

**Key Points:**

- Study applies rules of stoichiometry and enthalpy balance to understand carbon budgets of peatlands
- Methanogenesis does not result in deep peat formation as it requires too much energy to form residual organic matter at depth
- Deep peat formation could only be achieved if the dissolved organic matter in the peat pore water was the dominant electron acceptor

**Supporting Information:**

Supporting Information may be found in the online version of this article.

**Correspondence to:**

F. Worrall,  
Fred.Worrall@dur.ac.uk

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**Author Contributions:**

**Conceptualization:** Fred Worrall  
**Data curation:** Rob Rose  
**Formal analysis:** Gareth D. Clay, Catherine S. Moody, Katherine Heckman  
**Investigation:** Catherine S. Moody, Katherine Heckman  
**Methodology:** Fred Worrall  
**Project Administration:** Fred Worrall  
**Writing – original draft:** Fred Worrall  
**Writing – review & editing:** Gareth D. Clay, Catherine S. Moody, Tim P. Burt

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## Constraining the Carbon Budget of Peat Ecosystems: Application of Stoichiometry and Enthalpy Balances

Fred Worrall<sup>1</sup>, Ian M. Boothroyd<sup>1</sup>, Gareth D. Clay<sup>2</sup>, Catherine S. Moody<sup>3</sup>, Katherine Heckman<sup>4</sup>, Tim P. Burt<sup>5</sup>, and Rob Rose<sup>6</sup>

<sup>1</sup>Department of Earth Sciences, Science Laboratories, Durham University, Durham, UK, <sup>2</sup>Department of Geography, School of Environment, Education and Development, University of Manchester, Oxford Road, UK, <sup>3</sup>School of Geography, University of Leeds, Leeds, UK, <sup>4</sup>USDA Forest Service, Northern Research Station, Houghton, MI, USA, <sup>5</sup>Department of Geography, Science Laboratories, Durham University, Durham, UK, <sup>6</sup>Environmental Change Network, Centre for Ecology & Hydrology, University of Lancaster, Lancaster, UK

**Abstract** We consider how the stoichiometry and energy content of organic matter reservoirs and fluxes through and from a peatland enable the fluxes and storage of carbon within a peatland to be constrained. We include the elemental composition of the above- and below-ground biomass, litter, the peat profile, and the dissolved and particulate organic matter within a blanket bog in northern England for which the C budget has previously been measured. The study shows, based only on the elemental composition, and calculation of oxidation and energy contents, that: (a) Dissolved organic carbon (DOC) in first-order streams is significantly more oxidized than in peat pore water but that there was no significant difference in organic carbon oxidation state down the peat profile; (b) The occurrence and speciation of N uptake and release in the peatland with N used and recycled can be predicted; (c) The relatively high oxidation state of DOC in stream water acts as an endpoint for peat-forming reactions; (d) Methanogenesis does not result in deep peat formation as its requirement for energy consumes too much organic matter to form residual peat at depth; (e) Sulfate reduction does occur during the formation of deep peat; (f) Organic matter elemental composition could be constrained to within three bounding equations though the proportions of carbon species could not be specified. (g) The formation of deep peat in this catchment could only be achieved if the dissolved organic matter (DOM) in the peat pore water is the dominant electron acceptor and energy source in the production of residual organic matter; however, it is unclear as to the flux of DOM up or down the peat profile.

**Plain Language Summary** Peatlands are a vital terrestrial carbon store and so understanding their carbon budget has been a common measure of the health of those peatlands. Measuring carbon budgets a long and expensive process. However, we propose that the reactions of organic matter in peatlands must be constrained, like all chemical reactions, by stoichiometry and by enthalpy. Using elemental analysis of peat organic matter this study could reconstruct the C budget of a peatland and show which reactions are the most important.

### 1. Introduction

Within the terrestrial biosphere, northern peatlands store on the order of one third of the global soil carbon which is concentrated in 3% of the terrestrial surface (Turunen et al., 2002). Gorham (1991) estimated that between 270 and 450 Gtonnes C are stored in the global peatlands, whilst Hugelius et al. (2020) recently estimated  $415 \pm 150$  Gtonnes C. The very existence of peatlands relies on the fate of organic matter (i.e., slow decay of organic matter leading to long-term accumulation), and therefore, a peatland carbon budget is a statement of the ecosystem's future and thus the estimation of C budgets has been a common research target.

Initial approaches to C budgeting for peatlands was to measure the long-term, past 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 this approach estimate the species of carbon being lost as organic matter accumulates. Understanding the species of carbon that are lost, as opposed to those accumulated, is vital because carbon is sequestered from the atmosphere to a peatland as CO<sub>2</sub> but can be lost to the atmosphere as CO<sub>2</sub> or as the powerful greenhouse gas, CH<sub>4</sub> (Houghton et al., 1995). As an alternative, 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

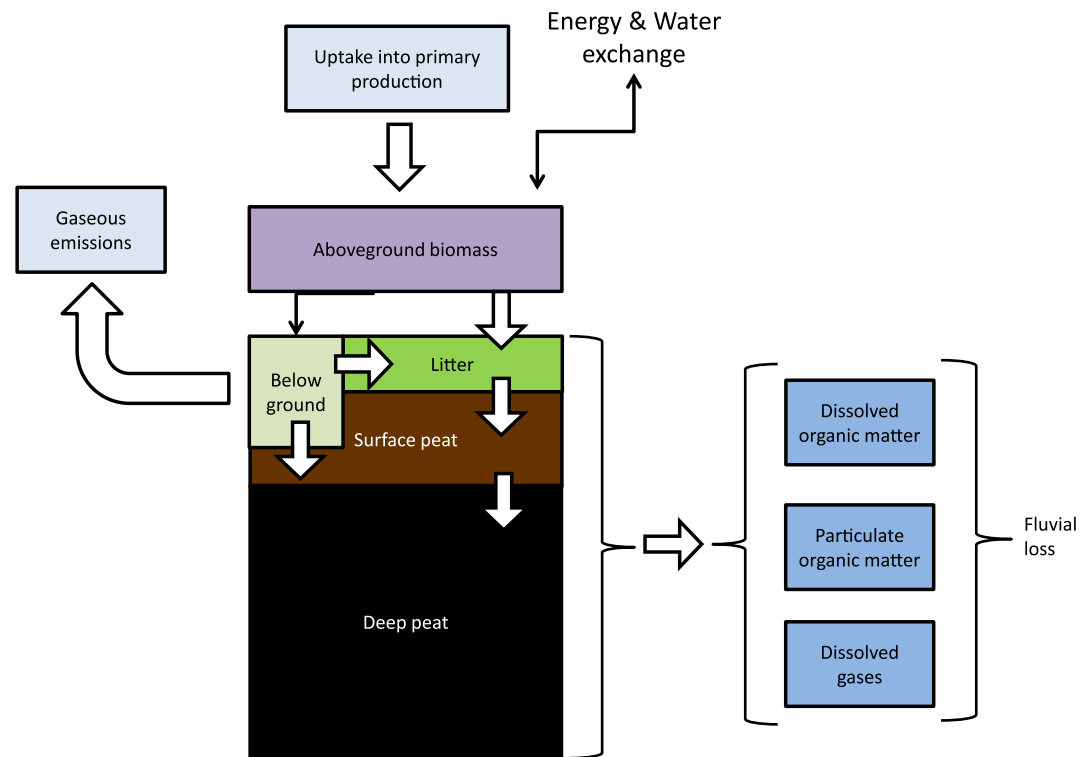
ecosystem and complete contemporary carbon budgets of peatlands are now common (e.g., Billett et al., 2004; Nilsson et al., 2008; Roulet et al., 2007; Worrall et al., 2003). If carbon is accumulating in peat soils, then the other elements in organic matter must also be accumulating. Contemporary elemental budgets for peatlands have been extended to include nitrogen (e.g., Hemond, 1983; Worrall et al., 2012), phosphorus (Worrall, Moody, et al., 2016) and sulfur (Blodau et al., 2007). Similarly, Worrall, Clay, et al. (2016) considered the transition of organic oxygen through a peat soil ecosystem and, although not classically an elemental budget as no inorganic O fluxes could be considered, the study still showed a peatland to be accumulating oxygen in the organic matter in deep peat soil at a rate of between 16 and 73 tonnes O km<sup>-2</sup> yr<sup>-1</sup>.

