AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2015JG003182

The effective oxidation state of a peatland

Fred Worrall[1], Gareth D. Clay[2], Catherine S. Moody[1], Tim P. Burt[3], and Rob Rose[4]

[1]Department of Earth Sciences, University of Durham, Durham, UK, [2]Geography, School of Environment, Education and Development, University of Manchester, Manchester, UK, [3]Department of Geography, University of Durham, Durham, UK, [4]Environmental Change Network, Centre for Ecology & Hydrology, University of Lancaster, Lancaster, UK

Key Points:

- First time oxidation state is considered for all carbon pools in a single ecosystem
- Shows the relative oxidation states of the terrestrial organic matter
- We can provide an estimate of global terrestrial sinks including fluvial fluxes

Correspondence to:
F. Worrall,
Fred.Worrall@dur.ac.uk

Citation:
Worrall, F., G. D. Clay, C. S. Moody, T. P. Burt, and R. Rose (2016), The effective oxidation state of a peatland, *J. Geophys. Res. Biogeosci.*, *121*, 145–158, doi:10.1002/2015JG003182.

Received 13 AUG 2015
Accepted 12 DEC 2015
Accepted article online 17 DEC 2015
Published online 15 JAN 2016

Abstract The oxidative ratio (OR) of the organic matter of the terrestrial biosphere is a key parameter in the understanding of the magnitude of the carbon sink represented both by the terrestrial biosphere and by the global oceans. However, no study has considered the oxidation state of all the organic pools and fluxes within one environment. In this study all organic matter pathways (dissolved organic matter, particulate organic matter, CO_2, and CH_4) were measured within an upland peat ecosystem in northern England. The study showed the following: (1) The peat soil of ecosystem was accumulating oxygen at a rate of between -16 and -73 t O $km^{-2}\,yr^{-1}$; (2) Although there was no significant variation in oxidation state in the peat profile, there was a significant increase in degree of unsaturation with depth; (3) The dissolved organic matter leaving the ecosystem was significantly more oxidized than the other carbon pools analyzed while the particulate organic matter was not significantly different from the peat soil profile; and (4) Assuming that all carbon flux from the site was as CO_2, the OR of the ecosystem was 1.07; when the nature and speciation of the release pathways were considered, the ecosystem OR was 1.04. At the global scale, correcting for the speciation of carbon fluxes means that the annual global fluxes of carbon to land = 1.49 ± 0.003 Gt C/yr and to the oceans = 2.01 ± 0.004 Gt C/yr.

1. Introduction

The carbon oxidation state (C_{ox}) of natural organic matter can be determined from the elemental composition of organic matter [*Masiello et al.*, 2008]:

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

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

The value of C_{ox} can range from +4 to −4 with the end-members being represented by CO_2 at the most oxidized end and CH_4 at the most reduced end. The value of C_{ox} not only represents an interesting amalgamated measure of the composition and properties of naturally occurring organic matter, but it can also be directly related to the oxidative ratio (OR) of the material. The OR represents the ratio of moles of oxygen (O_2) produced per mole carbon dioxide (CO_2) sequestered by the terrestrial biosphere. From *Masiello et al.* [2008] the OR value, assuming that the ultimate source of the N is N_2, is then calculated as follows:

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

The value of OR of an environment, and thus by extension C_{ox}, is a key parameter in understanding the magnitudes of global carbon sinks. *Keeling and Shertz* [1992] proposed that the magnitude of global carbon sinks, and more specifically the carbon sinks due to the terrestrial biosphere and the oceans, could be calculated from the relative changes in atmospheric gases. The relative changes of O_2 and carbon dioxide CO_2 concentrations have been used to refine estimates of terrestrial and oceanic carbon sinks of fossil fuel emissions [*Keeling et al.*, 1996; *Prentice et al.*, 2001]. *Battle et al.* [2000] proposed the following equations:

$$f_{\mathrm{land}} = -\frac{\mathrm{CS}}{\mathrm{OR}^{\mathrm{global}}_{\mathrm{terra}}} f_{\mathrm{fuel}} + \frac{1}{k_1 k_2 \mathrm{OR}^{\mathrm{global}}_{\mathrm{terra}}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} \tag{3}$$

$$f_{\mathrm{ocean}} = -\frac{1}{k_1}\frac{d(CO_2)}{dt} - \frac{1}{k_1 k_2 \mathrm{OR}^{\mathrm{global}}_{\mathrm{terra}}} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} - \frac{\mathrm{OR}^{\mathrm{global}}_{\mathrm{terra}} - \mathrm{CS}}{\mathrm{OR}^{\mathrm{global}}_{\mathrm{terra}}} f_{\mathrm{fuel}} - f_{\mathrm{cement}} \tag{4}$$

where: f_x = the annual flux of CO_2 (Gt C/yr) with x = land, ocean, fuel, or cement; (O_2/N_2) = the molar ratio of atmospheric O_2 and N_2; CS = the combustion stoichiometry (1.43 [*Battle et al*., 2000]); $OR_{\mathrm{terra}}^{\mathrm{global}}$ = the oxidative ratio of the global terrestrial biosphere; constants k_1 and k_2 = convert ppm in the atmosphere to per meg (which is ppm on a molecular basis for oxygen alone);the values are 0.471 and 4.8, respectively. *Battle et al*. [2000] refer to $OR_{\mathrm{terra}}^{\mathrm{global}}$ as the photosynthetic stoichiometry; this term is also known as α_B in the calculation of the atmospheric potential oxygen (APO [*Stephens et al*., 1998]).

Steinbach et al. [2011] showed that in the 12 years, 1996–2008, the global combustion stoichiometry (CS) varied from 1.39 to 1.42. The value of OR 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; *International Panel on Climate Change*, 2007; *Steinbach et al*., 2011], and *Keeling and Manning* [2014] have dismissed any attempt to update this value as trivial. This value of OR has been assumed to be fixed and true for all environments at all times. However, this value is based upon a 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, *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 IPCC represents the 97th percentile of observed values. When f_{land} is estimated as 1.4 ± 0.8 Gt C/yr, then an approximate 10% variation in the estimate of the OR value leads to a 10% change in the value of f_{land}. Similarly, a 0.1 decrease in OR leads to 8% change in the estimate of f_{ocean}.

The review of *Worrall et al*. [2013] had to make do with the data that were available in the literature rather than with data designed to consider oxidation state and could not consider any data from an environment where it was possible to compare different carbon reservoirs (e.g., soil organic matter versus biomass). Instead, *Worrall et al*. [2013] had to assume that the major control on OR was the differences between global soil taxa (e.g., Inceptisols) or global biomes (e.g., closed savannah [*Olson et al*., 2001]). Subsequently, *Clay and Worrall* [2015a] have shown no significant difference between soil taxa at least between mineral soil taxa (Oxisols, Ultisols, and Vertisols). Furthermore, *Clay and Worrall* [2015b] have shown that the difference in OR between simple carbon pools (soil, litter, and vegetation) was larger than differences between sites across the UK. It might be expected that C_{ox} is linked to the decomposability of organic matter, with more oxidized organic carbon decomposing more rapidly [*Kleber*, 2010]. This is plausible, because C_{ox} reflects the demand for O_2 in organic matter oxidation, with more reduced compounds demanding more O_2. In some contexts oxygen can be limiting (e.g., anaerobic marine sediments) and so more reduced compounds would therefore be expected to be more refractory, and indeed, oxygen exposure time has been linked to organic carbon preservation in marine sediments [*Hartnett et al*., 1998]. Equally, for terrestrial organic matter, litter bag experiments (where oxygen would not be limiting) have shown that the fraction of terrestrial organic matter remaining after decomposition is more reduced than the initial biomass [*Baldock et al*., 2004]. Easily respirable pools of soil carbon are likely to have lower OR values than bulk soil because the most respirable, or most readily turned over material, is more oxidized (e.g., glucose is more respirable and more oxidized than lignin); in other words, using whole soil values is a conservative estimate of $OR_{\mathrm{soil}}^{\mathrm{global}}$. Therefore, the aim of this study was to consider whether the oxidation state of the range of organic matter pools and fluxes within a single ecosystem would change the effective oxidation state of the whole ecosystem.

