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Key Points:

- Study evaluates the Sulfur (S) budget of a peatland to assess controls on C and greenhouse gas budgets
- The peat was accumulating 127 kg S/km²/yr, and reducing 0.25 t S/km²/yr, but in 8 out of 23 years the catchment was a net producer of S
- The peatland was capable of removing 71% of atmospheric deposition and diverting 0.47 t C/km²/yr are diverted from methanogenesis

Supporting Information:

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

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Sulfur Constraints on the Carbon Cycle of a Blanket Bog Peatland

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Abstract The reduction of sulfate (SO₄²⁻) represents an alternative terminal electron acceptor for the oxidation of organic matter in peat soils. The greenhouse gas budget in peatlands will be constrained by how much a peatland can utilize SO₄²⁻ reduction as an alternative to methanogenesis. Using records of atmospheric deposition and stream chemistry coupled with elemental analysis of peat soil, vegetation, particulate organic matter (POM) and dissolved organic matter (DOM), this study estimated a 23-years long sulfur (S) budget for a blanket bog-covered catchment in the North Pennines, England. The study showed that: (a) Atmospheric deposition of total S significantly declined over the study period from 2.4 to 0.5 t S/km²/yr. (b) Long term accumulation of S into deep peat at 1 m depth averaged 127 kg S/km²/yr. (c) Total S fluvial flux peaked as 4.5 t S/km²/yr with an average of 0.7 t S/km²/yr. (d) On average, over 23 years, 0.25 t S/km²/yr were reduced to either mineral sulphides or hydrogen sulphide; however, in eight out of the 23 years the catchment was a net producer of S to the streams of the catchment. At maximum observed, S reduction capacity the peatland was capable of a net removal of 71% of atmospheric S deposition. Allowing for the efficiency of energy transfer in the redox process and the oxidation state of peat organic matter means that for every mole of SO₄²⁻ reduced, 1.69 moles of CO₂ were produced, and an average of 0.47 t C/km²/yr are diverted from methanogenesis.

Plain Language Summary Peatlands are important terrestrial carbon (C) stores, with more carbon stored in peatlands than in the atmosphere. The very existence of peatlands relies on the fate or organic matter and the carbon budget is, therefore, a statement of ecosystem's future. The C budget of the peatland can be viewed as a series of reduction-oxidation reactions. Carbon dioxide (CO₂) from the atmosphere is fixed in to plant organic matter by photosynthesis. As organic matter transfers into the peat profile, the organic matter is transformed to CO₂, methane (CH₄), dissolved organic matter (DOM) and lost as particulate organic matter (POM). All but the transformation to POM requires a terminal electron acceptor, the most efficient of which is oxygen, followed by nitrate, but both of these are rapidly consumed in the water-logged conditions of peatlands which could lead to production of the powerful greenhouse gas—methane. The alternative electron acceptors that could limit organic matter loss are iron and sulfate. In this study, we use detailed long term records, coupled with elemental composition measurements, from an peatland in the UK to show that for every tonne of S removed by the peatland 0.23 tonnes of carbon are diverted from methane loss.

1. Introduction

Peatlands are important terrestrial carbon (C) stores, with an estimated 500 ± 100 Gt C in northern peatlands, over an area estimated to cover 3.2 million km² (Loisel et al., 2017; Yu, 2012). In the UK, 1.75 Gt C is estimated to be stored in peatlands (Joosten, 2009), of which 85%–92% is blanket bog (Clark et al., 2010; Lindsay, 1995). Given the magnitude of the store represented by peatlands it is important to understand the processes involved in peatland C cycling. Furthermore, a functioning peatland will sequester C from the atmosphere and provide a long-term store due to slow rates of decomposition under acidic, anaerobic conditions (Moore, 1989) and thus a well-functioning peatland can act to mitigate human-induced climate change.