The study of elemental budgets in any ecosystem, let alone peatlands, has been the staple of biogeochemists for decades (e.g., Fisher et al., 1968). Carbon budgets in peatlands have been viewed relative to different vegetation types with the differences in vegetation leading to different substrates from which peat soils can develop (Hargreaves et al., 2003). Budgets have also been considered relative to different land management (e.g., drainage–Rowson et al., 2010) or the impact of land use change (Clay et al., 2010). However, even these detailed studies consider budgets as C and not the molecules that move through the peatland. For example, primary productivity is viewed as sequestering C as CO<sub>2</sub> 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 macromolecular components of plants—lignin, carbohydrates (cellulose and hemicellulose), proteins and lipids (McDermitt & Loomis, 1981). It is this organic matter that is transformed back to CO<sub>2</sub> through root respiration, falls as litter, or released as plant exudates into the soil pores. It is the litter, or exudates, that transform into soil organic matter which may result in CO<sub>2</sub>, CH<sub>4</sub>, dissolved organic carbon (DOC) or particulate organic carbon (POC). So, if contemporary carbon budgets have been one step forward from the black box of the long-term accumulation approach whereby the different forms of release are considered, elemental budgets still offer no form of explanation as to what form the element is in.

Worrall et al. (2017) used thermogravimetric analysis to turn the C budget of a *Sphagnum*-dominated peatland into the budget of the main macromolecular species (cellulose, lignin, protein). They showed that cellulose was preferentially removed through the ecosystem, while lignin components were preferentially retained and came to dominate the organic matter accumulated at depth in the profile. Moody et al. (2018) combined a C budget with <sup>13</sup>C-NMR analysis to show that O-alkyl functional groups were disproportionately lost between primary production and accumulation in the deep peat, while C-alkyl functional groups were disproportionately preserved. The carbon lost as gases (CO<sub>2</sub> and CH<sub>4</sub>) was estimated to be composed of 93% polysaccharide- (or cellulose-) derived carbon and 7% lignin-derived carbon. However, no study has yet combined elemental and molecular budget information to understand the controls and limits on the C budget.

Based on a study of biochemical pathways, Penning de Vries et al. (1974) proposed that it was possible to understand and predict the cost of biomass development from proximate analysis of the composition of the biomass. That is, 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<sub>2</sub> produced from primary production 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. Percival et al. (1987) suggested that even 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. However, advances in technology means that elemental composition of organic matter is now readily available. The methods of Penning de Vries et al. (1974), McDermitt and Loomis (1981), and Percival et al. (1987) were only concerned with production values and the cost of biomass, but the logic of their approach, that is, that production is limited by the stoichiometry and energy (redox and thermodynamics), must also be true for accumulation of organic matter into litter and into soil.

Beer and Blodau (2007) constrained the organic matter turnover in the catotelm (synonymous with deep peat in this study) of a peat profile by considering the thermodynamics (Gibbs free energy change–ΔG) of each possible anaerobic fermentation and methanogenic reaction given the pore water conditions. Similarly, Worrall et al. (2018) considered ΔG down a peat profile and showed that there were no further soil organic matter transformations after 40 cm depth in the peat profile—the pore space had become closed and thermodynamic equilibrium achieved. The approach of Beer and Blodau (2007) did not consider the stoichiometric limits on any



**Figure 1.** Conceptual model of organic matter reservoirs and fluxes considered and sampled within this study. Boxes represent reservoirs or fluxes where the composition was known or was sampled and analyzed.

reaction and relied on the fact that the catotelm could be considered as a closed system with respect to its pore water, which meant that the aqueous equilibria could be considered. Therefore, existing proximate and elemental analytical approaches have only been applied to understand the development of biomass and the approach of Penning de Vries et al. (1974), McDermitt and Loomis (1981), and Percival et al. (1987) was based on oxygen as the only terminal electron acceptor (TEA). Although oxygen is the most energetically favorable TEA available in nature in peatlands, we would expect others to be important, including nitrogen (Hemond, 1983), iron (Zou et al., 2011), sulfur (Novak et al., 2005), and ultimately the organic matter itself (Loveley et al., 1996).

Therefore, the purpose of this study was to apply stoichiometric and energetic constraints on the C budget to improve our understanding of the transition of organic matter into and through a peatland.

## 2. Methods

The peatland ecosystem can be viewed as a series of organic matter pools and the fluxes between them (Figure 1). The approach taken here is that processes controlling exchange between organic matter pools in an ecosystem must be constrained by: (a) the relative stoichiometry of the organic matter in those pools; (b) the oxidation states of the organic matter; and (c) the available energy content.

This stoichiometric balance can be viewed in the context of the enthalpy change. In this study the assumption is that each reaction after photosynthesis must be exothermic with the photosynthetic process providing the initial input of energy and then subsequently the glucose is converted into biomass:



where:  $n$ ,  $d$ ,  $a$ ,  $b$ , and  $c$  are stoichiometric coefficients.

Equation 2 can be viewed in terms of the mass of material (in the case above the above-ground biomass) that can be produced per glucose molecule used (g of product/g of glucose = glucose value, GV), and the amount of glucose required to produce a known amount of product (g of glucose/g of product = glucose requirement, GR).

The GV for each process can be readily calculated using the method of McDermitt and Loomis (1981) whereby for the development of biomass from glucose:

$$\frac{[C]}{6} - \frac{r}{24} = \text{GV} \quad (3)$$

where:  $[C]$  = the number of carbon atoms in the molecular formula of the product; and  $r$  = the reduction level of the product. This formula is such because the molecular formula of glucose is  $C_6H_{12}O_6$  and that in its complete oxidation to  $CO_2$  it would release 24 electrons since the oxidation state of C in glucose is 0 and +4 in  $CO_2$ .

The reduction level ( $r$ ) is related to the oxidation state of carbon ( $C_{ox}$ ) within any molecule as defined by Masiello et al. (2008):

$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} = \frac{r}{[C]} \quad (4)$$

where:  $[X]$  = molar concentration of C, H, N or O.

Therefore, when the substrate is something other than glucose but with oxidation to  $CO_2$ , Equation 3 becomes a substrate equivalent (SEV):

$$\frac{[C]_{pro}}{[C]_{sub}} - \frac{C_{ox}^{pro}[C]_{pro}}{(C_{ox}^{CO_2} - C_{ox}^{sub})[C]_{sub}} = \text{SEV} \quad (5)$$

where:  $[C]_x$  = the molar concentration of C with  $x$  as *pro* is product and *sub* is substrate;  $C_{ox}^y$  = the oxidation state of the carbon with  $y$  as *pro* is product, *sub* is substrate, and  $CO_2$  is carbon dioxide.

Equation 5 represents the stoichiometric ratio corrected for the energy requirement of the reaction. It generalizes the approach of McDermitt and Loomis (1981) to any organic product from any organic substrate. It is formulated for  $O_2$  as the terminal electron acceptor.

It is not possible to transfer 100% of the energy content of the complete oxidation of glucose, or any other substrate, and different biochemical pathways have different energy efficiencies. Complete oxidation of glucose can produce 12 nucleotides (NADH) or 36 ATP molecules based on the release of 24 electrons per glucose molecule. The heat of combustion of glucose is  $15.6 \text{ MJ kg}^{-1}$  ( $2.8 \text{ MJ mol}^{-1}$ ) whereas for each nucleotide this is  $0.22 \text{ MJ mol}^{-1}$  and for ATP is  $0.053 \text{ MJ mol}^{-1}$ , that is, glucose energy conversion via NADH is 94% efficient and that via ATP is 68% efficient. Therefore, there is not a direct link between the energy content of the glucose (or substrate) molecule and the energy expended to make the product. The production value (PV) will always be less than GV (or SEV) as predicted by Equation 3 or 5, hence:

$$\text{PV} = E_g \text{GV} = E_g \text{SEV} \quad (6)$$

where:  $E_g$  = growth efficiency; GV = glucose value; SEV = substrate equivalent value; and PV = true production value. Lafitte and Loomis (1988) showed that the efficiency in plant processes varied between 0.84 and 0.89 and that range was used here.