2. Methods

The approach taken here was to measure the oxidation state of the organic matter between a series of carbon pools within the context of a known carbon budget.

2.1. Study Site

A peatland ecosystem was chosen for this study because it meant that substantial fluvial fluxes of organic matter could be considered alongside the large stores of organic matter in the soils and vegetation of this environment. Trout Beck is an 11.4 km^2 blanket peat catchment in the headwater of the River Tees (N54:41:18 W2:22:45; Figure 1). The study site lies within Moor House National Nature Reserve, 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 and Lane*, 1996].

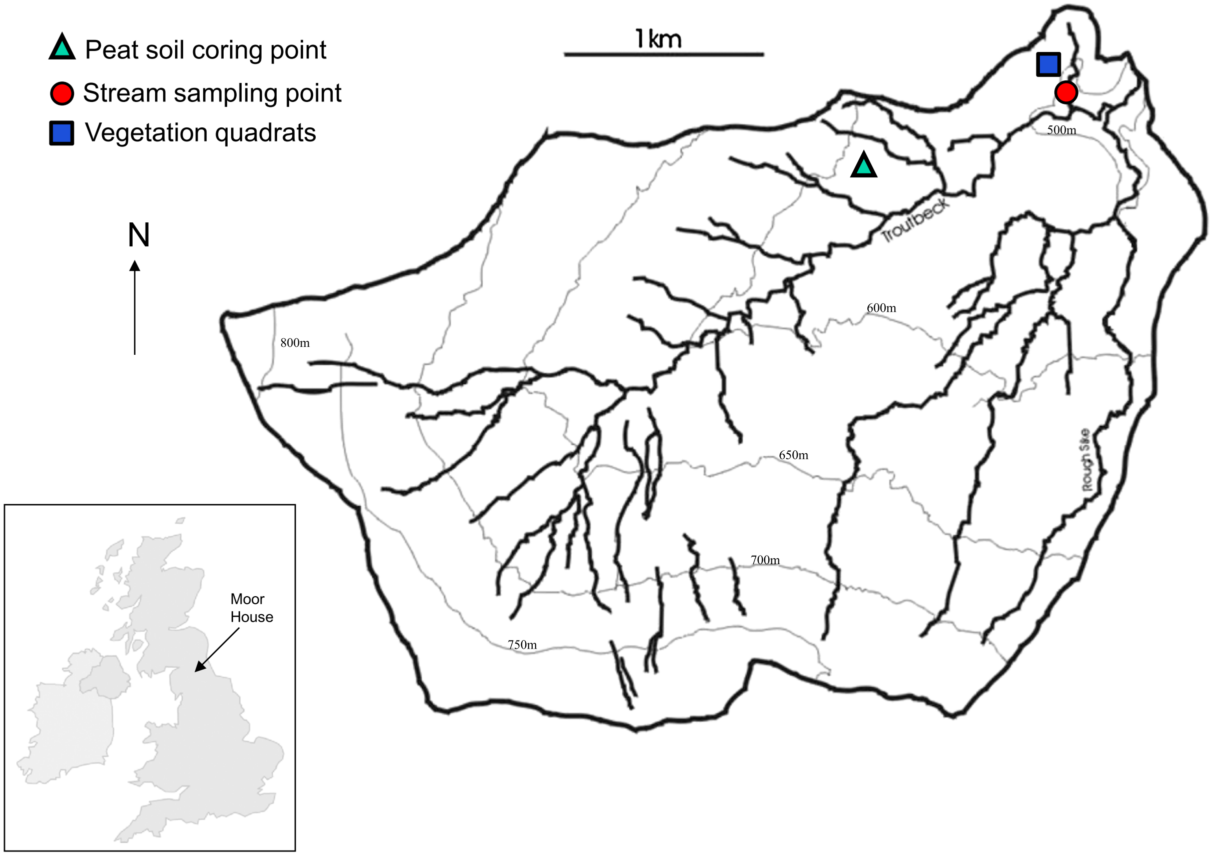

Figure 1. Location of the study site used in this study.

The Trout Beck catchment lies largely above 500 m above sea level; the highest point is the summit of Great Dun Fell at 848 m above sea level. 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]. The vegetation is dominated by *Eriophorum sp*. (cotton grass), *Calluna vulgaris* (heather), and *Sphagnum sp*. (moss).

2.2. Carbon and Dry Matter Budget

The study considers the ecosystem as a series of carbon pools and fluxes (Figure 2). The fluxes of carbon gases (CO_2 and CH_4) have a fixed molecular formula and so their C_{ox}, and OR does not require further measurement ($C_{ox} = +4$ and -4, respectively). The fluvial flux of dissolved gases is assumed to be overwhelmingly dominated by dissolved CO_2 [*Worrall et al.*, 2009].

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 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 a number of 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, i.e., the oxidation state that the whole environment behaves at because the relative importance of the carbon pools and fluxes has been taken into account. Once the effective oxidation state of an ecosystem is known, then its photosynthetic stoichiometry can be calculated. 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 carbon budget as follows:

$$100C_{pp} \Rightarrow 35C_R + 26C_{DOC} + 4C_{CH4} + 4C_{dissco2} + 9C_{POC} + 22C_{RES} \quad (5)$$

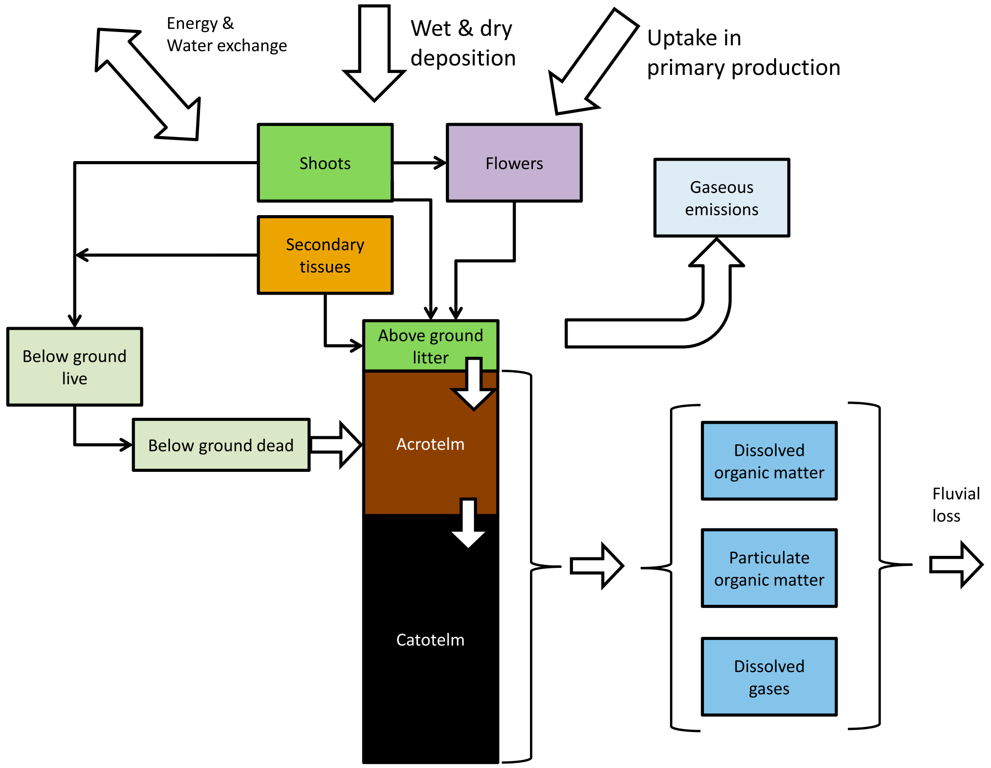

Figure 2. Schematic diagram of organic matter pools and fluxes considered by this study.

