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The oxygen budget of a peatland – new approach to estimating ecosystem oxidative ratio

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Abstract:

The oxidative ratio (OR) of an ecosystem in the terrestrial biosphere is defined as the ratio of the O_2 released from that ecosystem to the CO_2 adsorbed by that ecosystem. This study proposes that the OR of a terrestrial ecosystem could be calculated for the C budget of a peatland environment where stoichiometry and thermodynamics are constrained. Using detailed elemental analysis within an ecosystem with a known C and N budget it is possible to understand the amount of O_2 consumed.

The study shows that, for the study site, although the majority of the O_2 is consumed in the processing of organic-C (68%), 32% of O_2 consumption is due to oxidation of NH_4. The total amount of O_2 consumed by organic C processing is not dependent upon the pathway after surface peat formation: O_2 consumption is independent of production of DOC or CH_4 or of deep peat. This approach shows that allowing for stoichiometric, energy and energy transfer efficiency constrains the ecosystem OR = 0.88. The calculated OR is consistent with disproportionation of C occurring in the environment. The implication of OR < 1 is that the annual flux of C to the terrestrial biosphere has been underestimated by 12%.

1. Introduction

It has been suggested that the magnitude of global carbon sinks for both the terrestrial biosphere and the oceans could be determined by analyzing the relative changes in atmospheric gases, as proposed by Keeling and Shertz (1992). This method requires an understanding of the oxidative ratio (OR). For a terrestrial ecosystem, the OR represents the molar ratio of oxygen (O_2) produced relative to carbon dioxide (CO_2) sequestered. In simpler terms:

$$OR = \frac{mol(O_2)}{mol(CO_2)} \qquad \text{(i)}$$

Where: mol(O_2) = produced from the environment; mol(CO_2) = moles of CO_2 consumed by the environment. In a simple photosynthesis reaction where glucose is produced (Equation ii) the ratio of O_2 produced to CO_2 consumed (OR) is 1.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + O_2 \qquad \text{(ii)}$$

Taking the approach of Keeling and Shertz (1992), Battle et al. (2000) calculated the annual carbon flux to the terrestrial biosphere and the ocean using the following:

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

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

where: f_x= the annual flux of CO_2 (Gt C/yr) for ocean, fuel, cement or land; (O_2/N_2) = the molar ratio of atmospheric O_2 to N_2; CS = 1.43 (combustion stoichiometry - Battle et al., 2000); OR^{global}_{terra} = OR of the global terrestrial biosphere; constants K_1 = 0.471 and K_2 = 4.8. The constants K_1 and K_2 convert ppm in the atmosphere to per meg. The term OR^{global}_{terra} is also known as photosynthetic stoichiometry (Battle et al., 2000), as α_B in the estimation of the atmospheric potential oxygen (APO; Stephens et al., 1998) and is the reciprocal of apparent respiratory quotient (ARQ; Helm et al., 2021).

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

The first estimate of OR was 1.1 (Severinghaus, 1995; Keeling et al., 1996) and this value of OR has been used as OR_{terra}^{global} in multiple subsequent studies (e.g. IPCC, 2007, 2021; Steinbach et al. 2011; Nevison et al., 2015; Resplandy et al., 2016; Pickers et al., 2017; Hoshina et al., 2014; Resplandy et al., 2018; Pickers et al., 2022; Ishidoya et al., 2022). A global imbalance favouring oxygen production over carbon dioxide drawdown, indicated by an OR of 1.1, suggests a relatively reduced state of terrestrial organic carbon. Previous studies have often assumed a fixed OR value for all environments, but a review by Worrall et al. (2013) suggests a more realistic value of 1.03 ± 0.03. The commonly used value of 1.1, derived from a single Biosphere 2 experiment (Severinghaus, 1995), does not represent a global average and was not intended to be a universal OR value. Keeling and Manning (2014) suggested using a lower value of 1.05 and in recent years further studies have used this lower value (e.g., Resplandy et al. (2019) used a value of 1.05, based upon Randerson et al. (2006); Friedlingstein et al. (2023) also used 1.05 for global OR). Randerson et al. (2006) based their value on biomacromolecules composition of vegetation (e.g., lignin) and not of measurement of soils or vegetation. Although probably not the largest source of uncertainty in Equations (iii) and (iv), changes in OR_{terra}^{global} will have a direct consequence for the estimation of f_{land} and f_{ocean}.

There have been several approaches to calculating OR. The approach of Worrall et al. (2013) is based on the relationship, showed by Masiello et al. (2008), whereby OR can be estimated from the oxidation state of the carbon in the organic matter:

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]} \qquad \text{(v)}$$

$$C_{ox} = \frac{2[O]-[H]+3[N]}{[C]} \qquad \text{(vi)}$$

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

The C_{ox} is the oxidation state of the C in the analysed organic matter and is the nominal oxidation state of carbon (NOSC, LaRowe and van Cappellan, 2011). Worrall et al. (2013) used Equation (iii and iv) to calculate values of OR from compositional data in published literature, but to estimate a global value of OR they assumed that there was a significant and substantial difference in OR between different global soil taxa (e.g. vertisols) and between different global biomes (e.g. deciduous forest; Olson et al., 2001), and that therefore, the global estimate of OR was a stock or flux weighted combination of the OR of individual soil taxa and global biomes. Subsequent studies have shown that the significant difference in the OR were between soil, litter and vegetation and not between mineral soil taxa (Clay and Worrall 2015a, 2015b). Given that differences in OR are dominated by differences between organic carbon pools (e.g. between vegetation and soil), Worrall et al. (2015b) used a simple box model based upon differences between soil, litter and vegetation to calculate global OR. This box model also included the fluvial organic carbon both as dissolved (DOC) and particulate organic carbon (POC). This box model gave a median value of OR_{terra}^{global} = 1.034 ± 0.02 (Worrall et al. 2015b).