Table 1
Twenty-Year Average Concentration of Redox Active Species in Peat Soil Pore Water, Taken From Table 2 of Worrall et al. (2018)

	Mean concentration	
	Shallow (10 cm)	Deep (50 cm)
Sulfate (mg S/l)	0.11	0.02
Nitrate (mg N/l)	0.01	0.01
Ammonium (mg N/l)	0.06	0.42
Iron (mg Fe/l)	0.17	0.21
DOC (mg C/l)	21.3	17.5
Conductivity ($\mu\text{S}/\text{cm}$)	39.1	31.4
pH	4.3	4.6

DOC, dissolved organic carbon.

The very existence of peatlands relies on the fate of organic matter, and therefore, the C budget is a statement of the ecosystem's future. The estimation of C budgets has been a common research target and complete contemporary C budgets are now common (e.g., Billett et al., 2004; Nilsson et al., 2008; Roulet et al., 2007; Worrall et al., 2003). The C budget of the peatland can be viewed as a series of redox reactions (Worrall et al., 2017). The fixing of CO_2 to glucose converts the nominal oxidation state of the C (C_{ox} -Masiello et al., 2008) in CO_2 from the +4 state to carbon in glucose at the zero oxidation state. As organic matter transfers into the peat profile as litter and then to the deepest peats, the organic matter is transformed to CO_2 , CH_4 , dissolved organic matter (DOM) and lost as particulate organic matter (POM). POM has been shown to be a physical admixture of plant and soil components and is therefore not a product of biogeochemical transformation (Worrall et al., 2017). But the biogeochemical transformation of organic matter to release CO_2 and DOM is the release of highly oxidized forms of organic C ($\text{C}_{\text{ox}}[\text{CO}_2] = +4$ and $\text{C}_{\text{ox}}[\text{DOM}] = 0.4$ -Worrall et al., 2017) and requires an electron acceptor, that is, for oxidation there must also be reduction. Ultimately, organic matter can oxidize itself through a disproportionation reaction releasing both CO_2 and CH_4 (Blodau & Deppe, 2012)

The release of the most reduced form of C, methane (CH_4), from peatlands is critically important because of its large greenhouse gas warming potential relative to CO_2 . Methanogenesis is energetically the least favorable of the terminal electron acceptor (TEA) reactions and several electron acceptors are used prior to CH_4 production (LaRowe & Van Cappellan, 2011). The most energetically favorable TEA is O_2 but this appears to be rapidly removed in the water-logged, low permeable conditions of a peat profile (Worrall et al., 2012). Once O_2 no longer becomes a viable electron acceptor then the next most energetically favorable TEA is nitrate during denitrification. Indeed even in nutrient poor peatlands such as the ombrotrophic blanket bogs of the UK there is clear evidence of the removal of nitrate and generation of ammonium in peat soil pore water (Worrall et al., 2012). Furthermore, the complete removal of nitrate within the top 10 cm of the peat profile provided evidence of the lack of O_2 shallow in the peat profile (Worrall et al., 2012). In some minerotrophic systems, Fe represents a plausible electron acceptor (Smemo & Yavitt, 2011). However, in ombrotrophic peatlands the supply of Fe is from atmospheric deposition only and that is, small relative to deposition of nitrogen (N).

After N, the next important alternative electron acceptor is S. For ombrotrophic peatlands the processing of sulfate represents a constraint on how, and by what means, organic matter is and could be processed. The S budget of peatland represents a way to constrain the fate of peatlands because the presence of alternative electron acceptors such as SO_4^{2-} and Fe have been noted to suppress the primary anoxic form of C mineralization, methanogenesis (Smemo & Yavitt, 2011).

Thermodynamic constraints upon decomposition with depth in peat profiles have been observed (Beer & Blodau, 2007; Bonaiuti et al., 2020) and at Moor House, (an ombrotrophic blanket peat covered catchment in the UK), reactions were limited beyond 40 cm depth, allowing the long-term retention of organic matter in peat soil (Worrall et al., 2018). As a consequence, it was noted that studies at Moor House should consider the role of DOM at different depths in the soil profile. Furthermore, analysis of long-term water quality records at Moor House observed a decrease in SO_4^{2-} concentration in peat pore water between 10 and 50 cm depth (Table 1), and thus it was possible that SO_4^{2-} was a terminal electron acceptor, with preferential depletion of SO_4^{2-} by bacterial sulfate reduction inhibiting methanogenesis (Worrall et al., 2018).