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

Over the 13 years of study, 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. By far the biggest single component of the budget was the uptake of carbon by primary productivity (average across the study period of −176 t C km^{-2} yr^{-1}—budget status assessed relative to the atmosphere).

2.3. Sampling

Given the range of carbon pools and fluxes identified in Figure 2, the following sampling was carried out.

First, two locations in active, deep peat within the Cottage Hill Sike catchment were selected, and two peat cores were taken to 1 m depth with a gouge auger from areas of the order of 10 m apart. Two cores were taken to make a sufficient statistical test of variation with depth possible. The depth was selected to ensure coverage of both the acrotelm and catotelm [*Worrall et al.*, 2012]. 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, and then one sample taken between 95 and 100 cm depth. Peat core samples were dried at 105°C overnight and checked for no further mass loss and their bulk density measured prior to further processing.

Second, vegetation samples were collected from six quadrats. The six quadrats (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 sp.*, 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. Samples for quantitative biomass measurement were dried to 105°C and weighed to give an estimate of the total aboveground biomass, and the contribution from the dominant functional plant groups could be estimated, while for the litter and belowground biomass these samples were just 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 and assess the contribution of its components. It would be expected that the aboveground biomass would be weighted average of its components.

Finally, for the dissolved organic matter (DOM) samples of water from Cottage Hill Sike were collected monthly from October 2011 to September 2013 except for months where winter conditions precluded taking flowing water samples (21 samples in total). These samples were at least 25 liters, and on return to the laboratory the samples were allowed to settle with water tapped off from above the sediment layer and then evaporated to dryness to collect the total dissolved solids. By using settling as means of separation, no arbitrary filtration cutoff was being applied; rather, this study was defining DOM as being that component which was either colloidal or truly dissolved. The total dissolved solids for samples from Cottage Hill Sike would be expected to be predominantly organic matter, but the ash content (subsamples were ashed at 550°C and residual mass recorded) of the samples was analyzed, and all subsequent analysis were corrected so that all values are quoted on an ash-free basis. For the final two months of the DOM sampling, the settled sediment was recovered as a measure of the particulate organic matter (POM), dried to 105°C (overnight and checked for no further mass loss), and retained for subsequent analysis. As for DOM, it would be expected that suspended sediment from Cottage Hill Sike would be dominated by organic matter, but all samples were analyzed for their ash content and subsequent analyses adjusted for these values.

2.4. Sample 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. The ground samples were than subject to CHN and separately to O analysis on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler. Computer software used was Elemental Analysis Software (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 calculated for C, H, N, and O. All samples were corrected for their measured ash content.

In addition to the soil, vegetation, litter, DOM, and POM samples, this study also considered three standard materials. Lignin and humic acid were supplied from Aldrich and cellulose supplied from Whatman. If it is assumed that, with respect to the compositional data measured in this study, cellulose and hemicellulose are the same, then the next biggest component of plants found in a peatland system would be proteins [e.g., *McDermitt and Loomis*, 1981]. Standards of plant protein were not available, and so it was assumed that plant proteins were made of all the 22 standard, naturally occurring, proteinogenic amino acids, then the protein composition relevant to this study could be approximated. It was assumed that plant protein was composed of 100 amino acids chosen at random from the 22 proteinogenic amino acids, and then 500 of these random proteins were calculated. From this stochastic composition, measures relevant to this study were then themselves calculated as the median and the range of the distribution.

2.5. Oxidation State

The oxidation state of the measured compositions was calculated as per equation (1) and the OR by equation (2); however, for the modeled protein standard, the source of N is not N_2 (assumed to be NH_3 instead), and the more appropriate form of equation (2) is [*Masiello et al.*, 2008] as follows:

$$\mathrm{OR} = 1 - \frac{C_{\mathrm{OX}}}{4} + \frac{2[\mathrm{N}]}{[\mathrm{C}]} \tag{6}$$

Equation (1) assumes that there is no contribution to the C_{ox} from S or P, and it has been shown that the error in the OR of making such an assumption would be only ±0.0002, which is negligible compared to instrumental error [*Hockaday et al.*, 2009]. This additional uncertainty was added to the final calculation made in this study. Typically, the measurement precision is 0.01 with a natural variation from 0.92 to 1.12 (Table 1).

Table 1. The Median Composition of the Carbon Pools Considered by the Study[a]

	Elemental Analysis (mol/100 g)							
Carbon Pool/Type	C	H	N	O	C_{ox}	OR	Degree of Unsaturation (Ω)	Median Stoichiometry
DOM	3.8 ± 0.1	4.6 ± 0.2	0.12 ± 0.01	2.9 ± 0.1	0.40 ± 0.06	0.92 ± 0.01	2.42 ± 0.3	$C_{31}H_{38}NO_{24}$
POM	4.05 ± 0.02	6.40 ± 0.09	0.18 ± 0.01	2.50 ± 002	−0.21 ± 0.02	1.09 ± 0.01	1.76 ± 0.14	$C_{22}H_{35}NO_{14}$
Aboveground biomass	4.15 ± 0.12	6.30 ± 0.09	0.07 ± 0.015	2.55 ± 0.06	−0.26 ± 0.07	1.08 ± 0.01	1.98 ± 0.14	$C_{57}H_{86}NO_{35}$
Belowground biomass	4.23 ± 0.1	6.30 ± 0.09	0.09 ± 0.01	2.48 ± 0.06	−0.25 ± 0.06	1.08 ± 0.01	2.12 ± 0.14	$C_{49}H_{73}NO_{29}$
Grass and sedge	4.04 ± 0.1	6.30 ± 0.09	0.12 ± 0.01	2.59 ± 0.06	−0.19 ± 0.06	1.07 ± 0.01	1.95 ± 0.14	$C_{33}H_{52}NO_{21}$
Mosses	4.03 ± 0.1	6.30 ± 0.09	0.07 ± 0.01	2.65 ± 0.06	−0.19 ± 0.06	1.06 ± 0.01	1.92 ± 0.14	$C_{95}H_{145}NO_{56}$
Calluna	4.29 ± 0.1	6.58 ± 0.09	0.05 ± 0.01	2.53 ± 0.06	−0.32 ± 0.06	1.09 ± 0.01	2.03 ± 0.14	$C_{55}H_{86}NO_{46}$
Litter	4.17 ± 0.08	5.90 ± 0.1	0.167 ± 0.007	2.48 ± 0.08	−0.05 ± 0.04	1.05 ± 0.01	2.3 ± 0.2	$C_{25}H_{35}NO_{15}$
Peat soil	4.18 ± 0.01	6.00 ± 0.6	0.10 ± 0.01	2.53 ± 0.11	−0.15 ± 0.05	1.06 ± 0.03	2.2 ± 0.2	$C_{43}H_{62}NO_{26}$
Lignin	5.14 ± 0.01	6.03 ± 0.1	0.06 ± 0.005	1.81 ± 0.01	−0.43 ± 0.02	1.12 ± 0.01	3.14 ± 0.14	$C_{87}H_{103}NO_{31}$
Cellulose	3.60 ± 0.005	6.25 ± 0.24	0.00	3.21 ± 0.01	0.05 ± 0.02	0.99 ± 0.01	1.11 ± 0.14	CH_2O
Humic acid	2.99 ± 0.01	3.68 ± 0.09	0.06 ± 0.005	2.02 ± 0.02	0.19 ± 0.02	0.97 ± 0.01	2.18 ± 0.14	$C_{49}H_{60}NO_{33}$
Protein	4.72 ± 0.06	5.42 ± 0.17	1.24 ± 0.04	1.28 ± 0.05	0.18 ± 0.05	0.96 ± 0.01	3.63 ± 0.02	C_5H_5NO

[a] Variation is given as the interquartile range. Median stoichiometry is expressed relative to nitrogen content except for cellulose which expressed relative to carbon.