Other studies have used alternative methods to estimate OR. van der Laan et al. (2014) sampled atmospheric composition using aircraft flasks across western Russia and found an OR = 0.89. Faassen et al. (2023) used tall tower measurements (up to 125 m above forest surface) to measure OR and found daytime OR = 0.96 and night-time = 1.03. Battle et al. (2019) used six years of atmospheric measurement over a US forest and found values of 1.03. van Leeuwen and Meijer (2015) found OR = 1.04 based on atmospheric measurements in The Netherlands. Worrall et al. (2023) used long term water quality monitoring records of chemical oxygen

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

demand (COD) to measure the oxidation state of fluvial organic carbon and then incorporate this into a revised global estimate of OR, which yielded a median value of global OR = 1.059.

Worrall et al. (2016) applied the flux weighted approach to a single environment (upland blanket bog peatland) where the C budget was well constrained, which gave a value of OR = 1.04. As an alternative, Worrall et al. (2017), using the approach of Randerson et al. (2006), reconstructed the OR at the same site as Worrall et al. (2016) based upon a macromolecular budget, specifically the fate of the relative oxidised C biomacromolecules (e.g. carbohydrates) compared to relatively reduced C biomacromolecules (e.g. lignin). The preferential removal of carbohydrates relative to lignin meant that the OR that the atmosphere over the ecosystem experienced was 0.96 to 0.99. The organic matter accumulating in this ecosystem had OR > 1, whilst the OR of the material leaving the environment < 1. Given that C is fixed in the environment via photosynthesis as glucose, which has OR = 1, then we can see the processing of the fixed carbon through the environment results in a residual organic matter with OR > 1. Therefore, it is not surprising that the component lost to the atmosphere would have OR < 1.

Previous approaches to measuring OR have relied on extrapolation from elemental analysis (e.g. Worrall et al., 2013) or have relied upon a small number of expensive measurements (e.g. van der Lann et al., 2014). An alternative and new approach would be to measure the oxygen budget relative to the C budget so that Equation (i) could be used directly.

2. Approach

This study considered the elemental budgets and stoichiometry of the organic matter transition through a well-studied peatland. To calculate OR (Equation (i)) it would be necessary to understand both the C and the O budget of an ecosystem. Because peat soils are the accumulation of partially-decomposed organic matter (International Peatland Society, 2024)

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

the estimates of C budgets have been commonly reported. Initial approaches were based upon measurement of the dating of peat profiles (e.g. Turetsky et al., 2004). More recently, it has been possible to measure the range of contemporary carbon fluxes in and out of a peat ecosystem where the sum of these fluxes is the C budget (also known as C balance) (e.g. Worrall et al., 2003, Billett et al., 2004, Roulet et al., 2007, Nilsson et al., 2008). If organic matter is, or has been, accumulating in a peat soil then not only will C have accumulated but so too will other elements present in the organic matter. With respect to the problem of estimating OR these include the budgets of redox active elements: nitrogen (e.g. Hemond, 1983, Worrall et al., 2012), sulphur (Novak et al., 2005; Blodau et al., 2007; Boothroyd et al., 2021), and iron (Boothroyd et al., 2021). Indeed, Worrall et al. (2016) considered the accumulation of oxygen in the organic matter of deep peat soil and found between 16 and 73 tonnes O km^{-2} yr^{-1}, were accumulating each year. However, this estimation of O accumulation rate is not sufficient to solve Equation (i) and so not sufficient to calculate an OR for this ecosystem.

Worrall et al. (2022) applied the constraints of stoichiometry and energy to the flux and transition of C into, through and out of peat soil. The results showed how much of a series of terminal electron acceptors (TEAs: O_2, NO_3, SO_4 and C) were utilised in the production of deep peat and the resulting effluxes of CO_2, CH_4 and DOC. However, Worrall et al. (2022) only considered these constrains on organic matter budgets relative to the C budget of an ecosystem and not to other budgets. Therefore, this study builds on and advances previous work by applying stoichiometric and energetic constraints to understand the constraints on both the O and C budgets. If the O and C budget can be estimated, then the OR of the environment (Equation i) can be calculated.

3. Methods

The peatland ecosystem can be viewed as a system of organic matter reservoirs and the fluxes of organic matter between these pools (Fig. 1). In this study we use the same approach as Worrall et al. (2022) whereby the budget of any element of the organic matter in and through a peatland can be calculated given the constraints of the: (1) the relative stoichiometry; (2) the oxidation states of the organic carbon in the organic matter; and (3) the energy content of the organic matter in the important reservoirs.

McDermott and Loomis (1981) proposed that production of plant biomass could be viewed in terms of the amount of biomass of material that could be produced per mass of glucose utilised, known as the glucose value (GV). Worrall et al. (2022) generalised this approach for where the substrate could be something other than glucose but still with oxidation to CO_2. In this case rather than glucose value (GV) the resulting equation is for the substrate equivalent value (SEV):

$$\frac{[C]_{pro}}{[C]_{sub}} - \frac{C_{ox}^{pro}[C]_{pro}}{(C_{ox}^{CO2} - C_{ox}^{sub})[C]_{sub}} = SEV \qquad \text{(vii)}$$

where: $[C]_x$ = the molar concentration of C as product (*pro*) or as substrate (*sub*); and C_{ox}^{y} = the oxidation state of the carbon as product (*pro*), substrate (*sub*), or as CO_2. Equation (vii) represents the stoichiometric ratio between substrate and product corrected for the energy requirement of the reaction. It is formulated for O_2 as the terminal electron acceptor. In McDermott and Loomis (1981) it was only primary production that was considered (i.e. glucose to aboveground biomass) and therefore the substrate was always glucose and so C_{ox}^{sub} = 0, and $[C]_{sub}$- 3.33 mol C/100g. However, once the products of primary production are considered as transitioning in to and through a peat soil then C_{ox}^{sub} and $[C]_{sub}$ will not be the same values as for glucose.