Moor House is one of the most researched peatlands in the world. It was the first peatland for which a complete C budget was estimated (Worrall et al., 2003), where this budget included the fluxes of: dissolved organic carbon (DOC); particulate organic carbon (POC); dissolved CO_2 ; ecosystem respiration; primary productivity; and CH_4 . Worrall et al. (2012) calculated the multi-annual N budget for the peatland and showed that over a 17 year period the site was an average annual sink of total N of 0.7 tonnes $\text{N}/\text{km}^2/\text{yr}$ with up to 100% removal of nitrate-N between atmospheric deposition and fluvial loss from the study catchment.

Equally, the flux of N₂ and N₂O from the peatland meant that extensive denitrification was occurring as nitrate-N acted as a TEA. The loss of nitrate-N was observed in the peat pore water with nitrate reduced or denitrified within the 10 cm of the pore water profile and that NH₄ is the dominant form of inorganic N in the pore water (Table 1).

In the absence of oxidized inorganic N as a TEA the organic matter itself could act as a TEA. However, Worrall, Clay, et al. (2016) have shown that there is no significant change in the oxidation state of the accumulating organic matter at this site. Indeed Clay and Worrall (2015) have shown that there was no consistent or significant change in organic matter oxidation with depth for eight peatland sites across the UK. Lovley et al. (1996) have shown that DOM can act as a TEA and divert energy from methanogenesis, while Bauer et al. (2007) found that DOM could act as a redox buffer. Gao et al. (2019) found that CH₄ formation occurred only after the electron accepting capacity (EAC) of organic matter was depleted. Total EAC of organic matter was dominated by POM, which was key in inhibiting methanogenesis, but DOM was nonetheless important and it was speculated that DOM electron accepting moieties were more readily utilized as TEAs than POM and may influence POM reduction by electron shuttling (Gao et al., 2019).

Suppression of CH₄ production occurs because microbial groups can utilize TEAs such as NO₃⁻, Fe(III), Mn(III, IV) and SO₄²⁻ (Bridgham et al., 2013; Knorr et al., 2009) as oxidation of organic matter using these TEAs has a greater thermodynamic efficiency than methanogenesis (Lai, 2009). Consequently, bacterial sulfate reduction (BSR) could have both positive and negative climate change feedbacks (Vile et al., 2003), as BSR can both inhibit CH₄ production while promoting CO₂ production (Pester et al., 2012). Vile et al. (2003) investigated the role of S deposition on anaerobic C mineralization, demonstrating that BSR increased with higher levels of S deposition, suggesting an increased importance of sulfate as a TEA. Bacterial sulfate reduction led to demonstrably lower rates of CH₄ production at sites of higher S deposition, suggesting that methanogens were outcompeted for C and hydrogen by the SO₄²⁻ reducers (Vile et al., 2003). Bacterial sulfate reduction did not lead to elevated CO₂ emissions compared to a pristine site, though 26%–37% of CO₂ production at the polluted sites was attributed to BSR (Vile et al., 2003). Blodau et al. (2007) found that when BSR was suppressed using the inhibitor molybdate, CO₂ production was lowered by 20%–50%, demonstrating the role of BSR in anaerobic C mineralization.

Bacterial sulfate reduction is important because it is expected that for every mole of SO₄²⁻ reduced, two moles of CO₂ are produced (Vile et al., 2003) and consequently it is important to understand how much SO₄²⁻ is deposited and how much is lost in peatland systems to determine its potential impact on the carbon cycle. We hypothesize that a peatland has the ability to accumulate S but that it also may remove S as it accumulates organic matter that it also removes S via reducing SO₄²⁻ to S²⁻ and thus limiting organic matter decomposition to CH₄. Further, we hypothesize that the way to understand the impact of S cycling on the C cycle within peatlands is to measure the S budget within the context of the other elemental budgets of a peatland. Therefore, the purpose of this study was to consider the S budget of a peat catchment as a means of understanding controls on C and greenhouse gas budgets of these important global C stores.