In addition to the above parameters, the degree of unsaturation (the number of rings and *p* bonds within a molecule) was calculated where for molecules without any halogens the degree of unsaturation is [*McMurray*, 2004] as follows:

$$\Omega = C - \frac{H}{2} - \frac{N}{2} + 1 \tag{7}$$

where X = the number of atoms with X = C, H, and N. Pure alkane would have Ω = 0, and for benzene Ω = 4.

2.6. Statistical Analysis

Analysis of variance was used to assess differences between carbon pools and fluxes. For the case of DOM it was possible to include the month of sampling as factor. The normality of data was first assessed using the Anderson-Darling test [*Anderson and Darling*, 1952] and for the data sets considered here no transformation was found necessary. The significance of all factors was considered relative to a 95% probability of not being zero.

Because of the multivariate nature of the data set, principal component analysis was used to assess the differences between organic matter pools and fluxes on the basis of their molar contents of C, H, N, and O; C_{ox}; OR; and the degree of unsaturation (Ω). The data set was *z* transformed prior to principal component analysis to allow for the different scales of the variables included. 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].

2.7. Ecosystem OR

In *Worrall et al.* [2013] the value of OR_{terra}^{global} was calculated as a weighted sum of the OR of the global soils (OR_{soil}^{global}) and OR of the global vegetation (OR_{veg}^{global}) where the weighting was the proportion of the annual CO_2 flux from the soil and the vegetation pools, respectively. First, for this study, the OR of the study ecosystem will be considered as a weighted average of just two pools, the soil and the vegetation, that is,

$$OR_{ecosystem} = \varphi_{soil} OR_{soil} + \varphi_{veg} OR_{veg} \tag{8}$$

$$\varphi_{soil} + \varphi_{veg} = 1 \tag{9}$$

where φ_x = the proportion of the ecosystem C annual flux that is due to either soil or vegetation; and OR_x = the oxidative ratio with x = soil or vegetation. As a first attempt to understand the OR of this peat ecosystem and as comparison with previous studies, equation (8) was used given the previous values of $\varphi_{soil} = 0.27$ and $\varphi_{veg} = 0.73$ and, as in previous studies, the median values of all measured vegetation OR (taken here as the aboveground biomass) and soil OR (taken here as the average of the peat soil samples) were used.

The second approach was to consider the stock-weighted values for each of the sampled carbon pools at the study site. The stocks of the vegetative carbon pool were estimated from the study of *Forrest* [1971]. The stock of carbon in the soil carbon pool was estimated from the measurements of bulk density and carbon content measured as part of this study and given an assumption that it is the top 1 m of the peat profile that is interacting with the atmosphere.

The final approach used was to consider a residence time-weighted approach for the sampled carbon pools. The residence time was calculated as the stock/flux where the flux for the vegetation and litter pools was taken from *Forrest* [1971] and for the soil carbon pool from *Worrall et al.* [2009]. Finally, the ecosystem OR was calculated based on residence time weighting but also with respect to the form, or speciation, of the carbon loss from the environment, i.e., carbon is not just lost as CO_2 but as CO_2, CH_4, DOC, and POC. In many environments it may not be possible to consider all possible carbon flux pathways because they are either not measured, are too expensive to measure, or too impractical to measure. In other environments consideration of some carbon release pathways would be less relevant (e.g., CH_4 flux from grass pasture on mineral soils), and therefore, a comparson of a range of methods of increasing complexity is important.

3. Results

The vegetation types considered by the study all have negative C_{ox} values giving high OR values generally above that of all other organic matter pools in this ecosystem (Table 1). The values for the combined aboveground biomass are between those for the individual functional vegetation types confirming that the aboveground biomass is a simple mixture of the functional types present and demonstrating that the study has been successful in quantitatively recovering the aboveground biomass and its separate components. The most reduced vegetation type is *Calluna* with little difference between the mosses and the grass/sedges, with the former having a slightly higher C/N ratio than the latter. Similarly, *Calluna* has a larger degree of unsaturation than any of the other vegetation types. The difference between the functional vegetation types can be ascribed to the greater quantity of lignin in the *Calluna* compared to the other functional types. The values of C_{ox} for the combined aboveground biomass was consistent with it being a mixture of the functional groups of vegetation sampled (above ground biomass was composed of 78% *Calluna*, 17% *Eriophorum*, and 5% mosses). The combined aboveground biomass was not significantly different (probability of difference being zero, $p < 0.05$) from the belowground biomass with respect to all measures, except the degree of unsaturation where the aboveground biomass has a significantly lower value. The litter was more oxidized (higher C_{ox} and lower OR) and with a lower C/N ratio than the vegetation implying that, either litter is formed only from a component of the vegetation and not representative of it all, or as proposed by *Worrall et al.* [2012] litter represents a sink of N. The litter has a higher degree of unsaturation than the vegetation (both aboveground and belowground biomass) implying that condensation has occurred. Condensation is defined here as reactions that form carbon-carbon bonds, can involve an elimination reaction where two substituents are removed in reaction and form an additional carbon-carbon bond, and so cause an increase in the degree of unsaturation of the organic carbon. If the degree of unsaturation and C_{ox} are both increasing at the same time as C/N is decreasing, then we could hypothesis a relative loss of H and the formation of carbonyl groups.

The composition of the peat profile appears highly variable, and there is no significant change with depth for either C_{ox} or OR (Table 1 and Figure 3a). Given the classical explanation of peat formation based upon a diplotelmic model with a permamently anaerobic layer often within 10 s cm of the surface [*Ingram*, 1978], it would be expected that C_{ox} would decline with depth as the peat profile becomes more anaerobic, and therefore, an increase in OR with depth would be expected. Indeed, *Worrall et al.* [2012] noted a significant increase in the down profile C/N of the peat at this site at a depth of between 40 and 50 cm, which was interpreted as the acrotelm/catotelm boundary. The diplotelmic model of peat soils is that they rapidly become anaerobic due to excess organic matter and slow ingress of air due to persistent waterlogged conditions leading to successive use and exhaustion of redox couples [*Reddy and D'Angelo*, 1994]. However, this succession is noted mainly for inorganic species in soil water and, for peat soil water, concentrations are often low compared to mineral soils giving them very little buffering capacity with respect to redox conditions. Therefore, easily measured inorganic redox couples are rapidly transformed, e.g., Fe(III) to Fe(II), whereas the amount of reduction occurring is minimal in comparison to the amount of organic matter that could be oxidized, and so therefore dramatic changes in soil solution are not reflected in the substrate.