The 100% efficient transfer of energy in any reaction is not possible, and that includes the oxidation of glucose, or any other substrate, to CO_2. Furthermore, the extent of energy transfer efficiency depends upon the biochemical pathway by which oxidation occurs. Therefore, Equation (vii) is corrected for the energy transfer efficiency of the energy transfer:

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

where: PV = true production value, E_g = energy transfer efficiency, SEV = substrate equivalent value. In plant biochemical pathways the value of E_g has been shown to vary between 0.84 and 0.89 (Lafitte and Loomis, 1988) and that range was used here. Given Equations (vii) and (viii) it then becomes possible to calculate the amount of CO_2 produced per 100 C atoms going through a particular transition in the environment from a substrate (sub) such as aboveground biomass to a product (pro) such as litter:

$$[C]_{CO2} = \frac{100}{[C]_{sub}}\left([C]_{sub} - PV[C]_{pro}\right) \qquad \text{(ix)}$$

Equations (vii)-(ix) were applied to the organic matter reservoirs and fluxes shown in Fig. 1 with the reactions considered being:

1) Primary production as glucose to aboveground biomass
2) Primary production as glucose to below ground biomass
3) Aboveground biomass to litter
4) Litter to surface peat
5) Surface peat to deep peat
6) Surface peat to stream water DOM

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

Organic matter was assumed to move from belowground biomass to litter at the same rate as aboveground biomass moving to litter. Surface peat could become deep peat through three possible processes: conversion to CO_2, DOM or CH_4. DOM was considered a final product in its own right, and its formation did not lead to deep peat formation due to the low energy released during its formation requiring more surface peat OM to be processed. Thus, stream water DOM was treated as a separate loss pathway. Knowing the potential energy and carbon content for each reaction or transition in Fig. 1, and the elemental composition of the organic matter, the oxygen consumption could be calculated.

Worrall et al. (2022) provided balanced reactions for each of the above transitions (Fig. 1). Once the PV and $[C]_{CO2}$ are known for each of the reactions listed above (1 through 6), then the reactions were balanced with respect to C, carbon oxidation state (C_{ox}), O and N. Reactions were finally balanced with respect to H, and it was assumed that plentiful protons were available, i.e. charge balance was not explicitly required. The balanced reactions were assessed relative to the appropriate TEA and respective fluxes of CO_2 and other carbon species, but the consequences for the flux of O_2 was not considered. Furthermore, the role of TEAs other than O_2 have consequences for O_2 consumption and these non-organic matter, O_2 consumption processes were considered. Specifically, we consider the regeneration of NO_3 from NH_4 where the regeneration of NO_3 from NH_4 requires O_2 consumption. However, for S we assume that SO_4 is not regenerated because H_2S is lost as gas from ecosystem and that regeneration of SO_4 from organic-S is negligible.

3.1 Uncertainty analysis

The triplicate measurements of the composition of the aboveground biomass, below ground biomass, litter, peat soil and DOM were used to give the median and the interquartile range (IQR) of all elemental analysis. Second, the value of E_g (Equation viii) is taken as varying between 0.85 and 0.89. An estimate of the uncertainty in the OR estimate was made assuming uniform distribution between these ranges, sampling 500 times from within those distributions, and with stochastic combination.

3.2 Study site

The study was conducted at the Moor House National Nature Reserve (NNR) blanket peat catchment, located in the headwaters of the River Tees in northern England (54.6883° N, 2.3792° W; Fig. 2). This site is part of the UK Environmental Change Network (ECN) and provides valuable chemical and hydrological data from the Trout Beck catchment, as detailed by Sykes and Lane (1996).

The study site is situated at a high altitude, primarily above 500 meters (1,640 feet) above sea level. The highest point in the catchment is 848 metres above sea level. The underlying bedrock consists of Carboniferous limestone, sandstone, and shale formations, interspersed with intrusions of dolerite known as the Whin Sill (Johnson and Dunham, 1963; Burt and Tucker, 2020).

A layer of glacial till covers this solid geology, hindering drainage and contributing to the initiation of an extensive blanket peat during the Holocene epoch. The region experiences a cold climate, with a mean annual temperature of 5.2°C (averaging period: 1931 to 2000). Air frosts occur on over 100 days per year (period considered: 1991 to 2000, Holden and Rose, 2001). Annual precipitation is high, averaging 1953 mm (averaging period: 1953 to 1997, Burt et al., 1998), with significant snowfall. Snow cover at 500 meters persists for an average of 55 days annually (Archer and Stewart, 1995).

The vegetation is characterized by a dominance of cotton grass (*Eriophorum spp.*), heather (*Calluna vulgaris*), and moss (*Sphagnum spp.*). There had been no prescribed burning in the catchment since 1954 (Garnett et al., 2000).