Once the production value (PV) is known, and the stoichiometry of the substrate and product are known, then the amount of  $CO_2$  produced ( $[C]_{CO_2}$ ) per 100 C atoms of the substrate can be calculated as:

$$[C]_{CO_2} = \frac{100}{[C]_{sub}} ([C]_{sub} - \text{PV}[C]_{pro}) \quad (7)$$

Equations 3–7 were applied to the organic matter reservoirs and fluxes shown in Figure 1 and the reactions considered were:

1. Primary production (glucose) to above-ground biomass
2. Primary production (glucose) to below-ground biomass

3. Above-ground biomass to litter
4. Below-ground biomass to litter
5. Litter to surface peat
6. Surface peat to deep peat

Where the deep peat is defined as the peat composition at 1 m depth in the peat profile on the basis of evidence from Worrall et al. (2018) that showed there was no further change in the peat below 40 cm at the study site (see Study Site). Deep peat in this study is the same as catotlemic peat for this site. Further, the reaction of surface to deep peat (reaction 6) was considered separately via the production of dissolved organic matter (DOM), CO<sub>2</sub> and CH<sub>4</sub>.

Once the PV and [C]<sub>CO2</sub> are known for each reaction listed above, then the consequences for N and O follow. It was assumed that inorganic N and O were available, but the species were not constant and alternative electron acceptors were available (e.g., SO<sub>4</sub>). However, as described below, the presence of terminal electron acceptors other than N and O were used as means of testing, validating and constraining the predictions of this approach. The reactions were balanced with respect to C, carbon oxidation state (C<sub>ox</sub>), O and N. Reactions were finally balanced with respect to H, but it was assumed that plentiful protons were available. Equations 3–7 were fitted to the 6 pathways identified using a simulated annealing approach based upon minimizing the root mean square error.

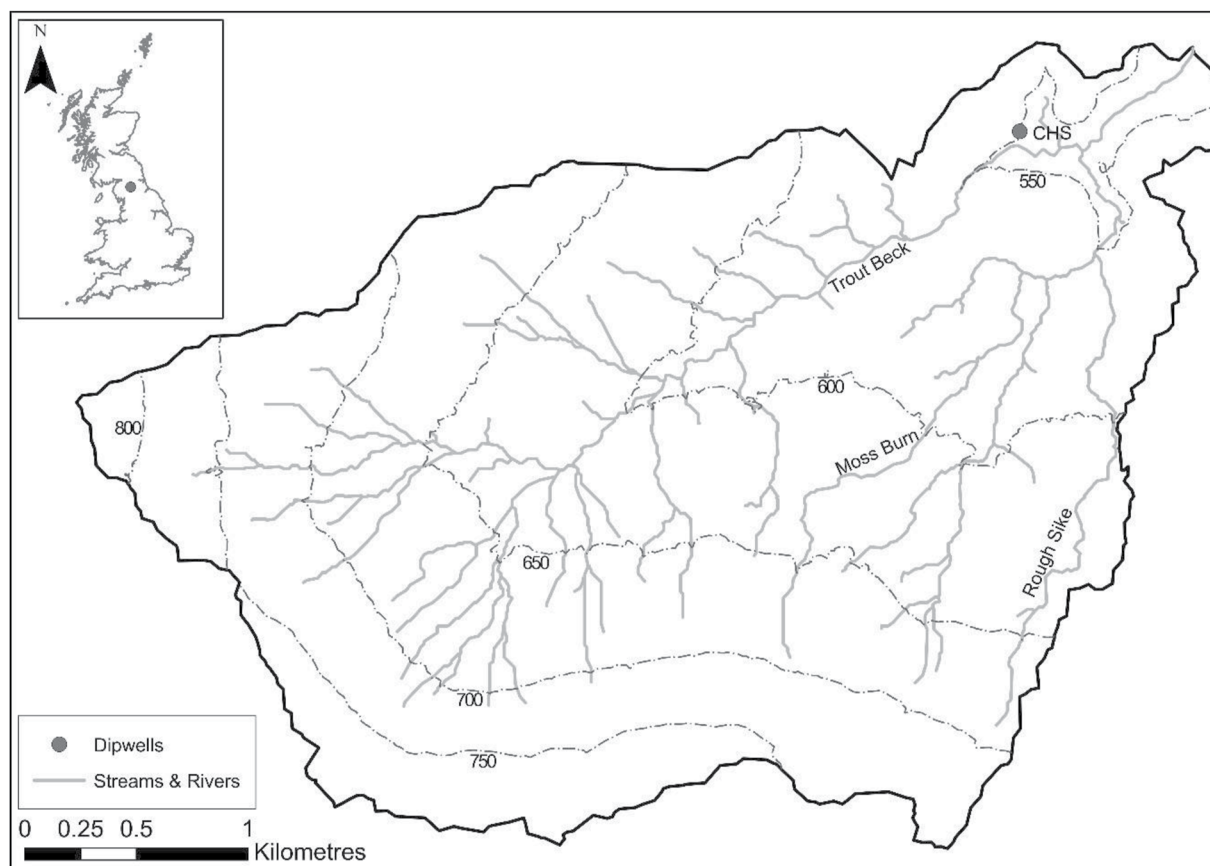
It has already been recognised that there is an uncertainty associated with the value of  $E_g$  (growth efficiency) but there is also a sampling and measurement variance associated with the measurement of the elemental composition of the organic matter reservoirs and pathways. Therefore, to assess the uncertainty in the above calculations, the transition between primary productivity and litter was considered. The transition between primary productivity and litter is the first transition between two measured compositions, as opposed to the first transition considered (glucose to primary productivity) where one of the compositions (glucose) has a fixed composition. The replicate measurements of the composition of the above-ground biomass and litter were used to give the median and the interquartile range (IQR). Using the IQR, 200 values were drawn at random assuming the ranges defined uniform distributions. Production value (PV) and [C]<sub>CO2</sub> were then calculated and the errors read from the resulting distributions.

To constrain and validate the predictions of the above calculations, it was possible to compare to observations of the presence and distribution of terminal electron acceptors (Boothroyd et al., 2021) and the elemental budget, already available for the study site (Boothroyd et al., 2021; Worrall et al., 2009, 2012).

## 2.1. Study Site

The study site was the Moor House National Nature Reserve blanket peat catchment in the headwaters of the River Tees (54°41'18"N, 2°22'45"W; Figure 2). The study site lies within Moor House National Nature Reserve (NNR), a terrestrial and freshwater site which is part of the UK Environmental Change Network (ECN). The ECN collects various chemical and hydrological data from the Trout Beck catchment relevant to this study (Sykes & Lane, 1996).

The study site lies largely above 500 m O.D.; the highest point in the reserve is the summit of Great Dun Fell at 848 m O.D. The underlying geology is a succession of Carboniferous limestones, sands and shales with intrusions of the doleritic Whin Sill (Burt & Tucker, 2020; Johnson & Dunham, 1963). This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat during the Holocene. The mean annual temperature (1931–2000) was 5.2°C; air frosts were recorded on over 100 days in a year (1991–2000, Holden, J. & Rose, R. (2001)). Mean annual precipitation (1953–1997) was 1953 mm (Burt et al., 1998) with snow representing a noteworthy proportion: annual average snow cover at 500 m is 55 days (Archer & Stewart, 1995). The vegetation is dominated by *Eriophorum sp.* (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum sp.* (moss). Except for an area of experimental plots, none of the catchment area has experienced prescribed burning or wild-fire since 1954 (Garnett et al., 2000).



**Figure 2.** Map of Moor House study catchment. CHS shows Cottage Hill Sike stream water sampling location. Numbers refer to altitude in meters.

## 2.2. Carbon and Dry Matter Budget

The study considers the ecosystem as a series of carbon pools and fluxes (Figure 1). The dry matter budget of the catchment was first recorded by Forrest (1971) who studied the productive ecology of the dominant species. Forrest (1971) did include litter production rates but not their subsequent decay and peat formation rates, so this study will combine the study of dry matter production with a carbon budget. The study site has been the subject of several studies of the carbon budget of its peat soils and these carbon budgets can be used in conjunction with the elemental analysis to constrain the effective oxidation state and the photosynthetic stoichiometry. 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) but reported in the N budget for the site (Worrall et al., 2012). Worrall et al. (2009) summarized the carbon budget as:

$$100C_{pp} \Rightarrow 35C_R + 26C_{DOC} + 4C_{CH_4} + 4C_{dissco_2} + 9C_{POC} + 22C_{RES} \quad (8)$$

(±4.7) (±21) (±0.6) (±4) (±4.5) (±26)

where:  $C_x$  = carbon from the following uptake or release pathways, where  $x$  is: pp = primary productivity,  $R$  = net ecosystem respiration, DOC = dissolved organic carbon;  $CH_4$  = methane;  $dissco_2$  = dissolved  $CO_2$ ; POC = particulate organic carbon; and RES = residual carbon stored in the soil. The values in the parentheses beneath the coefficients in Equation (viii) are the 95th percentile confidence interval.