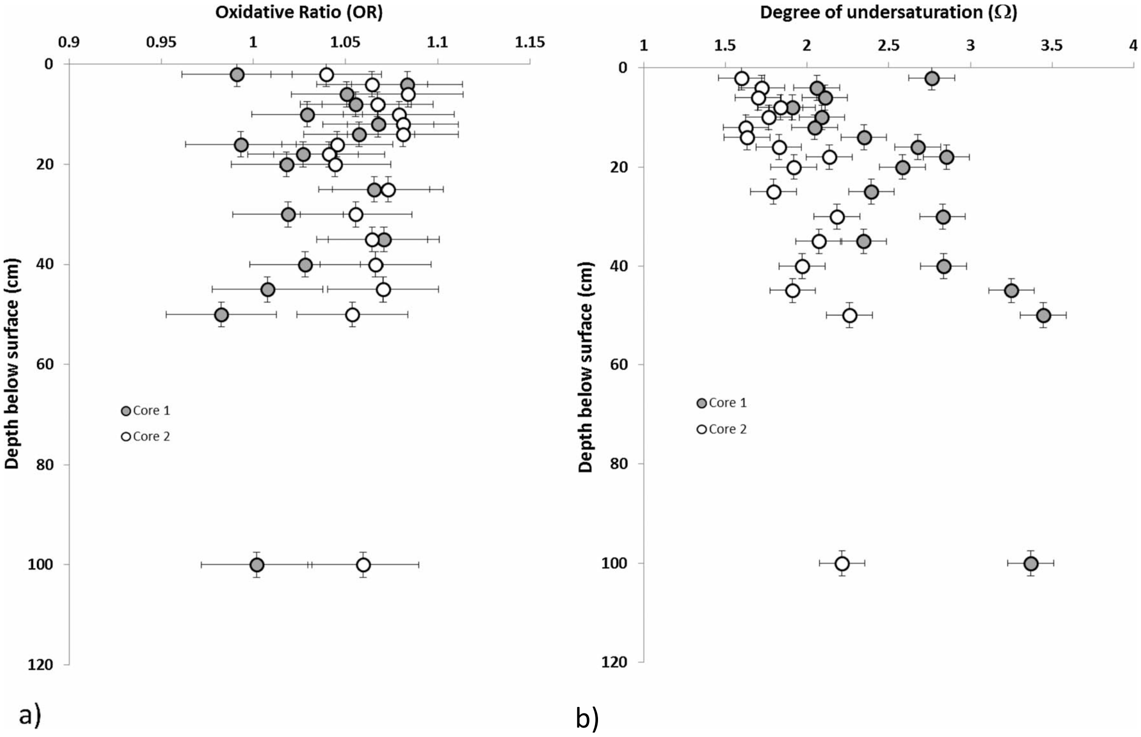

Figure 3. The average peat profile for (a) the oxidative ratio (OR) and (b) the degree of unsaturation (Ω).

An alternative explanation of the lack of coherent down-profile change in C_{ox} and OR may relate to changing deposition of organic matter over the several centuries represented in the cores taken from the site, e.g., a change in the dominant vegetation. Given the lack of significant change with depth in C_{ox} or OR, only one set of values need be reported (Table 1); these values show that it would be difficult to show a difference between the peat soil and the litter and vegetation pools.

While no significant down profile change in C_{ox} or OR could be found, there is a significant increase in the degree of unsaturation with depth in the profile (Figure 3b), where the best fit equation for the peat soil samples is as follows:

$$\begin{array}{ll}\Omega = \underset{(0.11)}{2.07} + \underset{(0.003)}{0.01}d & r^2 = 0.22,\ n = 33\end{array} \tag{10}$$

where d = depth in the peat profile from the soil surface (cm).

The values in the brackets are the standard error in the coefficient or *y* intercept showing that both the coefficient of depth and the *y* intercept value are significantly different from zero ($P < 0.05$). The *y* intercept value of equation (10) was not significantly different from the degree of unsaturation of the litter samples.

The humic acid standard used in this study does not appear to be representative of the humification processes occurring in the peat profile. Compared to the humic acid standard, the peat is more reduced, and the humic acid standard appears more like the highly oxidized DOM. *Worrall et al.* [2013] compared elemental results from 74 extracted soil humic acids from 16 studies and found a range of OR values 0.88 to 1.12, i.e., humic acids have a very broad range of compositions, and use of one standard of unknown source would not be justified in future studies.

It has been proposed that the origin of particulate organic matter (POM) from peatlands is physical (i.e., by water and wind erosion) and not biogeochemical [*Evans and Warburton*, 2005], and therefore, we could hypothesize that the composition of POM would reflect the peat soil from which the particles are eroded. In this study there was no significant difference between the C_{ox} and OR values for POM and the peat soil profile (Table 1). The highest value of OR among all field samples was for a sample of POM (OR = 1.099),

Table 2. The Loadings of the Variables on the Principal Components Along With the Variance Explained

Variable	PC1	PC2
C	0.38	0.37
H	0.46	−0.27
N	0.07	0.62
O	−0.31	−0.55
C_{ox}	−0.53	0.20
OR	0.52	−0.24
W	−0.21	0.52
% variance explained	54	88

although it was still slightly lower than the OR of the lignin standard, which might suggest that woody fragments get eroded into the suspended sediment.

Conversely, DOM was significantly different from the peat profile and was the most oxidized organic matter analyzed for this study (Table 1). *Worrall et al.* [2013] did consider DOM in their review and found two studies with sufficient elemental information such that an OR could be calculated for DOM from rivers or lakes [*Martin et al.*, 2006; *Davis et al.*, 1999]. That review found an OR range of 0.87 to 0.95 with a median of 0.91, i.e., very similar to the highly oxidized material found in this study. Furthermore, fulvic acid compositions were found not to be significantly different from those of the reviewed composition of DOM, which has a range of 0.82 to 1.26, with a median value of 0.91 [*Ussiri and Johnson*, 2003; *Maie et al.*, 2004; *Martin et al.*, 2006; *Neves-Fernandes et al.*, 2010]. There was no significant seasonal cycle in the DOM composition suggesting that DOM composition may be more related to immediate hydroclimatic context of each month's sampling, for example, the composition might be more closely related to occurrence of rain and runoff events in the days before sampling. The lowest degree of unsaturation in the DOM samples never exceeded 3 but was as low as 1.14.

The principal component analysis of the compositional variation between sample types showed that only two components had eigenvalues >1, and together they explained 88% of the variation in the data (Table 2). The first component is dominated by the negative correlation between C_{ox} and OR and, while C_{ox} increases with increasing O content, the OR increases with increasing C and H content—there appears to be no role for N content. In contrast, the second principal component has a high positive loading for N content, which positively correlates with C_{ox} and C content but negatively correlates with O and H, i.e., the second component is then the contribution to oxidation state from the nitrogen.

Plotting the scores on components 1 and 2 for all the samples and standards shows clear patterns of differentiation (Figure 4). First, the vegetation samples appear to lie dominantly on a line between lignin and cellulose standards and, if this were interpreted as a mixing line, then the plant samples would be approximately

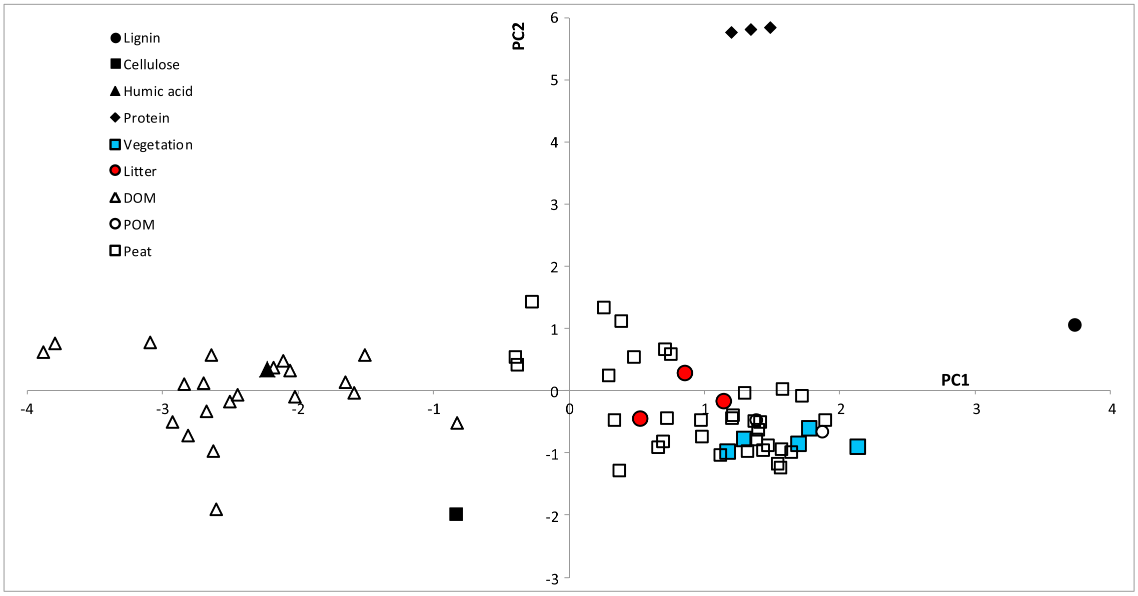

Figure 4. Comparison of PC1 and PC2 for all samples and standards with the vegetation and litter samples emphasized.