3.3 Carbon & nitrogen budget

The carbon budget for the study site was established using the findings of Worrall et al. (2009), with updates incorporated from the N budget presented in Worrall et al. (2012). The C budget can be summarized as follows:

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

$$(\pm 4.7) \quad (\pm 21) \quad (\pm 0.6) \quad (\pm 4) \quad (\pm 4.5) \quad (\pm 26)$$

where: C_x = carbon in that flux or reservoir, with x as: pp = primary production, R = net ecosystem respiration, DOC = dissolved organic carbon; CH4 = methane; dissco2 = dissolved CO_2; POC = particulate organic carbon; and RES = residual carbon stored as peat. The values in the parentheses beneath the coefficients in Equation (vi) are the 95th percentile confidence interval.

Additionally, the budgets for nitrogen, sulphur, and iron for this study site have been documented in previous research (Worrall et al. 2012, Boothroyd et al., 2021). These established budgets can be utilized to validate and refine the predictions generated by the new methodology in this study.

3.4 Sampling

No additional sampling was undertaken during for this study that had not already been described in Worrall et al. (2022).

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

4. Results

The results of the elemental analysis are summarised in Table 1 (Figure 3). Given the stoichiometry of the organic matter reservoirs and fluxes, the formation of aboveground biomass from glucose (i.e., primary production) at this site leads to following best-fit reaction:

$$C_6H_{12}O_6 + 0.08NH_4^+ \rightarrow 0.08C_{57}H_{86}NO_{35} + 1.44CO_2 + 0.78H_2O + 3.32H^+ \quad \text{(xi)}$$

It follows from Equation (xi), that for every 100 moles of C fixed as glucose then 76 moles of C will be fixed as aboveground biomass and 24 moles will be lost as CO_2. No O_2 was consumed in this reaction, but NH_4 was required. For every 100 moles C fixed as glucose then 1.33 moles N as NH_4 are required. Given the range in triplicate measurements of elemental composition and the accepted range on E_g then the inter-quartile range (IQR) on $[C]_{CO2}$ (Equation ix) is ±3%.

For the production of belowground biomass from glucose (primary production):

$$C_6H_{12}O_6 + 0.1NH_4^+ \rightarrow 0.1C_{49}H_{73}NO_{29} + 1.2CO_2 + 0.91H_2O + 4H^+ \quad \text{(xii)}$$

For 100 moles of C sequestered as glucose 26.5 moles C are released as CO_2 and 73.5 moles retained as biomass. As for Equation (xi) there is no O_2 consumption in this reaction and 1.6 moles of NH_4 is consumed for every 100 C fixed as glucose.

For the conversion of aboveground biomass to litter the best-fit equation was:

$$C_{57}H_{86}NO_{35} + 0.92NO_3^- + 4.63O_2 \rightarrow 1.92C_{25}H_{35}NO_{15} + 9.1CO_2 + 18.8H^+ \quad \text{(xiii)}$$

The conversion of litter from aboveground biomass does require O and N, and because O is required then it was assumed that the N addition would be in the form of NO_3. Given 100 moles C as aboveground biomass then 84 moles C as litter would be produced and 16 moles C converted to CO_2. Further, that 8.1 moles of O and 1.6 moles of N as NO_3 would be consumed for every 100 moles C as aboveground biomass.

For reaction of litter to the surface peat the best-fit reaction is:

$$C_{25}H_{35}NO_{15} + 3.65O_2 \rightarrow 0.53C_{39}H_{56}NO_{26} + 4.26CO_2 + 0.47NH_4^+ + 3.91H^+ \quad \text{(xiv)}$$

For every 100 moles C in this transition, 17 moles are lost as CO_2 and 83 moles are converted to surface peat. For every 100 moles of C as litter making this transition then 14.6 moles of O are consumed, while 1.9 moles of N (as NH_4) are produced. The NH_4 produced is then available to be recycled in other reactions in the environment, particularly as a form of N supply to aboveground biomass (Equations xi & xii). To convert this substrate, litter, this reaction does not require N as a terminal electron acceptor, and because this reaction will occur near the peat surface then oxygen will be consumed in the conversion of NH_4 to NO_3.

For the pathway from surface peat to deep peat without the production of CH_4 or DOM the best-fit reaction is:

$$C_{39}H_{56}NO_{26} + 1.54SO_4 \rightarrow 0.43C_{75}H_{107}NO_{45} + 6.41CO_2 + 1.54H_2S + 0.53NH_4^+ + 4.75H^+ \quad \text{(xv)}$$

The relative C/N ratios indicate that nitrogen (N) is released during the transformation of surface peat to deep peat, similar to the process of surface peat formation (Equation xiv). This released N contributes to nutrient recycling for primary production, as noted in Equation (xii). The oxidation states of the substrate and product suggest the need for an oxidant. Given the release of N, sulphate (SO_4) is likely the terminal electron acceptor. So for the pathway from surface peat to deep peat for every 100 moles of carbon (C) transitioning through this pathway, 83 moles of C are lost as CO_2, 16 moles as CH_4, and 1.4 moles of N are produced as NH_4.

For the pathway from surface peat to stream water DOM the best-fit reaction is:

$$C_{39}H_{56}NO_{26} + 2.29NO_3^- \rightarrow 1.18C_{31}H_{38}NO_{24} + 2.27CO_2 + 2.29NH_4^+ + 2H^+ \quad \text{(xvi)}$$

This pathway results in the loss of only 6% of the carbon as CO_2, indicating the highly oxidized state of the stream water dissolved organic matter (DOM). The formation of stream water DOM in this pathway does not require an N source but does necessitate an oxidant. While O may act as the oxidant higher in the peat profile, Equation (xiv) suggests nitrate (NO_3^-) as the terminal electron acceptor. In the pathway described by Equation (xvi), for every 100 moles of carbon lost as dissolved organic carbon (DOC), 6.2 moles of carbon are lost as CO_2, and 6.3 moles of nitrogen are reduced from nitrate to ammonium ($NH4^+$).