2. Approach and Methodology

The approach taken here was to analyze the S content of the organic matter in a series of organic matter pools and pathways with the addition of measuring the fluxes of S in to and out of a peatland all within the context of other known elemental and dry matter budgets (Figure 1). This study defined the S budget as:

$$S_{\text{atmdep}} = S_{\text{peat}} + S_{\text{fluvial}} + S_{\text{reduced}} \quad (1)$$

where: S_x = the annual export of S (t S/km²/yr) with atmdep = atmospheric deposition; peat = S stored accumulated at depth in the peat soil; fluvial = the loss of S in the streams of the catchment; and reduced = the S reduced to sulphide (S²⁻). In Equation 1 the production of S_{reduced} was taken as consisting of both production and loss of sulphide as H₂S and for storage as mineral sulphides (typically FeS). The budget is for total S which means inorganic and organic components were considered as well as dissolved, colloidal, particulate and gaseous forms. For the purpose of this study S_{reduced} is given as positive when there was net loss relative to the atmospheric inputs and negative when there is net gain across the peatland. The sign convention also means that accumulation within the peatland would be a positive value. The methodology

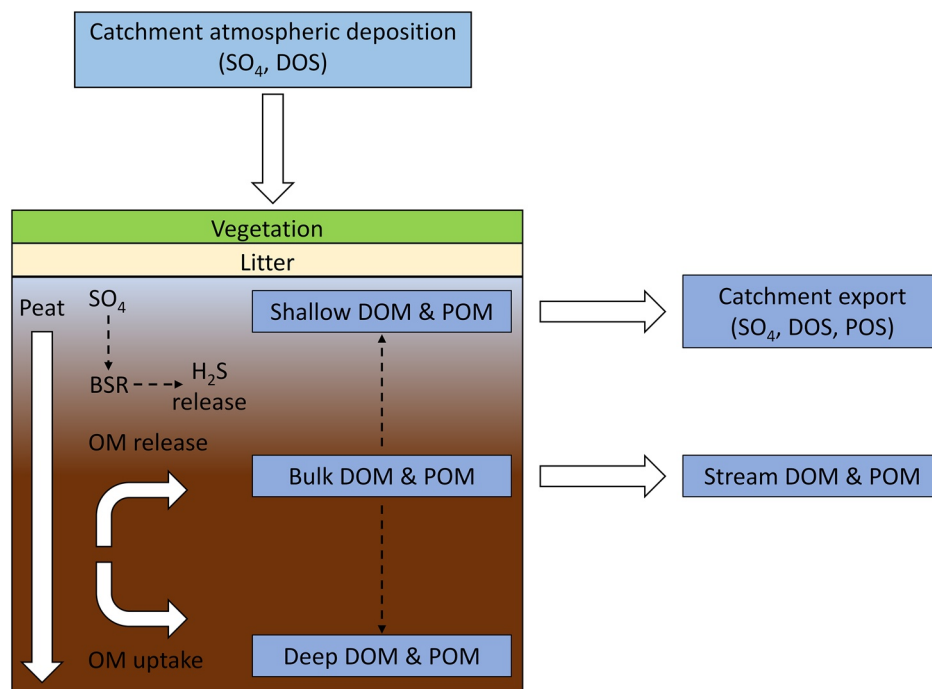


Figure 1. Conceptual model of organic matter pools and catchment sulfur species studied. Dissolved organic matter (DOM) and particulate organic matter (POM) are dissolved and particulate organic matter. Shallow, bulk and deep DOM & POM are from peat pore water. Catchment budget includes precipitation inputs and fluvial exports from shallow soil water, Cottage Hill Sike and Trout Beck using environmental change network datasets.