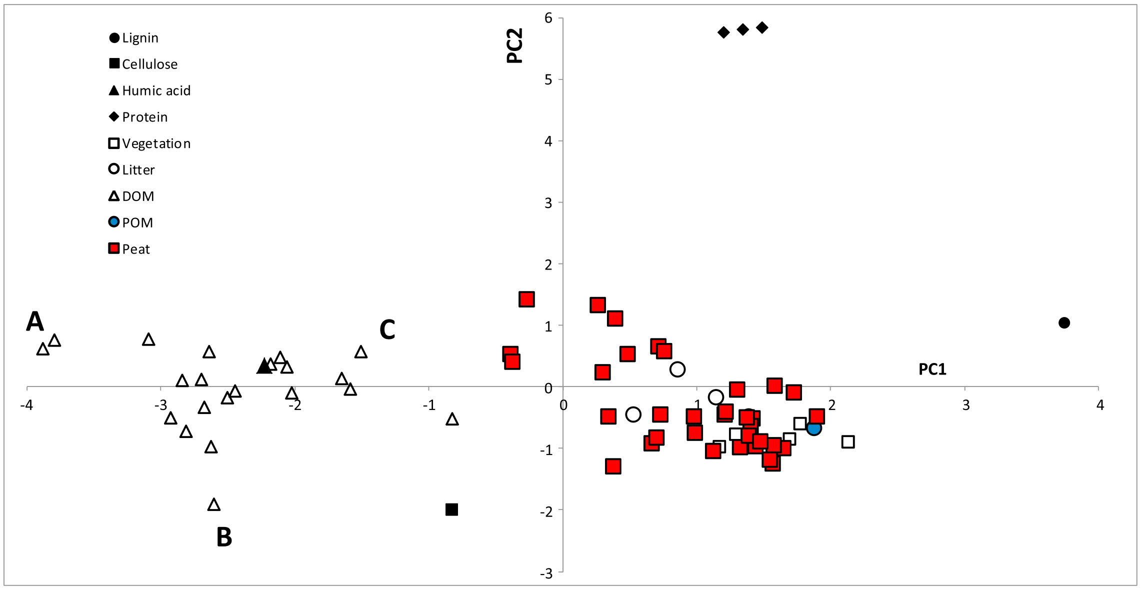

Figure 5. Comparison of PC1 and PC2 for all samples and standards with the peat soil samples emphasized.

50:50 lignin:cellulose. However, the protein standard plots at very high positive values of PC2 (Figure 4) and quite clearly separate from all other samples. The plot of the vegetation samples between the lignin and cellulose implies limited protein content which is unlikely. In comparison, the litter samples plot at lower values of PC1 and higher values of PC2 than the plant samples. Plotting at lower PC1 and higher PC2 values than the plant samples would mean that the litter samples would be more oxidized and have higher N compositions than plants.

The samples from the peat profile plotted in Figure 4 are approximately circumscribed by the standards. It is possible to suggest that the peat profile samples follow a broad trend from close to where the vegetation samples plot to lower values of PC1 and higher values of PC2 (Figure 4). This broad trend covers where both the litter samples and the POM samples plot. The trend has a credible interpretation with peat soils evolving away from vegetation and litter inputs, and that POM is material physically eroded from the peat profile and so therefore shares it composition. There is a significant relationship between the depth in the peat soil and the values of PC1 and PC2 ($\text{depth} = 19.4 + 20.7\text{PC1} + 13\text{PC2}$, $r^2 = 0.27$, $n = 33$, $P < 0.05$) with the deepest peat soil samples plotting at the highest values of PC2 and the lowest of PC1. The trend of peat soil with depth implies that the POM samples come from an equivalent depth of between 41 and 49 cm depth in the profile. If one end of peat soil sample trend is associated with the vegetation samples, which are themselves controlled by cellulose and lignin compositions, it is not clear what the composition of the high PC2 end-member is composed of. Relative to the standards, it is clear that the trend in peat samples is not evolving toward anyone of the standards, but it is possible that it is evolving toward a mixture of any of the three of humic acid, protein, or cellulose; however, it is not possible to judge in what combination.

The DOM samples clearly plot apart from all other field samples and at lower values of PC1, implying these samples are all more oxidized than any other field sample (Figure 5). The humic acid standard plots within the area of the DOM samples, suggesting that the DOM measured here are variations of the humic acid composition. The DOM composition could be described by a mixing system of three end-members (A–C) where A represents the low PC1 end-member and has an average composition of $C_{32}H_{36}NO_{21}$ ($C_{ox} = 0.28$, $OR = 0.95$), but in particular, this sample has a high degree of unsaturation ($\Omega = 2.95$). Composition B has an average composition of $C_{32}H_{61}NO_{35}$ ($C_{ox} = 0.34$, $OR = 0.94$) with the lowest degree of unsaturation of any sample considered in this study ($\Omega = 1.14$), while composition C is the most oxidized end-member ($C_{34}H_{34}NO_{26}$, $C_{ox} = 0.34$, $OR = 0.86$) with the highest degree of unsaturation of any DOM sample analyzed ($\Omega = 3.02$). The trends B and C are parallel to the line between the cellulose and protein standards and so may represent the same compositional change, i.e., addition of N, increased saturation and moderate decrease in oxidation

Table 3. The Stock, Flux, and Residence Time Values Used by This Study in the Calculation of Ecosystem OR

Carbon Pool	Stock[a] (gC/m^2)	Flux[b] ($gC/m^2/yr$)	Residence Time (year)
Calluna	774	176	4.4
Eriophorum	175	87	2.0
Sphagnum	50	23	2.2
Below ground	134	23	3.0
Litter	589	91	6.5
Peat	81850	88	930

[a] Based upon *Forrest* [1971].
[b] Based upon *Worrall et al.* [2009, 2012].

status. One DOM sample does not conform to this pattern and that is the DOM sampled in November 2011 which has a composition of $C_{25}H_{36}NO_{18}$ ($C_{ox} = 0.14$, $OR = 0.99$, $\Omega = 2.05$)—this is the most reduced DOM sample found in this study. The clear distinction between the soluble and insoluble organic matter in this study means that it is possible to say that organic matter will be soluble if it meets the following inequality:

$$1.44 > \frac{[C]}{[O]} \quad (11)$$

3.1. Ecosystem OR

The study has used four methods for calculating ecosystem OR, and these methods are of increasing complexity and rely on increasing levels of information about the ecosystems stocks and fluxes of carbon. Applying the simplest method first, equation (8) gives an ecosystem OR of 1.067 ± 0.009. The stocks, fluxes, and residence times of the sampled carbon pools are given in Table 3. When stock weighted the ecosystem, OR is 1.06 ± 0.04. When flux weighted the ecosystem, OR was 1.077 ± 0.004. However, these calculations assume that the release from the environment is as CO_2, but this is not the case for a peatland where release from the peatland can also be as DOC, POC, and CH_4. The OR of CH_4 is 2, and the values for DOC and POC have been reported above. Flux weighting by the individual pathways based on equation (5) gives the ecosystem OR as 1.042 ± 0.004. This much lower ecosystem OR is due to the large flux out of the peatland of highly oxidized DOC, even when the release of the highly reduced CH_4 was included in the calculation

4. Discussion

4.1. Source of POM

The study has shown that POM is sourced from physical erosion of the peat, and its generation does not represent an oxidation, or indeed reduction, of organic matter. Furthermore, this study would suggest that the most likely source is not the soil surface and suggests bank erosion rather than surface erosion. However, at least one POM sample did show signs of that POM included vegetation, which is readily explained if a component of runoff in a peat catchment comes across the soil surface and entrains litter material. *Shuttleworth et al.* [2015] have shown that the relative contribution of surface and gully wall peat to POM depends on the level of vegetation cover.