There is also the pathway from surface to deep peat via methane production:

$$C_{39}H_{56}NO_{26} + 7.56H_2O \rightarrow 16.78CH_4 + 22.22CO_2 + NH_4^+ \quad \text{(xvii)}$$

The oxidation state (C_{ox}) and C/N ratio changes during the reaction suggest nitrogen (N) is released. The high energy requirement for CH_4 production inhibits the formation of residues like deep peat. Equation (xvii) shows a disproportionation reaction, where both reduced and oxidized forms of carbon (C) are produced from the initial substrate. The CO_2 to CH_4 ratio in Equation (xvii) depends on the substrate's C_{ox}, for example, glucose ($C_{ox} = 0$) would yield CO_2

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

and CH_4 in equal proportions. However, slightly reduced surface peat (C_{ox} = -0.1) favours CO_2 production. It was assumed sufficient acid-base groups were present for charge balance. The deep peat substrate's C_{ox} limits the available oxygen for CO_2 production, crucial for the reaction's energetics. For every 100 moles of C in surface peat, 46 moles become CH_4, 54 moles are lost as CO_2, and 2.5 moles of N are released as N.

If we consider 100 moles C fixed as glucose, we can then propagate the progress of C released and O_2 consumed (Table 2 and summarised in Fig. 3). Because the reaction of C from surface peat onwards does not consume O, the total amount of O_2 consumed by organic C processing is not dependent upon the pathway after surface peat formation (i.e. is independent of production of DOC or CH_4 or of deep peat). For every 100 moles of C fixed in photosynthesis 7.8 moles of O_2 are consumed, therefore 92.2 moles of O_2 are released, i.e. an OR = 0.92.

Across the reactions considered, 2.9 moles N as NO_3 and 1.3 moles of N as NH_4 are required, while 3.4 moles of N as NH_4 are produced (assuming Equation x). To meet this N requirement would mean that 2.1 moles of NH_4 must be converted to NO_3 which in turn means that 3.2 moles of O_2 will be consumed. The complete conversion of NH_4 to NO_3 would still require 0.8 moles of N as NO_3 which would be supplied from atmospheric deposition, i.e. the recycling of N predicted above is not sufficient for the required supply of NO_3. Worrall et al. (2012) suggest that atmospheric deposition would supply between 0.1 and 0.46 moles N as NO_3, but they also note that the deposition at the study site was not significantly changing. However, there would be sufficient supply of N if atmospheric NH_4 deposition could be oxidised. By accounting for O_2 consumption of this additional N from NH_4 deposition means, in total, 11.5 moles of O_2 are consumed, and thus yields a mean OR = 0.88.

5. Discussion

https://doi.org/10.5194/egusphere-2025-1469
Preprint. Discussion started: 22 April 2025

The study has proposed an independent method for finding the OR of an ecosystem via understanding the element analysis of organic matter fluxes and reservoirs in an environment constrained by stoichiometric and energy balances. Previous approaches have been based upon the OR calculated from the CHNO composition of individual organic matter pools (e.g. peat soil; Worrall et al., 2016) or from the degradation of biomacromolecules (Randerson et al., 2006; Worrall et al. 2017), but not from the actual O and C budgets as required by the definition of Equation (i) and now demonstrated in this study.

Previously for this site, Worrall et al. (2016) gave a value of OR = 1.04, assuming that the OR was that of residual components after processing of organic matter and weighted by the relative magnitudes of environmental fluxes. Alternatively, Worrall et al. (2017) estimated the OR of the component of the organic matter that was returned to the atmosphere and not that which was fixed into the environment, i.e. that organic matter that was processed through, and out of, the environment, rather than the OR of the fixed organic matter that remained as the residual in the environment. The value given by Worrall et al. (2017) was 0.96 – 0.99, but this estimate did not account for E_g (Equation viii). By accounting for E_g (E_g = 0.84 to 0.89) in the study of Worrall et al. (2017) would lead to a revised value for OR = 0.82 to 0.88.

Other published measurements of OR range between ~0.9 and 1.05 (e.g., van der Laan et al., 2014; van Leeuwen and Meijer, 2015; Faassen et al., 2023). Some studies have found larger values of OR from gas flux measurements (e.g., 0.7 – 1.6 from a range of forested sites, Seibt et al., 2004) implying that a range of results was possible. This study has found an OR = 0.88, which is consistent with the values found by Worrall et al. (2017) (once E_g is accounted for) and nearer the bottom range of other previous values.

How can values of OR < 1 be explained? We could consider the process of organic carbon fixation and transfers through, into and out of terrestrial environments as being a disproportionation reaction. Disproportionation is a redox reaction in which an element (e.g.

C) undergoes both oxidation and reduction to form two different products but the weighted sum of which is the oxidation state of the element in the reactants. It has been little considered that by reporting OR > 1 this means that the organic carbon in the terrestrial ecosystem is relatively reduced compared to carbon fixed as glucose through photosynthesis which by definition OR = 1. Accepting a value of OR > 1 assumes that the atmosphere is interacting with a reduced form of terrestrial OM and that this is the residual of the turnover of photosynthetic products. But to form reduced products from glucose an oxidised form of OM must also have been produced. The fact that collected and analysed samples give reduced values of OR (relative to glucose) means that the oxidised form has been lost. Therefore, it is the oxidised forms of carbon in terrestrial organic matter that have turned over (i.e. decomposed) to the atmosphere. Previous studies (e.g. Keeling and Shertz, 1992; Stephens et al., 1998; Keeling et al., 1996; Prentice et al., 2001; Langenfelds et al., 1999) have assumed that it is the reduced and residual forms that have interacted with the atmosphere, whereas, by definition, it must be organic matter with OR < 1 that is interacting with the atmosphere. Therefore, we propose that organic carbon, once fixed in primary productivity, is subject to disproportionation and this would leave more reduced OM in soils and biomass while a more oxidised form interacts with the atmosphere.

