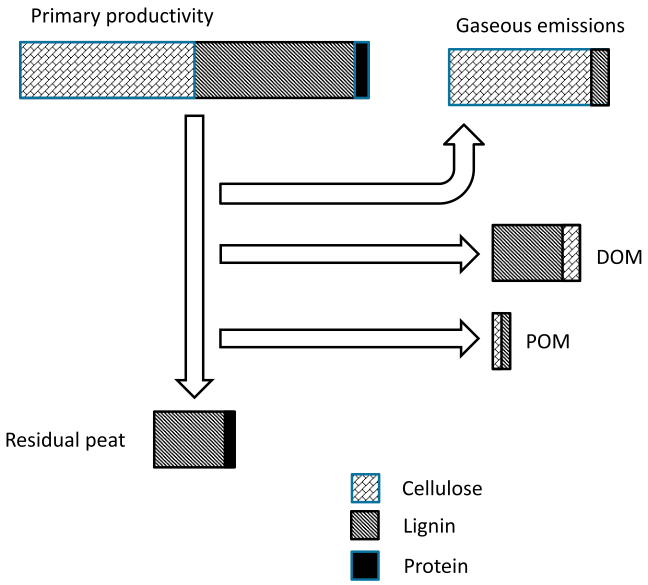

Figure 10. Schematic representation of equation (2) scaled for the size of its carbon flux and composition as predicted from equation (1) and from Figure 8.

estimates derived in this study (based upon an OR = 0.975—the median of the range estimated from this study of 0.96 to 0.99) then f_{land} = 1.60 Gt C/yr and f_{oceans} = 1.88 Gt C/yr.

5. Conclusions

The study has shown that thermogravimetric analysis (TGA) can distinguish between the organic matter fluxes and reservoirs across a peatland ecosystem. The comparison of the TGA in the context of a known carbon budget for the site shows that while primary productivity sequesters carbon from the atmosphere which is transformed into lignin and polysaccharides, it is the polysaccharides that are preferentially lost through degradation and the residual peat at 1 m depth is predominantly lignin-like. The loss of particulate organic matter (POM) is shown to be from erosion of peat soil and vegetation, while the dissolved organic matter (DOM) appears to be the degradation product of lignin with only a small contribution from polysaccharides. Of 100 g of C taken up as primary productivity (50% polysaccharide-C; 46% lignin-C) 22 g of C would be left as residual peat at 1 m depth of which 95% was lignin-C. Of the 100 g of C taken up as primary productivity 26 g of C was lost via DOM flux of which 81% was lignin-C; 9g of C was lost via POM flux which was 89% lignin-C. Therefore, of the 100 g of C taken up as primary productivity, 46 g would be lost as CO_2 and CH_4 fluxes of which between 89 and 95% was polysaccharide-C. The composition lost from the peat via all pathways would then be between 92 and 95% polysaccharide-C and up to 8% lignin-C. The dominate role in CO_2 release for polysaccharides means that the oxidative ratio (OR) of the ecosystem is between 0.96 and 0.99 and not 1.04 as previously thought and if true for other environments would have radical consequences for the value of OR (1.1) as used by the IPCC.

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