outlined below means that this study can estimate S_{atmdep} , S_{peat} , and $S_{fluvial}$, and thus Equation 1 is balanced by $S_{reduced}$. Obviously, Equation 1 is a simplification of the ways in which S can partition through a peatland, but Equation 1 is consistent with the level of information available across a catchment and with the analytical techniques applicable at catchment scale. There will be other processes that are operating but this study can observed the net impact, for example, H₂S produced at depth in the anoxic then oxidized in near surfaces layers to SO₄ may then be lost from the peat as SO₄ in water flow to the streams of the catchment—this would be counted as $S_{fluvial}$. A simple Fe budget was considered so that supply and change in storage of mineral sulphides could be considered.

Uncertainty in estimates are generated from the combination of the uncertainties in each of the pathways as outlined in the methods above.

2.1. Study Site

The study was undertaken at Moor House National Nature Reserve (Figure 2) in the North Pennines, United Kingdom (UK). Moor House is an upland blanket bog, with the sampling locations around 550 m altitude. The study focused on the Trout Beck (TB) and Cottage Hill Sike (CHS) catchments. The TB is an 11.4 km² catchment in the headwater of the River Tees with 90% peat soil cover (N 54°41'18" W 2°22'45"; Figure 2). The site has been well studied so this study could draw upon existing budgets for dry matter (Forrest, 1971); carbon (Worrall et al., 2003, 2009); nitrogen (Worrall et al., 2012), phosphorus (Worrall, Moody, et al., 2016) and energy (Worrall et al., 2015). Between 1991 and 2006 the mean annual temperature was 5.8°C; air frosts were recorded on 99 days in a year; and the mean number of days with snow cover was 41, and the mean annual precipitation was 2012 mm (Holden & Rose, 2011). The vegetation of the site is dominated by *Eriophorum sp.* (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum sp.* (moss). This study considered the boundary of the processes and budgets to be exported to the atmosphere and streams from the soils and biomass of the study catchment. For example, DOM or POM export from the soil profile were included.