This study has assumed that sulphur plays no role in the consumption of O_2, that the role of sulphur as a TEA results in the release of H_2S, and that there is no oxidation of sulphide. Furthermore, we assume that no organic-S becomes oxidised within the soil column. If there is oxidation of sulphides or of organic-S within this terrestrial environment, then that leads to a lower value of OR. Equation (xiv) implies that for every 100 moles C fixed from the atmosphere in primary production then 2.01 moles of S as sulphate would be consumed. However, if this was all regenerated (i.e. oxidised to SO_4 and no loss as H_2S or formation of stable stores of solid sulphides) then it would consume 4.02 moles O_2. Accounting for this

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additional O_2 consumption, if there were complete regeneration of sulphur, then the OR would decrease from the current estimate of 0.88 to be 0.8.

How is it possible to have an ecosystem OR = 0.88? The OR of glucose is 1 ($C_{ox} = 0$) but the OR of cellulose is 0.98 ($C_{ox} = 0.05$). Equally, the OR of lignin is 1.11 ($C_{ox} = -0.43$) and that of gluten (a plant protein) is OR = 1.18 ($C_{ox} = 0.03$). The OR measured for this ecosystem (OR = 0.88) implies that the lost composition is more oxidised than the carbohydrates (e.g. cellulose, OR = 0.98). A simple resolution is that the lost composition contains a small proportion of amino acids. Common amino acids have a high positive C_{ox} and low OR, and therefore a simple admixture of amino acids and carbohydrates would have OR < 1. Therefore the disproportionation reaction in this ecosystem is one of the preferential removal of carbohydrates and transformation of proteins with the preferential preservation of lignin-like molecules. Such a set of reactions amongst the biomacromolecules would give the OR observed.

In the case of peatlands, this study site is accumulating C and has been doing so for at least decades if not centuries, but what would happen if the ecosystem were a net source of C? In this scenario the environment would be oxidising and actively consuming O_2 which would mean that OR would be even lower than at present. However, if a system was becoming a net source of carbon, then net uptake of CO_2 would decrease. The approach outlined in this study assumes a net uptake of CO_2 and it is thus unclear how OR would be defined in a net source environment.

Can this method be applied elsewhere? The method used here required the C and N budgets to be known, but it needed to know these from stoichiometric and energy constraints and not necessarily from direct flux measurements. Peatlands are generally considered low nutrient systems and are reliant on the recycling of their nutrients in the soil profile with relatively low inputs from external sources (in the case of this study that is atmospheric deposition). In peat ecosystems with higher external inputs of nitrate then regeneration of NH_4 maybe reduced and OR would be larger. This study site is a blanket bog which by definition means that water runs off from the peat taking N species away in that runoff. Alternatively, in peat ecosystems that are raised bogs the hydrological loss is instead dominated by evaporation, which means that a raised bog exists in a "soup bowl" (Glatzel et al., 2023). In the "soup bowl" analogy there is no pathway for nutrients to leave and so NH_4 will be recycled lowering OR.

The implication of OR < 1 can be explored through application of Equations (iii) and (iv). Assuming all values are as described above then Equation (ii) approximates to:

$$f_{land} = 3.15 - 1.58OR \qquad \text{(xviii)}$$

Therefore, a decrease of 0.1 in the value of OR would result in a 0.16 increase in the global flux to land. At the presently accepted value of $OR_{terra}^{global} = 1.1$ then f_{land} = 1.38 Gt C/yr, at the preferred value calculated from this study (OR = 0.88) then f_{land} = 1.55 Gt C/yr (0.17 Gt C/yr) more than present value).

6. Conclusions

This study presents a new method for calculating the O budget and the OR for an ecosystem from a knowledge of the elemental composition and C and N budgets of that ecosystem given stoichiometric and thermodynamic constraints. The estimation of the O budget in the context of the C budget makes it possible for oxidative ratio (OR) of an environment to be calculated. The value of the ecosystem OR was 0.88, 68% of the O_2 consumption was due to oxidation of organic C and 32% was due to oxidation of NH_4. The value estimated by this study is in line with the uptake, processing and transfer of organic matter through this terrestrial ecosystem being a disproportionation reaction of the C. That is, C fixed as glucose in photosynthesis must lose an oxidised form of C if what is left behind is more reduced than glucose. The implication of OR < 1 at global scale, would be that global terrestrial C sinks have been underestimated by 12%.

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Competing interests

The authors know of no competing interests.

Author contributions

FW and CH contributed to the study conception. Material preparation, data collection and chemical analysis were performed by GDC and CM. The data analysis and first draft of the manuscript was done by FW and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data Availability statement

The data used for this study can be found in the tables and in the Supplementary Material.