Over the 13 years of the study considered by Worrall et al. (2012), the total carbon flux varied between  $-20$  and  $-91$  tonnes  $C \text{ km}^{-2} \text{ yr}^{-1}$  and by far the biggest single component of the budget was the uptake of carbon by primary productivity (average across the study period of  $176$  tonnes  $C \text{ km}^{-2} \text{ yr}^{-1}$ ). Given the confidence intervals for Equation 8, it is possible at approximately a 5% chance that the peat soils were a net source; however, this was never observed during the 13 years. Furthermore, the N, S and Fe budgets for this study site have been published

(Boothroyd et al., 2021; Worrall et al., 2012) and these can be used to confirm and constrain the predictions of this approach.

### 2.3. Sampling

Given the range of carbon pools and fluxes identified in Figure 1 the following sampling was carried out.

Peat cores to 1 m depth in two locations were collected with a gouge auger. Both 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, then one sample taken between 95 and 100 cm depth. Peat core samples were dried at 105°C and their bulk density measured prior to further processing.

Six quadrats (0.5 × 0.5 m) were randomly located in the Cottage Hill Sike catchment. In three of the quadrats the entire above-ground biomass was quantitatively recovered. For the three other quadrats, the total above-ground, living biomass was collected but separated by functional group: shrubs (dominantly *Calluna vulgaris*, henceforward referred to as *Calluna*); grasses and sedges (dominantly *Eriophorum sp.*, henceforward referred to as grass/sedge); and mosses (including *Sphagnum spp.*, henceforward referred to as mosses). From within these quadrats samples of litter and below-ground biomass were recovered but not quantitatively. Quantitative biomass samples were dried to 105°C and weighed before further analysis while for the litter and below-ground biomass these samples were dried to 105°C before further analysis.

Three sources of DOM were sampled: first, stream water from a first-order stream, that is, as water emerges from the peat profile of water; second, from shallow peat pore water; and third, from deep peat pore water. First-order stream samples were collected monthly from October 2011 to September 2013 except for months where winter conditions precluded taking flowing water samples (21 samples in total). For peat soil pore water, 12 dipwells were installed horizontally into a gully wall, with six each at shallow (mean 28 ± 3 cm) and deep (mean 75 ± 6 cm) depths in November 2016—the sampling and seasonal differences in the DOM composition are discussed in Boothroyd et al. (2021). All the dipwells had holes every 10 cm and were blocked with rubber bungs at both ends to allow infilling of peat pore water. The dipwells were all 1 m long with at least 90 cm inserted into the peat. The pore water from the sets of dipwells at the two depths in the gully wall were drained for pore water samples monthly from December 2016 to March 2017. The DOM and POM were extracted from the water samples using methods developed by Worrall, Clay, et al. (2016) and Boothroyd et al. (2021). Water samples were allowed to settle overnight (a minimum of 16 hr) prior to sample preparation to allow separation of particulate (POM) and dissolved (DOM) components. Peat pore water was subsequently extracted by syringing water from the surface so as not to disturb the settling layer of particulates. First-order stream water samples were drained from the 20 L water carrier directly via a tap that was above the settled layer. All supernatant samples were placed into evaporating dishes and placed in a drying oven at ~80°C until all water was evaporated and DOM could be recovered as a solid sample for compositional analysis. By using settling as means of separation, no arbitrary filtration cut-off was being applied, rather this study was defining DOM as being that component which was either colloidal or truly dissolved.

The DOM composition  $C_{ox}$  values were tested using analysis of variance (ANOVA). The ANOVA was considered with one factor which was the source of the DOM sample, this factor had three levels—first-order stream, shallow peat pore water, and deep peat pore water. The  $C_{ox}$  were tested for normality (using the Anderson-Darling test) prior to ANOVA and it was unnecessary to transform the data. Post hoc analysis was performed between factor levels using the Tukey test. This ANOVA was performed as we had hypothesized that there would be a significant difference in the  $C_{ox}$  of DOM across the peatland, and if so this would have consequences for the role of DOM as product of the reactions of organic matter entering peat soil.

### 2.4. Radiocarbon Dating

To understand the rates of transformation and the sources of the transformation products, peat soil samples and DOM samples from both the stream and soil water were selected for radiocarbon dating. Samples were graphitized in preparation for  $^{14}C$  abundance measurement at the Carbon, Water and Soils Research Lab in Houghton, Michigan. Peat samples were treated with successive washes of acid (1 N HCl) and base (1 N NaOH) to remove any materials which may have adhered to the surfaces of the organics. Dissolved organic matter samples received

no chemical pre-treatment. Samples were then weighed into quartz tubes and sealed under vacuum. Samples were combusted at 900°C for 6 hr with cupric oxide (CuO) and silver (Ag) in sealed quartz test tubes to form CO<sub>2</sub> gas. The CO<sub>2</sub> was then reduced to graphite through heating at 570°C in the presence of hydrogen (H<sub>2</sub>) gas and an iron (Fe) catalyst (Vogel et al., 1987). Graphite targets were then analyzed for radiocarbon abundance by Accelerator Mass Spectrometry at the DirectAMS facility in Bothell, WA (Zoppi et al., 2007), and corrected for mass-dependent fractionation following Stuiver and Polach (1977). Long term depth and carbon accumulation rates were calculated from the least squares regression between radiocarbon ages and depth and depth corrected for bulk density and C content of peat samples.

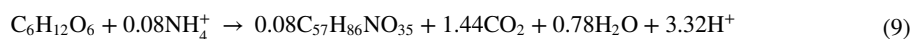
### 2.5. Sample Analysis

Triplicate samples of all the collected samples (above-ground and below-ground vegetation, litter, peat soil, and DOM) once dried to 105°C, were then milled to a sub-mm powder using a Spex 6770 Freezer Mill. The ground samples were then subject to CHN and 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 and O set ups, a 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, three times on the CHN set up and a further three times on O set up, and a mean calculated for C, H, N and O. All samples were corrected for their measured ash content. Measurements for S content were made using a 121 Vario MAX CNS analyzer (Elementar, Langensfeld, Germany). Based on duplicate measurements of S content, high precision was achieved with relative standard deviation (RSD) of 0.51%.

## 3. Results

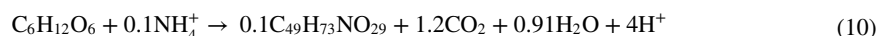
The results of the elemental analysis are summarized in Table 1 (See also Table S2 in Supporting Information S1), the SEV are given in Table 2, and illustrated in Figure 3. The ANOVA of the DOM  $C_{ox}$  values showed there was significant difference ( $P < 0.01$ ) due to the source of the DOM and that this difference explained 45% of the variance in the original data set. The post hoc analysis shows that the significance difference was due to the difference between stream water DOM and the peat pore water DOM but that there was no significant difference between the shallow and deep peat pore water DOM. The stream water DOM is highly oxidized ( $C_{ox} = 0.4$ ) compared to the reduced DOM of the peat pore water (shallow  $C_{ox} = -0.3$ ; deep  $C_{ox} = -0.22$ ). This result gives us separate possibilities for assessing the transformation of surface to deep peat (reaction 6).

For the formation of above-ground biomass from primary productivity (glucose) at this site leads to a stoichiometry of:



In the case of Equation (9) the comparative C:N ratios of the substrate and product shows that additional N is required; however, the comparative  $C_{ox}$  of the substrate and product shows that an electron acceptor is not required. In a peat profile, reducing conditions will persist especially at root depth and so the form of nitrogen supplied to the roots would be ammonium and not nitrate. The glucose value (GV) of the above-ground biomass was  $0.61 \pm 0.01$  g of product/g of glucose. Equation 9 implies that for every 1g of above-ground biomass 0.55 g of C is sequestered from the atmosphere. Further, that for every 100 C fixed as glucose then 76 C will be fixed as above-ground biomass and 24 will be lost as CO<sub>2</sub>.