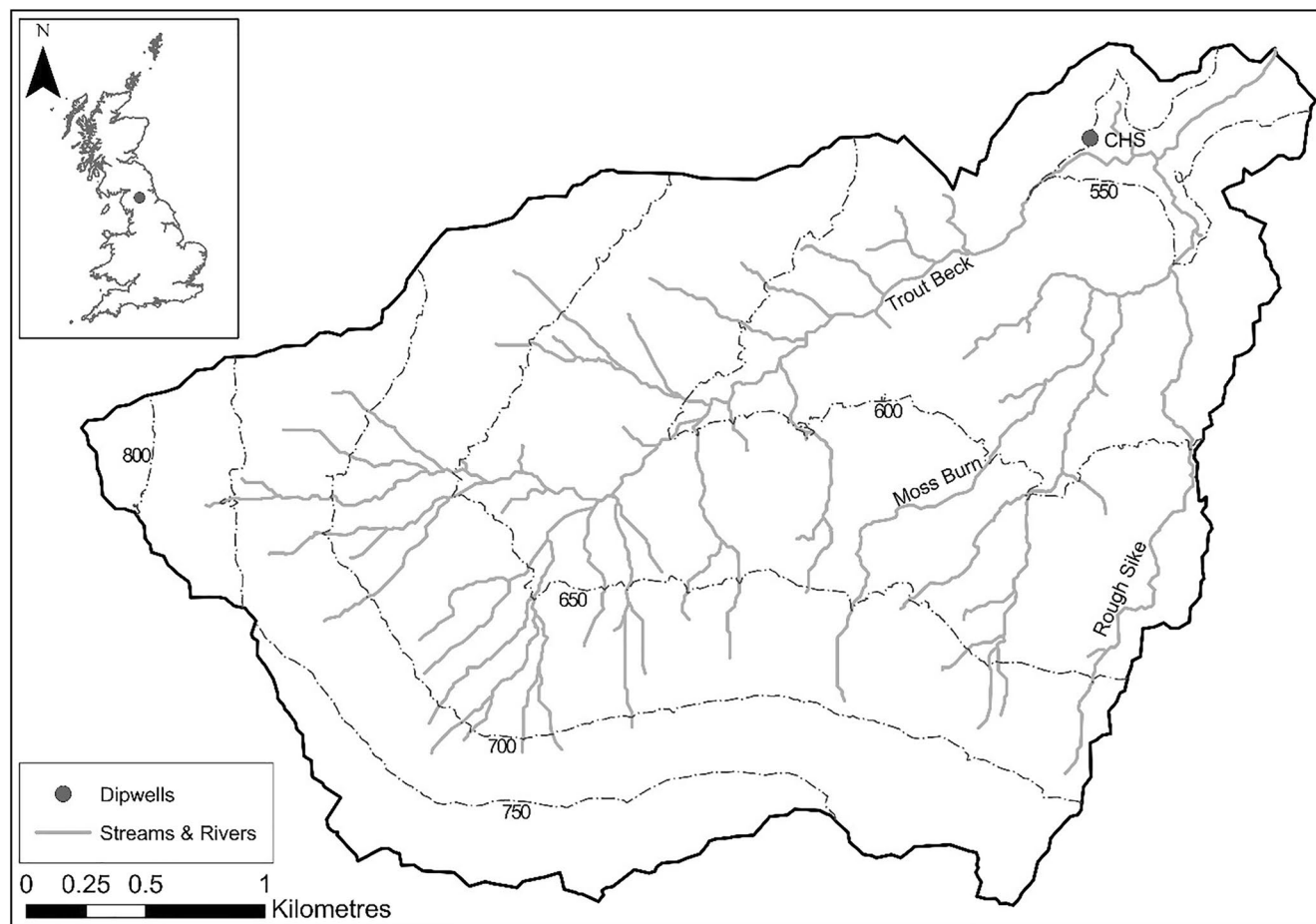


Figure 2. Map of Moor House study catchment. Cottage hill sike shows Cottage Hill Sike stream water sampling location. Numbers refer to altitude in meters.

2.2. Field Sampling

The study considered the following pools and pathways shown in Figure 1: the peat profile; vegetation; litter; DOM in the peat soil pore water; and the DOM and POM in a first-order stream.

For peat soil pore water, 12 dipwells were installed horizontally in to a gully wall, with six each at shallow (mean 28 ± 3 cm) and deep (mean 75 ± 6 cm) depths in November 2016. A further six dipwells were installed on the gully interfluvium in December 2016, allowing collection of soil pore water samples from January to March 2017. Dipwells on the gully interfluvium were sampled without consideration of sample depth as these dipwells were installed so as to ensure sufficient water volume in each sample (typically between 4 and 6 L) for complete analysis of DOM and POM. Samples of DOM and POM from the gully interfluvium are henceforward referred to as bulk DOM and POM. All the dipwells had holes every 10 cm and were blocked with rubber bungs at both ends to allow infilling of peat pore water. The dipwells were all 1 m long with at least 90 cm inserted in to the peat. It is not known whether flow of peat pore water at 90 cm from the gully wall is vertical or horizontal toward the gully and whether the flow direction will alter the composition of the pore water DOM. The pore water from the sets of dipwells at the two depths in the gully wall were drained for pore water samples monthly from December 2016 to March 2017.

For samples of stream water DOM and POM, 20 L of water were collected from CHS, a first-order stream draining the catchment that included all the other sampling sites. First-order stream samples were collected on the same visits as for the porewater samples. Analysis of previously collected and preserved samples from the study of Worrall, Moody, et al. (2016) were also included in this study.

For peat soil samples, two 1 m deep soil cores were collected in March 2017 from the same gully inter-fluve close to where the dipwells were located. The cores were subdivided as follows: 2 cm increments for 0–20 cm; 5 cm increments for 20–50 cm; 10 cm increments for 50–90 cm; and 5 cm increments for 90–100 cm. The sampling regime allowed more detail at the top and bottom of the core. Samples were sealed in polyethylene bags prior to analysis.