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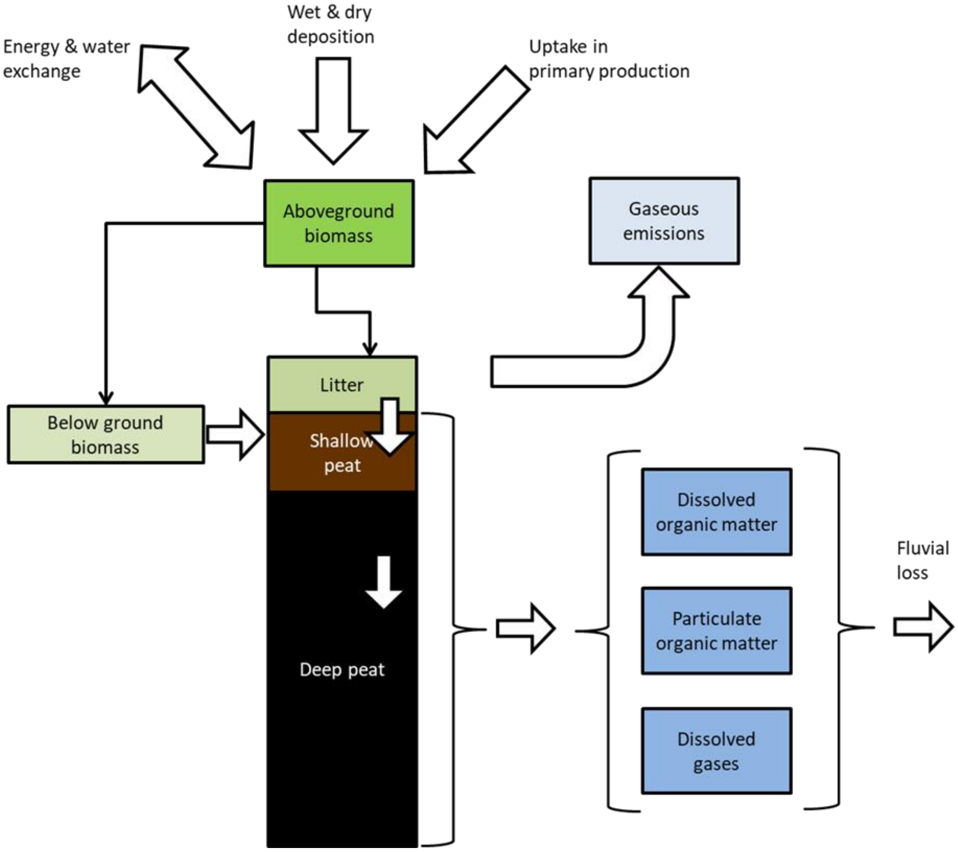

Figure. 1. A schematic diagram of organic matter fluxes and reservoirs, with each arrow representing a carbon flux and boxes being the organic matter reservoirs.

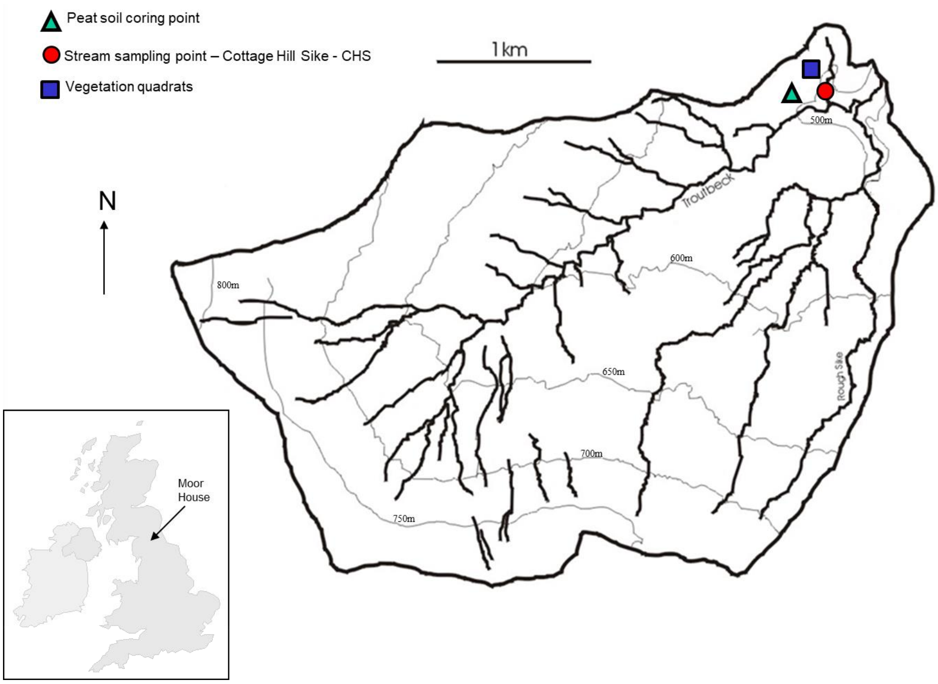

Figure. 2. Map of the study catchment. CHS is Cottage Hill Sike, the stream water sampling location. Numbers refer to altitude in metres above sea level.