For below-ground biomass from primary productivity (glucose):



This would give the GV of the below-ground biomass as  $0.67 \pm 0.01$  g of product/g of glucose; and Equation 10 implies that for every 1g of below-ground biomass 0.56 g of C is sequestered from the atmosphere. Given that Forrest (1971) found that total primary productivity divided 67% to above-ground biomass, then for 100g C sequestered as glucose 26.5 g C are released as CO<sub>2</sub> and 73.5 g retained as biomass be that above- or below-ground biomass.

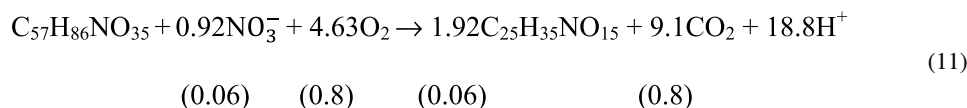


**Table 1**  
The Average Composition of the Carbon Pools Considered by the Study

Carbon pool	Elemental analysis (mol/100g)				Median stoichiometry	C <sub>ox</sub>
	C	H	N	O		
DOM first-order stream	3.8 ± 0.1	4.6 ± 0.2	0.12 ± 0.01	2.9 ± 0.1	C <sub>31</sub> H <sub>38</sub> NO <sub>24</sub>	0.4 ± 0.08
DOM shallow peat porewater	4.17 ± 0.18	5.24 ± 0.19	0.14 ± 0.009	2.06 ± 0.03	C <sub>29</sub> H <sub>41</sub> NO <sub>15</sub>	-0.31 ± 0.05
DOM deep peat porewater	4.05 ± 0.16	5.80 ± 0.65	0.13 ± 0.005	1.97 ± 0.08	C <sub>30</sub> H <sub>39</sub> NO <sub>15</sub>	-0.22 ± 0.16
POM	4.05 ± 0.02	6.40 ± 0.09	0.18 ± 0.01	2.50 ± 0.02	C <sub>22</sub> H <sub>35</sub> NO <sub>14</sub>	-0.21 ± 0.03
Above-ground biomass	4.15 ± 0.12	6.30 ± 0.09	0.07 ± 0.015	2.55 ± 0.06	C <sub>57</sub> H <sub>86</sub> NO <sub>35</sub>	-0.26 ± 0.04
Below-ground biomass	4.23 ± 0.1	6.30 ± 0.09	0.09 ± 0.01	2.48 ± 0.06	C <sub>49</sub> H <sub>73</sub> NO <sub>29</sub>	-0.25 ± 0.04
Grass and sedge	4.04 ± 0.1	6.30 ± 0.09	0.12 ± 0.01	2.59 ± 0.06	C <sub>33</sub> H <sub>52</sub> NO <sub>21</sub>	-0.19 ± 0.04
Mosses	4.03 ± 0.1	6.30 ± 0.09	0.07 ± 0.01	2.65 ± 0.06	C <sub>95</sub> H <sub>145</sub> NO <sub>56</sub>	-0.19 ± 0.04
Calluna	4.29 ± 0.1	6.58 ± 0.09	0.05 ± 0.01	2.53 ± 0.06	C <sub>55</sub> H <sub>86</sub> NO <sub>46</sub>	-0.32 ± 0.04
Litter	4.17 ± 0.08	5.90 ± 0.1	0.167 ± 0.007	2.48 ± 0.08	C <sub>25</sub> H <sub>35</sub> NO <sub>15</sub>	-0.05 ± 0.05
Peat soil (0–5 cm)	4.18 ± 0.01	6.00 ± 0.6	0.10 ± 0.01	2.53 ± 0.11	C <sub>39</sub> H <sub>56</sub> NO <sub>26</sub>	-0.10 ± 0.15
Peat soil (45–50 cm)	4.44 ± 0.4	5.3 ± 1.4	0.08 ± 0.02	2.40 ± 0.24	C <sub>57</sub> H <sub>68</sub> NO <sub>31</sub>	-0.02 ± 0.33
Peat soil (90–100 cm)	4.47 ± 0.21	5.27 ± 0.76	0.08 ± 0.02	2.37 ± 0.13	C <sub>75</sub> H <sub>107</sub> NO <sub>45</sub>	-0.07 ± 0.18
Lignin	5.14 ± 0.01	6.03 ± 0.1	0.06 ± 0.005	1.81 ± 0.01	C <sub>87</sub> H <sub>103</sub> NO <sub>31</sub>	-0.43 ± 0.02
Cellulose	3.60 ± 0.005	6.25 ± 0.24	0.00	3.21 ± 0.01	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.05 ± 0.06
Humic acid	2.99 ± 0.01	3.68 ± 0.09	0.06 ± 0.005	2.02 ± 0.02	C <sub>49</sub> H <sub>60</sub> NO <sub>33</sub>	0.19 ± 0.04
Protein	4.72 ± 0.06	5.42 ± 0.17	1.24 ± 0.04	1.28 ± 0.05	C <sub>5</sub> H <sub>5</sub> NO	0.18 ± 0.05

Note. Variation is given as the 95th percentile range. Median stoichiometry is expressed relative to nitrogen content except for cellulose which expressed relative to carbon. For comparison values for lignin, cellulose, protein (gluten) and humic acid have been added from Worrall, Clay, et al. (2016).

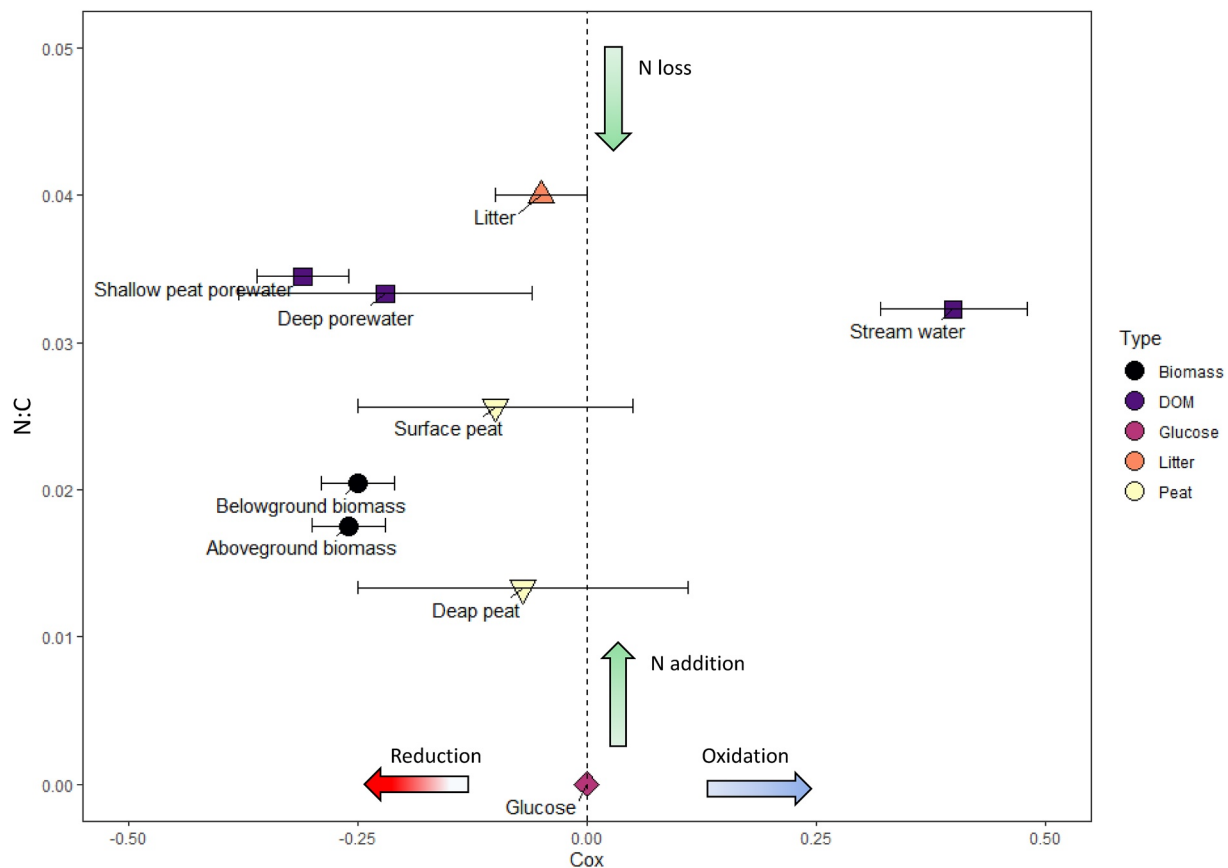
With regard to the production of litter from above-ground biomass, the best-fit equation was:



Given that uncertainty analysis was performed on this transition, the numbers in the brackets represent the semi-interquartile range in the coefficients. For future transitions and reactions these semi-interquartile ranges were expressed as percentage variation in the coefficients: ±3% in the PV and ±9% in the [C]<sub>CO2</sub>. In the case of production of litter, the C:N ratio of the substrate and the product means that a source of N is required and given that production is occurring at the surface exposed to atmosphere, it has been assumed that nitrate is available and that oxygen is present as the electron acceptor. Given 100 g C as above-ground biomass, then 84g C would

**Table 2**  
The Estimated Production Value (PV), CO<sub>2</sub> Production Rate (C-CO<sub>2</sub> per 100 C of Substrate), and Substrate Equivalent Value (SEV)

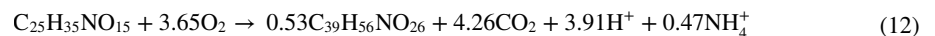
Substrate	Product	PV (g product/g substrate)	[C] <sub>CO2</sub> (C-CO <sub>2</sub> per 100 C of substrate)	SEV (g product/g substrate)
Glucose	Aboveground biomass	1.08 ± 0.05	1.21	1.25 ± 0.03
Glucose	Belowground biomass	1.10 ± 0.05	1.20	1.27 ± 0.03
Aboveground biomass	Litter	0.92 ± 0.04	9.11	1.07 ± 0.04
Litter	Surface peat	0.89 ± 0.03	4.26	1.01 ± 0.02
Surface peat	DOM	0.82 ± 0.05	2.27	0.93 ± 0.05
Surface peat	Deep peat	0.96 ± 0.06	6.41	1.10 ± 0.07
Surface peat	CH <sub>4</sub>	28.7 ± 1.4	22.22	32.68 ± 1.15



**Figure 3.** Summary of analyzed compositions with N:C versus  $C_{ox}$  and illustrating the reaction trends. Data are given as mean and confidence interval for the  $C_{ox}$  and N:C, for the latter the confidence interval is smaller than the size of the plotted point.  $CH_4$  and  $CO_2$  would plot outwith the frame of the plot at  $-4$  and  $+4$  respectively. Note that this plot uses N:C, and not C:N, so that samples respect their relative position with depth through the peat profile.

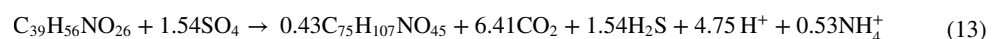
become litter and 16 g C lost as  $CO_2$ . At steady state of 100 g C sequestered as glucose primary production, 61 g C would remain as litter and 38 g C would be lost as  $CO_2$ .

For the litter to the surface peat:



For every 100 C making this transition 17 g are lost as  $CO_2$  and 83 g are retained as surface peat. Given the assumption of steady state, then of the 100 g C fixed as glucose then 51 enter surface peat and 49 g C are lost as  $CO_2$ . In the case of transfer of litter to surface peat, the respective C:N ratios of the substrate and product means that N is lost in to solution. This production of N (as  $NH_4^+$ ) into the solution is recycling it to be available for other reactions and particularly for nutrients to grow above-ground biomass (Equation 9). However, given the fact that the reaction will occur near the surface and that N is not needed as an electron acceptor to convert the substrate, then oxygen is available for conversion of ammonium to nitrate.

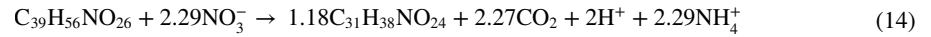
The production of deep peat without the production of DOM or  $CH_4$ , is



As with the production of surface peat, the relative C:N ratios show that N will have been released by this reaction, again the process by which the nutrient is recycled to primary production. The relative oxidation states of the substrate and product shows that an oxidant is required, but given that N is released, then an alternative to N is required. In this case we have assumed that sulfate would be the terminal electron acceptor. For every 100 g C transitioning from surface to deep peat then 16 g C would be lost as  $CO_2$ . Again, assuming steady state, then of

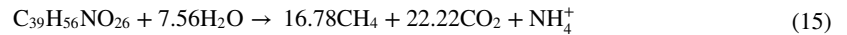
100 g C sequestered as glucose entering as primary production, 47 g C would be left as deep peat and 53 g C would be lost as CO<sub>2</sub>.

When the pathway to stream water DOM is considered then:



Through this pathway only 6% of the C would be lost as CO<sub>2</sub> which reflects the highly oxidized nature of the stream water DOM. Second, stream water DOM formation does not require an N source but does require an oxidant. If the process were occurring high in the profile, then the oxidant may well be oxygen but in Equation 14 we have given nitrate as the terminal electron acceptor. For every 100g C exported as DOM, 7 g C are lost as CO<sub>2</sub>, and for every 100 g C fixed as glucose then this production to DOM would mean that 50 g C would be lost as CO<sub>2</sub>, but it is more appropriate to consider the amount of CO<sub>2</sub> produced per DOC and so for every 100 g C lost as DOC then 6 g C are lost as CO<sub>2</sub>. When DOM was considered as the oxidized end product rather than CO<sub>2</sub>, as in Equation 13, then there is no formation of deep peat; the energy released in the formation of DOM was too small to make it possible to form any deep peat. That is the formation of stream water DOM is an end in itself and not a pathway to deep peat.

Finally, there is the possibility of methane production:



The change in C<sub>ox</sub> and C; N across the reaction means that N is released but also that there are no residual products (i.e., deep peat) as the energy required to produce CH<sub>4</sub> is too great. Equation 15 can be viewed as a disproportionation reaction as both reduced and oxidized forms of C are produced relative to the initial substrate. In this case the balance of CO<sub>2</sub> to CH<sub>4</sub> in Equation (15) is governed by the C<sub>ox</sub> of the substrate. If it were glucose (C<sub>ox</sub> = 0) reacting to CH<sub>4</sub>, then exactly the same amount of CH<sub>4</sub> and CO<sub>2</sub> would be produced. However, the surface peat is slightly reduced (C<sub>ox</sub> = -0.1; Table 1), and therefore produces more CO<sub>2</sub> than CH<sub>4</sub>. Note that in our approach we have assumed that there are sufficient acid-base groups to give charge balance. The C<sub>ox</sub> of the substrate means there is insufficient oxygen for the amount of CO<sub>2</sub> required for the energetics of the reaction. For every 100 g C produced as CH<sub>4</sub> then 135 g C would be lost as CO<sub>2</sub>, but for every 100 g C sequestered as glucose none would be left as deep peat and 78 g will have formed CO<sub>2</sub> and 22 g as CH<sub>4</sub>.