4.2. Source of DOM

Conversely, the study has shown that DOM is marked out by its oxidation state relative to the other organic matter in the ecosystem. Therefore, we can propose that the creation of DOM is due to the oxidation of the organic matter; the ultimate product will be CO_2, but the intermediate product is oxidized organic matter that can be soluble. The data do show a variation in the oxidation of the DOM (e.g., the variation between composition A and C; Figure 5). This creates a hypothesis that the composition of the DOM is set by the amount of time for oxidation, and therefore is set by the timing between runoff events; the longer the time between runoff events (rainstorms) in the catchment, the longer there is to oxidize the DOM.

4.3. Storage of O in Organic Matter

The catchment has been assessed to be storing −20 to −91 t C km^{-2} yr^{-1} and accumulating −1.0 to +2.5 t N km^{-2} yr^{-1}, i.e., in some years the peat soil was a source of N to the catchment [*Worrall et al.*, 2012]. It is not possible to judge the complete oxygen budget of this catchment, as we have not considered the inorganic fluxes of oxygen; however, given the composition of the peat soil was $C_{43}H_{62}NO_{26}$ and from the amount of residual carbon storage predicted in equation (5), then if carbon is accumulating at the rate given above and the composition of the deep peat soil is as measured within this study, then the amount of oxygen accumulating in the peat as part of the accumulating organic matter each year is between −16 and −73 t O km^{-2} yr^{-1}.

Table 4. The Ranges of OR and φ Values Used for Equations (12) and (13). $\varphi^{terra}_{POM} = 0\text{–}12\%$ for All Soils Except for Histosols, Mollisols, and Gelisols.$\varphi^{terra}_{DOM} = 0$ and $\varphi^{terra}_{CH4} = 0$ for all Soils Except for Histosols, Mollisols, and Gelisols

Oxidative Ratio (OR)	Preferred Range	Proportion of Annual Flux (φ)	Preferred Value
OR^{global}_{soil}	1.02 to 1.11	φ^{terra}_{soil}	0.24
OR^{global}_{veg}	1.05 to 1.10	φ^{terra}_{veg}	0.64
OR^{global}_{DOM}	0.91 to 0.94	φ^{terra}_{DOM}	0.08
OR^{global}_{POM}	1.05 to 1.14	φ^{terra}_{POM}	0.025
OR^{global}_{CH4}	2.00	φ^{terra}_{CH4}	0.015

4.4. Improved Estimate for Global Terrestrial Biospheric OR

The study has shown that the OR of the peatland ecosystem should also include a consideration of the form in which fluxes leave the environment and where relevant and practical inclusion of all pathways would be beneficial. Equation (3) as applied to the global terrestrial biosphere should include a consideration of the release from the soil and vegetation carbon pools as DOM, POM, and CH_4; therefore, equation (8) can be reformulated as follows:

$$OR^{global}_{terra} = \varphi^{terra}_{soil}OR^{global}_{soil} + \varphi^{terra}_{veg}OR^{global}_{veg} + \varphi^{terra}_{DOM}OR^{global}_{DOM} + \varphi^{terra}_{POM}OR^{global}_{POM} + \varphi^{terra}_{CH4}OR^{global}_{CH4} \tag{12}$$

$$\varphi^{terra}_{soil} + \varphi^{terra}_{veg} + \varphi^{terra}_{DOM} + \varphi^{terra}_{POM} + \varphi^{terra}_{CH4} = 1 \tag{13}$$

where φ^{terra}_{DOM} = the proportion of the terrestrial biosphere C annual flux that is due to DOM flux; φ^{terra}_{POM} = the proportion of the terrestrial biosphere C annual flux that is due to POM flux; φ^{terra}_{CH4} = the proportion of the terrestrial biosphere C annual flux that is due to methane; and φ^{terra}_{soil} and φ^{terra}_{veg} are as previously defined (Table 4).

In many environments the proportion of the carbon flux that is due to DOM, POM, or CH_4 is very low or negligible, and it is perhaps only in a peatland environment where all such exchanges are relevant. However, we assumed that all soils exported some carbon as particulates, and so φ^{terra}_{POM} was zero in any of the environments chosen. Therefore, to assess the impact of considering the nature of the fluxes from the environment, Histosols, Mollisols, and Gelisols were taken as exporting carbon as DOM, POM, and CH_4 in proportion to that predicted by equation (5), but that for all other soil orders export via CH_4 or DOM was negligible. It was assumed that all soils exported some carbon as particulates; in Histosols such as peat where the soil is approximately 100% organic matter then the erosion will be 100% organic carbon, but in mineral soils the organic carbon content of the particulate flux will be lower, and so will be the fraction of the carbon pool turned over via this mechanism. In the absence of further information, the value of φ^{terra}_{POM} was allowed to vary between 0 and 12% (based upon the POM fluxes reported for the UK [*Worrall et al*., 2014]) for all soil orders other than Histosols, Mollisols, and Gelisols. The value of OR^{global}_{CH4} is 2, and the value of OR^{global}_{DOM} OR will be 0.92 with an interquartile range of 0.91 to 0.94 based on this study and those reported from the meta-analysis of *Worrall et al*. [2013]. The value of OR^{terra}_{POM} was taken as the same as the soil from which it eroded. Given these corrections, the calculation in equations (12) and (13) was performed 100 times drawing at random from the ranges specified (Table 4), and from these hundred values the median value OR^{terra}_{global} was 1.034 with an interquartile range of 1.032 to 1.036. Applying the currently used value of OR ($OR^{terra}_{global} = 1.1$) and leaving all other terms equal in equation (3), then $f_{land} = 1.40$ Gt C/yr, and $f_{ocean} = 2.11$ Gt C/yr. Taking the estimate of OR^{terra}_{global} from *Worrall et al*. [2013], then $f_{land} = 1.48$ Gt C/yr, and $f_{ocean} = 2.03$ Gt C/yr. Based upon the correction found here and the additional values of OR for other soils and environment published within the studies of *Clay and Worrall* [2015a, 2015b], the values would now be $f_{land} = 1.49 \pm 0.003$ Gt C/yr, and $f_{ocean} = 2.01 \pm 0.004$ Gt C/yr. Note that the combined sample size of this study and that of *Worrall et al*. [2013] and *Clay and Worrall* [2015a, 2015b] is 806 organic matter samples.

5. Conclusions

The study has shown that while the composition of peat soils evolved with depth from vegetation and litter, this evolution was in terms of carbon unsaturation and not oxidation status. The POM was sourced from bank erosion and wash off of vegetation into streams, while DOM was distinguished by $[C][O] < 1.44$. The amount of oxygen accumulating in the peat soil of the study site each year was between -16 and -73 t O km^{-2} yr^{-1}. The study shows that the oxidative ratio (OR) for an ecosystem needs to be corrected for the form and speciation of the carbon release pathways. The estimation of ecosystem OR should not assume that all release from any ecosystem is as CO_2. Allowing for the nature of the release pathway meant that the OR of this peatland ecosystem was 1.04 rather than 1.07. Applying the correction to a database of global OR values reduced the estimate of OR 1.04 to 1.034 which in turn means the annual flux of carbon to the terrestrial biosphere would be 1.49 Gt C/yr, and the flux to the oceans would be 2.01 Gt C/yr.

Acknowledgments
The authors are grateful the Environmental Change Network for the data from the Moor House site. The data used in this study are available in the paper and at http://www.ecn.ac.uk/data.

References

Anderson, T. W., and D. A. Darling (1952), Asymptotic theory of certain "goodness-of-fit" criteria based on stochastic processes, *Ann. Math. Stat.*, *23*, 193–212.

Baldock, J. A., C. A. Masiello, Y. Gelinas, and J. I. Hedges (2004), Cycling and composition of organic matter in terrestrial and marine ecosystems, *Mar. Chem.*, *92*, 39–64.