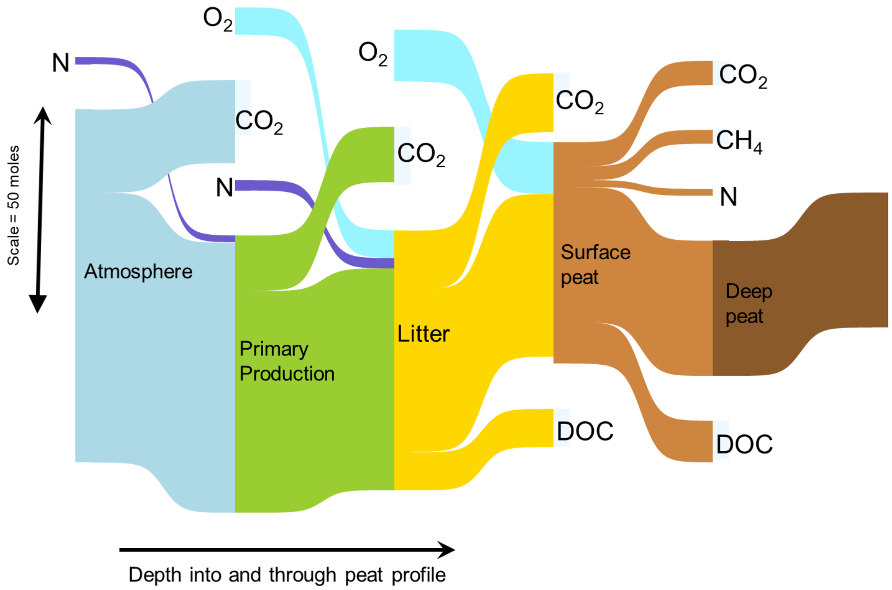

Figure. 3. Sankey diagram of the of the organic matter fluxes relative C,O and N as given in Table 2 and Equation (x), i.e. line thickness is proportional to moles of the element, through environmental compartments given in Table 2.

Table 1. Median composition of the carbon pools examined in the study, with variation indicated by the 95th percentile range. Median stoichiometry is expressed relative to nitrogen content, except for cellulose, which is expressed relative to carbon.

Carbon reservoir (or flux)	Elemental composition (mol/100g)			
	C	H	N	O
DOM first order stream	3.8±0.1	4.6±0.2	0.12±0.01	2.9±0.1
DOM shallow peat porewater	4.17±0.18	5.24±0.19	0.14±0.009	2.06±0.03
DOM deep peat porewater	4.05±0.16	5.80±0.65	0.13±0.005	1.97±0.08
POM	4.05±0.02	6.40±0.09	0.18±0.01	2.50±002
Aboveground biomass	4.15±0.12	6.30±0.09	0.07±0.015	2.55±0.06
Below ground biomass	4.23±0.1	6.30±0.09	0.09±0.01	2.48±0.06
Grass or sedge	4.04±0.1	6.30±0.09	0.12±0.01	2.59±0.06
Mosses	4.03±0.1	6.30±0.09	0.07±0.01	2.65±0.06
Calluna	4.29±0.1	6.58±0.09	0.05±0.01	2.53±0.06
Litter	4.17±0.08	5.90±0.1	0.167±0.007	2.48±0.08
Peat soil (0-5 cm)	4.18±0.01	6.00±0.6	0.10±0.01	2.53±0.11
Peat soil (45-50 cm)	4.44±0.4	5.3±1.4	0.08±0.02	2.40±0.24
Peat soil (90-100 cm)	4.47±0.21	5.27±0.76	0.08±0.02	2.37±0.13
Lignin	5.14±0.01	6.03±0.1	0.06±0.005	1.81±0.01
Cellulose	3.60±0.005	6.25±0.24	0.00	3.21±0.01
Humic acid	2.99±0.01	3.68±0.09	0.06±0.005	2.02±0.02
Protein	4.72±0.06	5.42±0.17	1.24±0.04	1.28±0.05

Carbon reservoir (or flux)	Median stoichiometry	Median C_{ox}
DOM first order stream	$C_{31}H_{38}NO_{24}$	0.4±0.08
DOM shallow peat porewater	$C_{29}H_{41}NO_{15}$	-0.31±0.05
DOM deep peat porewater	$C_{30}H_{39}NO_{15}$	-0.22±0.16
POM	$C_{22}H_{35}NO_{14}$	-0.21±0.03
Aboveground biomass	$C_{57}H_{86}NO_{35}$	-0.26±0.04
Below ground biomass	$C_{49}H_{73}NO_{29}$	-0.25±0.04
Grass or sedge	$C_{33}H_{52}NO_{21}$	-0.19±0.04
Mosses	$C_{95}H_{145}NO_{56}$	-0.19±0.04
Calluna	$C_{55}H_{86}NO_{46}$	-0.32±0.04
Litter	$C_{25}H_{35}NO_{15}$	-0.05±0.05
Peat soil (0-5 cm)	$C_{39}H_{56}NO_{26}$	-0.10±0.15
Peat soil (45-50 cm)	$C_{57}H_{68}NO_{31}$	-0.02±0.33
Peat soil (90-100 cm)	$C_{75}H_{107}NO_{45}$	-0.07±0.18
Lignin	$C_{87}H_{103}NO_{31}$	-0.43±0.02
Cellulose	$C_6H_{10}O_5$	0.05±0.06
Humic acid	$C_{49}H_{60}NO_{33}$	0.19±0.04
Protein	C_5H_5NO	0.18±0.05

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Table 2. Transformations between different organic matter reservoirs (see Methods). For each reaction: the estimated moles C as CO_2 production; moles O_2 consumed; moles of N consumed; and moles of N produced. All expressed per 100 moles of C of substrate.

Substrate	Product	C as CO_2 produced	O_2 consumed
Glucose	Aboveground biomass	24	0
Glucose	Belowground biomass	23	0
Aboveground biomass	Litter	16	8.1
Litter	Surface peat	17	14.6
Surface peat	DOM	5.8	0
Surface peat	Deep peat	16	0
Surface peat	CH_4	54	0

Substrate	Product	N consumed	N produced
Glucose	Aboveground biomass	1.3	0
Glucose	Belowground biomass	1.7	0
Aboveground biomass	Litter	1.6	0
Litter	Surface peat	0	1.9
Surface peat	DOM	0	5.9
Surface peat	Deep peat	0	1.4
Surface peat	CH_4	0	2.6