The problem is that we know that all three of Equations 13–15 must be occurring as residual peat, DOM and CH<sub>4</sub> are all produced from most peatlands and certainly from this peatland (Worrall et al., 2003). Therefore, we can consider a series of simultaneous reactions. First, the carbon budget of any peatland can be considered as:

$$\alpha C_{pp} - \beta C_{POC} = \chi C_{DOM} + \delta C_{CH_4} + \epsilon C_{RES} + \gamma C_{CO_2} \quad (16)$$

where:  $\alpha, \beta, \chi, \delta, \epsilon, \gamma = \text{constants}$ . Equation (16) is a generalization of Equation 8 where  $C_{POC}$  has been considered as entirely a result of physical rather than biogeochemical process and so taken as subtracting from the primary productivity ( $C_{PP}$ ). From the above values of  $C_{CO_2}$  for each of the processes that produce deep peat, DOM and CH<sub>4</sub> ( $C_{RES}$ ,  $C_{DOM}$ , and  $C_{CH_4}$ ) (Equations 9–15), therefore Equation (16) becomes:

$$C_{CO_2} = 0.07C_{DOM} + 3.54C_{CH_4} + 1.13C_{RES} \quad (17)$$

Therefore, combining Equations 16 and 17:

$$C_{pp} - C_{POC} = 1.07C_{DOM} + 4.35C_{CH_4} + 2.13C_{RES} \quad (18)$$

Note that the form of the coefficients in Equation (18) comes from Equations 5 and 6 which for example, for DOM gives:

$$1.07 = 2 - E_g SEV_{pp}^{DOM} \frac{[C]_{DOM}}{[C]_{pp}} \quad (19)$$

Equation 18 has too many unknowns to solve. However, it is possible to compare Equation 18 to Equation 8. Equation 18 predicts that  $C_{pp} - C_{POC} = 92 \pm 4$ , whereas the observed value based on Equation 8,  $C_{pp} - C_{POC} = 91 \pm 5$ , that is, the two values overlap within the stated uncertainties.

**Table 3**  
Concentrations of Redox Active Species in the Soil Water of the Study Site

	Shallow (10 cm)		Deep (50 cm)	
	Median	IQR	Median	IQR
Sulfate <sup>a</sup>	0.11	0.05 to 0.20	0.02	0.00 to 0.04
Nitrate	0.01	0.00 to 0.02	0.01	0.00 to 0.02
Ammonium <sup>a</sup>	0.06	0.04 to 0.08	0.42	0.39 to 0.46
Iron <sup>a</sup>	0.17	0.13 to 0.24	0.21	0.18 to 0.24
DOC <sup>a</sup>	21.3	18.0 to 26.7	17.5	16.4 to 18.8
Conductivity <sup>a</sup>	39.1	32.6 to 45.1	31.4	29.6 to 35.2
pH <sup>a</sup>	4.3	4.1 to 4.4	4.6	4.2 to 4.6

<sup>a</sup>Denotes Comparison Between the Shallow and Deep Soil Water Samples That are Significantly Different.

### 3.1. Radiocarbon Ages

For the DOM at Moor House the shallow peat pore water had a date of 1515–1740 <sup>14</sup>C yr BP; the deep peat pore water had a date of 2060–2205 <sup>14</sup>C yr BP; and the stream water DOM is measured as modern (all dates supplied in Table S3 in Supporting Information S1).

The best-fit depth accumulation is:

$$\text{Depth} = 0.047 \text{Age} \quad n = 10, \quad r^2 = 0.98 \quad (20)$$

(0.002)

The best fit C accumulation ( $C_{\text{sum}}$  gC/cm<sup>2</sup>) is:

$$C_{\text{sum}} = 40 \text{Age} \quad n = 10, \quad r^2 = 0.98 \quad (21)$$

(1.4)

where: Age in <sup>14</sup>C year BP.

Therefore, the long term carbon accumulation rate (LARCA) for Moor House is  $-40 \pm 2.7$  gC cm<sup>-2</sup> yr<sup>-1</sup>. This LARCA value is within the range of the C budget published for this site ( $-20$  to  $-90$  g cm<sup>-2</sup> yr<sup>-1</sup>; Worrall et al., 2012). Given the nominal depth of sampling of the peat pore water DOC at Moor House of 25 and 75 cm, then the expected ages of the DOC that would in equilibrium with the surrounding peat would be 722 years BP and 1550 years BP respectively. The ages of the pore water DOC are older than their putative depths but they are also much older than the DOC that was present in the first-order stream.

## 4. Discussion

This study used a well-studied catchment and showed that the measured carbon budget is constrained by the stoichiometry and redox status of the organic carbon. The study could constrain the C budget to within three bounding equations (Equations 13–15) but could not specify the proportion of the carbon release species.

If the first test of the approach of this study was a comparison to the known C budget of the study catchment (Equation 8), a possible further test of this approach is to consider the change in the observed soil pore water redox species. Between October 1992 and December 2014, the soil water at 10 and 50 cm depths at the study site were sampled in a nest of six suction samplers 538 and 534 times respectively (Boothroyd et al., 2021). The concentration ranges of the redox-active elements for which there were monitoring records are detailed and compared in Table 3; conductivity and pH are included for context. Even by 10 cm depth nitrate is present in only residual quantities; ammonium is detectable and increases in concentration by 50 cm depth. This change in N species is consistent with the processes proposed in Equations 10–14, that is, that nitrate is only present in the litter layer and that it is ammonium that is recycled and available to plant roots at depth.

Sulfate is being removed between depths of 10 and 50 cm and this is consistent with Equation 13. Equation 13 implies that for every mole of SO<sub>4</sub>, 4.13 mol of CO<sub>2</sub> are produced, or in mass terms, for every g of S-SO<sub>4</sub> removed then 1.54 g of C-CO<sub>2</sub> is produced. Furthermore, that for every 1 g of surface peat, then 0.78 g of deep peat would be formed via the pathway described in Equation 13. Alternatively, 1 g of C entering as surface peat would result in 0.82 g as deep peat, but this transition would require 0.11 g S-SO<sub>4</sub>. Boothroyd et al. (2021) examined the S budget of this peatland and found that the maximum capacity to reduce atmospherically deposited SO<sub>4</sub> was 1.75 tonnes S km<sup>-2</sup> yr<sup>-1</sup>, which would mean that 15.9 tonnes C km<sup>-2</sup> yr<sup>-1</sup> was being processed by this route which would produce 13.0 tonnes C km<sup>-2</sup> yr<sup>-1</sup> as deep peat ( $C_{\text{RES}}$ –Equation 13). Given the C budget for this site is between  $-20$  and  $-91$  tonnes C km<sup>-2</sup> yr<sup>-1</sup> with a median value of 56 tonnes C km<sup>-2</sup> yr<sup>-1</sup> (Worrall et al., 2012), this means that Equation 13 represents between 14% and 62% of deep peat production.

The above approach only considered O, N, S and C as terminal electron acceptors. The routine monitoring of peat pore water did include Fe but did not differentiate between ferric and ferrous iron. Analysis of the pore water does show a significant increase in Fe in pore water with depth suggesting that Fe might be reduced and mobilized in the deeper peat pore water and that Fe could be terminal electron acceptor. Boothroyd et al. (2021)

did consider the total Fe budget of the studied peatland and showed that, while the atmospheric deposition flux of Fe to the peatland varied from 8.7 to 129 kg Fe km<sup>-2</sup> yr<sup>-1</sup>, there was a significant decline in flux over the period. The concentration of Fe in the peat pore water (Table 3) is at least an order of magnitude higher than the concentration in the precipitation: the concentration of Fe in precipitation had a median value of 0.02 mg l<sup>-1</sup> in 1992 but declined to a median 0.00 mg l<sup>-1</sup> by 2012. Equally, the average concentration of Fe in the Cottage Hill Sike (Figure 2–CHS) was 0.52 mg l<sup>-1</sup>. The flux of Fe from CHS was between 0.38 and 1.39 tonnes Fe km<sup>-2</sup> yr<sup>-1</sup> with no significant trend over the study period. Therefore, this peat-covered catchment is actually a net source of Fe. The source of Fe in the study catchment is likely to be mineral sulphides in the underlying rocks. Given the nature of the study catchment, the flux values and concentrations of Fe present, then Fe does not represent an important terminal electron acceptor at this site. In many terrestrial environments Mn can act as a terminal electron acceptor: there is no information on Mn for this catchment.

The concentration of DOC in the peat soil water is far in excess of the other monitored redox components, and, furthermore, there is a significant decrease in the DOC concentrations between the monitored depths, which could imply that DOM is being consumed (Table 3). The elemental analysis performed in this study has shown that the DOM in the first-order stream is oxic relative to the DOM in peat pore water. Data from this study shows that if a mole of DOC of the stream water composition (Table 1) did transition into DOC in the shallow peat pore water then an average of 0.7 mol of electrons would be available. Note that this is not the same as the redox buffering capacity of the DOM as measured by Bauer et al. (2007). Therefore, the transition from surface to deep peat based upon using surface water DOM as a terminal electron acceptor would be:



Equation 22 shows that for every 1 g of surface peat then 0.82 g of deep peat would be formed via the pathway described in Equation 13. Alternatively, 1 g of C entering as surface peat would result in 0.85 g of C as deep peat, but this transition would require 0.79 g DOC, resulting in 0.74 g of DOC in the peat pore water and releasing 0.19 g of C as CO<sub>2</sub>. Unlike for SO<sub>4</sub>, for Equation 22 we have no measure of how much DOM makes the transition into the deep peat pore water. For the study catchment the DOC flux via stream water is between 12 and 85 tonnes C km<sup>-2</sup> yr<sup>-1</sup> (median = 47 tonnes C km<sup>-2</sup> yr<sup>-1</sup>) and so there is considerable amount of DOC available.