Battle, M., M. I. Bender, P. P. Tans, J. W. C. White, J. T. Ellis, T. Conway, and R. J. Francey (2000), Global carbon sinks and their variability inferred from atmospheric O-2 and delta C-13, *Science*, *287*(5462), 2467–2470.

Chatfield, C., and A. J. Collins (1980), *Introduction to Multivariate Analysis*, Chapman and Hall, London.

Clay, G. D., and F. Worrall (2015a), Oxidative ratio (OR) of Southern African soils and vegetation: Updating the global OR estimate, *Catena*, *126*, 126–133.

Clay, G. D., and F. Worrall (2015b), Estimating the oxidative ratio of UK peats and agricultural soils, *Soil Use Manage.*, *31*(1), 77–88.

Davis, W. D., C. T. Erickson, C. T. Johnston, J. J. Delfino, and J. E. Porter (1999), Quantitative fourier transform infrared spectroscopic investigation of humic substance functional group composition, *Chemosphere*, *38*, 2913–2928.

Evans, M. G., and J. Warburton (2005), Sediment budget for an eroding peat-moorland catchment in Northern England, *Earth Surf. Processes Landforms*, *30*, 557–577.

Evans, M. G., T. P. Burt, J. Holden, and J. K. Adamson (1999), Runoff generation and water table fluctuations in blanket peat: Evidence from UK data spanning the dry summer of 1995, *J. Hydrol.*, *221*, 141–160.

Forrest, G. I. (1971), Structure and production of North Pennine blanket bog vegetation, *J. Ecol.*, *59*(2), 453–479.

Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol (1998), Influence of oxygen exposure time on organic carbon preservation in continental margin sediments, *Nature*, *391*, 572–575.

Hockaday, W. C., C. A. Masiello, J. T. Randerson, R. J. Smernik, J. A. Baldock, O. A. Chadwick, and J. W. Harden (2009), Measurement of soil carbon oxidation state and oxidative ratio by C-13 nuclear magnetic resonance, *J. Geophys. Res.*, *114*, G02014, doi:10.1029/2008JG000803.

Holden, J., and R. Rose (2011), Temperature and surface lapse rate change: A study of the UK's longest upland instrumental record, *Int. J. Climatol.*, *31*(6), 907–919.

Ingram, H. A. P. (1978), Soil layers in mires: Function and terminology, *J. Soil Sci.*, *29*, 224–227.

International Panel on Climate Change (2007), *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon et al., Cambridge Univ. Press, Cambridge, U. K., and New York.

Johnson, G. A. L., and K. Dunham (1963), *The Geology of Moor House*, Nature Conservancy Council, HMSO, London.

Keeling, R. F., and A. C. Manning (2014), Studies of recent changes in atmospheric O_2 content, in *Treatise on Geochemistry*, vol. 5–15, 2nd ed., edited by H. D. Holland and K. K. Turekian, pp. 385–404, Elsevier, Oxford.

Keeling, R. F., and S. R. Shertz (1992), Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle, *Nature*, *35*, 723–727.

Keeling, R. F., S. C. Piper, and M. Heimann (1996), Global and hemispheric CO_2 sinks deduced from changes in atmospheric O_2 concentration, *Nature*, *381*, 218–221.

Kleber, M. (2010), What is recalcitrant soil organic matter?, *Environ. Chem.*, *7*, 320–332.

Langenfelds, R. L., R. J. Francey, L. P. Steele, M. Battle, R. F. Keeling, and W. F. Budd (1999), Partitioning of the global fossil CO_2 sink using a 19 year trend in atmospheric O_2, *Geophys. Res. Lett.*, *26*(13), 1897–1900, doi:10.1029/1999GL900446.

Maie, N., A. Watanabe, and M. Kimura (2004), Chemical characteristics and potential source of fulvic acids leached from the plow layer of paddy soil, *Geoderma*, *120*, 309–3232.

Martin, M., L. Celi, E. Bonifacio, S. Nardi, and E. Barberis (2006), Characteristics of soil organic matter in a limnic histosol of the alpine morainic system, *Soil Sci.*, *171*, 527–540.

Masiello, C. A., M. E. Gallagher, J. T. Randerson, R. M. Deco, and O. A. Chadwick (2008), Evaluating two experimental approaches for measuring ecosystem carbon oxidation state and oxidative ratio, *J. Geophys. Res.*, *113*, G03010, doi:10.1029/2007JG000534.

McDermitt, D. K., and R. S. Loomis (1981), Elemental composition of biomass and its relation to energy content, growth efficiency, and growth yield, *Ann. Bot.*, *48*, 275–290.

McMurray, J. E. (2004), *Organic Chemistry*, 6th ed., Brooks Cole, London.

Neves-Fernandes, A., M. Giovanela, V. I. Esteves, M. Marta, and S. Sierra (2010), Elemental and spectral properties of peat and soil samples and their respective humic substances, *J. Mol. Struct.*, *971*, 33–38.

Olson, J. S., J. A. Watts, and L. T. Allison (2001), *Major World Ecosystem Complexes Ranked by Carbon in Live Vegetation: A database*, Carbon Dioxide Information Analysis Center, Oak Ridge Natl. Lab., Oak Ridge, Tenn.

Prentice, I. C., et al. (2001), The carbon cycle and atmospheric carbon dioxide, in *Climate Change 2001, The Scientific Basis, Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., Cambridge Univ. Press, Cambridge, U. K.

Reddy, K. R., and E. M. D'Angelo (1994), Soil processes regulating water quality in wetlands, in *Global Wetlands: Old World and New*, edited by J. W. Mitsch, pp. 309–324, Elsevier, New York.

Severinghaus, J. P. (1995), Studies of the terrestrial O_2 and carbon cycles in sand dunes gases and in Biosphere 2, PhD thesis, Columbia Univ.

Shuttleworth, E. L., M. G. Evans, S. M. Hutchinson, and J. J. Rothwell (2015), Peatland restoration: Controls on sediment production and reductions in carbon and pollutant export, *Earth Surf. Processes Landforms*, *40*(4), 459–472.

Steinbach, J., C. Gerbig, C. Rodenbeck, U. Karstens, C. Minejima, and H. Mukai (2011), The CO_2 release and oxygen uptake from fossil fuel emission estimate (COFFEE) dataset: Effects from varying oxidative ratios, *Atmos. Chem. Phys.*, *11*, 6855–6870.

Stephens, B. B., R. F. Keeling, M. Heimann, K. D. Six, R. Murnane, and K. Caldeira (1998), Testing global ocean carbon cycle models using measurements of atmospheric O_2 and CO_2 concentration, *Global Biogeochem. Cycles*, *12*(2), 213–230, doi:10.1029/97GB03500.

Sykes, J. M., and A. M. J. Lane (1996), *The United Kingdom Environmental Change Network: Protocols for Standard Measurements of Terrestrial Sites*, 220 pp., Nat. Environ. Res. Council, London.

Ussiri, D. A. N., and C. E. Johnson (2003), Characterization of organic matter in a northern hardwood forest soil by ^{13}C NMR spectroscopy and chemical methods, *Geoderma*, *111*, 123–149.

Worrall, F., T. P. Burt, J. G. Rowson, J. Warburton, and J. K. Adamson (2009), The multi-annual carbon budget of a peat-covered catchment, *Sci. Total Environ.*, *407*(13), 4084–4094.

Worrall, F., G. D. Clay, T. P. Burt, and R. Rose (2012), The multi-annual nitrogen budget of a peat-covered catchment—Changing from sink to source?, *Sci. Total Environ.*, *433*, 176–188.

Worrall, F., G. D. Clay, C. A. Masiello, and G. Mynheer (2013), Estimating the oxidative ratio of terrestrial biosphere carbon—Global carbon sinks have been underestimated, *Biogeochemistry*, *115*(1–3), 23–32.

Worrall, F., T. P. Burt, and N. J. K. Howden (2014), The fluvial flux of particulate organic matter from the UK: Quantifying in-stream losses and carbon sinks, *J. Hydrol.*, *519*, 611–625.