This analysis assumes several things about the nature of flow paths of the DOM. First, that the first-order stream water DOM represents the oxidized end member of the DOM composition and that this oxic DOM is created at depths shallower than sampled in this study, that is, less than 25 cm depth. This first assumption is supported by the evidence of Equation 14 that the oxic stream water DOM was created whilst there was still nitrate but not oxygen available. Second, that there is some transfer of DOM through the peat profile. Studies of the flow paths in the catchment have shown that sampled peat pore water, as summarized in Table 3, does contribute to the first-order streams (Worrall et al., 2003), but this study did not consider the transfer of DOC. Equally, Clay et al. (2010) showed the link between peat pore water and surface runoff composition, but again DOC was not considered in that study.

Alternatively, there does not have to be flux of water down the peat profile for there to be a flux and loss of DOC down the peat profile: there could be diffusion of DOC down the peat profile driven by loss of DOC at depth. Observations of the peat pore water DOC concentrations (Table 3) shows that there is a long-term concentration difference of 3.8 mgC l<sup>-1</sup> (or a difference of 18%) between 10 and 50 cm depth in the peat profile. This concentration difference could be due to turnover of DOC down the peat profile, and which could provide energy for the formation of deep peat. Lovley et al. (1996) have shown that DOM can act as a TEA and divert energy from methanogenesis, while Bauer et al. (2007) found that DOM could act as a redox buffer. Gao et al. (2019) found that CH<sub>4</sub> formation occurred only after the electron accepting capacity (EAC) of organic matter was depleted. Gao et al. (2019) found that the total EAC of organic matter was dominated by POM, which was key in inhibiting methanogenesis, but DOM was nonetheless important and it was speculated that DOM electron accepting moieties were more readily utilized as TEAs than POM and may influence POM reduction by electron shuttling (Gao et al., 2019). However, and as with the flux DOC between peat pore water and the first-order stream (Equation 22), we do not know how much DOC makes the transition down the peat profile and therefore how much DOC is lost. Although there is no significant difference in C<sub>ox</sub> down the peat profile, there is a significant change in the degree of unsaturation down the peat profile (Clay & Worrall, 2015) and that implies that condensation reactions are occurring down the peat profile. The radiocarbon ages of stream and soil water DOM suggest that

there is no mixing between these two types of DOM. The distinct ages of the stream and soil water DOM does confirm that the reactions represented by Equations 14 and 22 are distinct pathways. Furthermore, the difference in radiocarbon ages between the stream water of peat pore water DOC suggests diffusion and loss of DOC down through a static pore water profile rather than flow and mixing of water. Given the S budget for this study area can account for an average 59% of the deep peat production then the DOC pathway of Equation 22 might have to account for between 38% and 86% with a median of 62% of the deep peat production or a median value 35 tonnes C km<sup>-2</sup> yr<sup>-1</sup>. The production of 35 tonnes C km<sup>-2</sup> yr<sup>-1</sup> of deep peat via the pathway given in Equation 22 results in a 2.1 tonnes C km<sup>-2</sup> yr<sup>-1</sup> loss of DOM or only 4.4% of the median DOC flux from the streams of the study site, that is, only a small proportion of the DOC flux needs to be diverted to give the required terminal electron acceptors. As noted above, Beer and Blodau (2007) showed that the peat soil water was closed at depth and that this limited the extent of reaction. This closure at depth implies that there is no, or at least negligible, transfer of DOM down the profile even by diffusion. It should also be noted that the approach of Beer and Blodau (2007) provides an alternative approach to that of this study, but comes to a similar conclusion. Future research, must consider the transfer of material in and out of peat porewater.

This has been a detailed study of one peatland in northern England—how would these results apply to other settings? In Equation 13 this study has highlighted that presence of SO<sub>4</sub> is vital for the storage of C in deep peat and its role in diverting from reaction pathways that do not result in deep C storage, for example, methanogenesis (Equation 15). Gauci, Fowler, et al. (2004) found, in experimental peat mesocosms, that an addition of 1.5 tonnes S km<sup>-2</sup> yr<sup>-1</sup> led to 30% suppression of CH<sub>4</sub> flux. Furthermore, Gauci, Matthews, et al. (2004) have shown that atmospheric deposition of S to peatlands has decreased CH<sub>4</sub> over industrial history and possibly suppressing CH<sub>4</sub> by the same amount expected from climate change over the same period of their study. Review of Transboundary Atmospheric Pollution (RoTAP, 2012) concluded that atmospheric deposition of S peaked in the 1970s with S emissions having peaked in the UK in 1969 (Zhao et al., 1998). Curtis and Simpson (2014) considered S deposition at 12 upland sites across the UK and found that between 1988 and 2007, 11 of the 12 sites considered showed significant declines over that period with S deposition typically decreasing by a factor of two. Indeed, at the study site there has been a significant decline in S deposition over 23 years of record to 2019 at an average rate 0.03 tonnes S km<sup>-2</sup> yr<sup>-2</sup> from a peak of 2.4 tonnes S km<sup>-2</sup> yr<sup>-1</sup> (Boothroyd et al., 2021). Therefore, we can not only expect that the suppression of CH<sub>4</sub> emissions from peatlands will be decreasing, that is, CH<sub>4</sub> emissions from peatlands will rise, but given Equations 13–15 that storage of deep peat will decrease as S deposition decreases. Equation 13 means that 7.4 tonnes C km<sup>-2</sup> yr<sup>-1</sup> are stored as deep peat at this site for every 1 tonne S km<sup>-2</sup> yr<sup>-1</sup> of S removal from deposition, and so if S deposition at this site is declining at a rate of 0.03 tonnes S km<sup>-2</sup> yr<sup>-2</sup>, then deep C storage is declining at a rate of 0.22 tonnes C km<sup>-2</sup> yr<sup>-1</sup>.

The change in atmospheric S deposition is not independent of other C pathways and decreases in S deposition across the Northern Hemisphere have been related to increases in loss of DOC in rivers from peat headwaters (de Wit et al., 2021; Montieth et al., 2007); this has also been observed within this study catchment (Clark et al., 2005). If decreasing S deposition is leading to increased loss of DOC from peat catchments, this not only means an increase in the direct loss of C from peatlands but also that deep peat formation may be limited via Equation 14 or Equation 22. The nature of blanket bogs is that they exist on slopes and so naturally drain and so DOM is a more important component of the C budget than in other peat deposits such as raised bogs. Therefore, in other settings the processing of DOM to surface water DOM may not be such an important pathway; rather, the transition between shallow and deep peat pore water may become the important alternative redox pathway. Alternatively, the flushing of water through blanket bogs such as that in this study does not occur for peats in raised bogs and the relatively stable water table in raised bogs may lead to greater preservation of organic matter.

## 5. Conclusions

This study has been able to reproduce the C budget of a blanket bog based upon a knowledge of the elemental composition of the major organic matter stores and pathways. The results show that methanogenesis does not result in deep peat formation and the presence of long-term peat storage in this ecosystem relies on sulfate reduction and the processing of pore water DOM. The DOC of the stream water is significantly oxidized relative to the DOC in the peat pore water and its role as a terminal electron acceptor dominates the production of deep peat over the role of sulfate reduction. Given declining S deposition in this study and globally, then the critical constraint is the amount of DOM processing up and down the peat profile.

## Data Availability Statement

All of the equations of the study are collected in Table S1 in Supporting Information S1. The elemental data used in this study is given Table S2 in Supporting Information S1. The radiocarbon dates are given in Table S3 in Supporting Information S1. In addition, data are available from University of Durham data repository <https://collections.durham.ac.uk/%20and%20ark:/32150/r1s7526c436>; <https://doi.org/10.15128/r1s7526c436>.

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