Sampling during this study drew upon samples collected and preserved from a previous study (Worrall, Moody, et al., 2016). Vegetation samples were collected from six quadrats (0.25 m², 0.5 × 0.5 m) located in the Cottage Hill Sike catchment and chosen to cover the three main plant functional groups—shrubs (dominantly *Calluna vulgaris*, henceforward referred to as *Calluna*); grasses and sedges (dominantly *Eriophorum spp.*, henceforward referred to as grass/sedge); and mosses (including *Sphagnum spp.*, henceforward referred to as mosses). In three of the quadrats, the entire above-ground biomass was quantitatively recovered. For the three other quadrats, the total above-ground biomass was collected but separated by functional group. From within these quadrats, samples of litter and below-ground biomass were recovered but not quantitatively. The sampled litter and below-ground biomass underwent compositional analysis alongside the vegetation samples separated by plant functional group.

2.3. Laboratory Analysis

Water samples were allowed to settle overnight prior to sample preparation to allow separation of particulate and dissolved components. Peat pore water was subsequently extracted by syringing water from the surface so as not to disturb the settling layer of particulates. First-order stream water samples were drained from the 20 L water carrier directly via a tap that was above the settled layer. All supernatant samples were placed into evaporating dishes and placed in a drying oven at ~80°C until all water was evaporated and DOM could be recovered as a solid sample for compositional analysis. The settled layer from the peat pore water and stream water samples was filtered using 0.6 μm glass-fiber filter paper (Advantec, Japan) and the residue taken as constituting the POM. The filter papers were oven dried overnight and the POM residue removed from the filter paper after drying.

Peat profile samples were dried at 105°C for 24 h, or until a steady sample weight was achieved. Samples were weighed to determine bulk density (ρ_{bd}). Woody and vegetative tissue was subsequently removed from soil samples. Vegetation samples were air dried and then oven dried for 24 h.

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

Both soil and vegetation samples were homogenised using a cryomill using a SPEX SamplePrep 6,770 Freezer/Mill (Stanmore, UK) for three minutes at 12 cycles per second.

Dissolved organic matter, POM, soil, vegetation and litter samples were analyzed for carbon, hydrogen, nitrogen and oxygen (CHNO) content using a COSTECH ECS 4010 Elemental Combustion System with pneumatic auto sampler. Separate analyses were performed for CHN and O. Samples were analyzed in triplicate with data calibrated against a suite of acetanilide standards. Calibration curves were based on linear or quadratic regression, with an $R^2 > 0.999$. Every 24 samples, acetanilide was measured in duplicate as a check for drift. CHNO content was determined as the mean of each triplicate analysis and samples that had a relative standard error > 5% were re-run as a check against analytical error or sample heterogeneity. Measurements for S content were made using a 121 Vario MAX CNS analyzer (Elementar, Langensfeld, Germany). Based on duplicate measurements of S content, high precision was achieved with relative standard deviation (RSD) of 0.51%.

CHNOS content was converted from weight percent into molar concentration, from which the atomic ratios of C:S, C:N, H:C, and O:C were determined. Carbon oxidation state (C_{ox} —Equation 1) and oxidative ratio (OR—Equation 2) were derived using Masiello et al. (2008):

$$C_{ox} = \frac{2O - H + 3N - 2S}{C} \quad (2)$$

$$OR = 1 - \frac{C_{OX}}{4} + \frac{3N}{4C} \quad (3)$$

where: O, H, N, S and C are the molar concentrations of each element.

Degree of unsaturation (Ω -Equation 4) was derived as:

$$\Omega = C - \frac{H}{2} + \frac{N}{2} + 1 \quad (4)$$

2.4. Long Term Water Quality Monitoring

The study site lies within Moor House National Nature Reserve (NNR), a terrestrial and freshwater site which is part of the UK Environmental Change Network (ECN). The ECN collects various chemical and hydrological data from the Trout Beck catchment relevant to this study (Sykes & Lane, 1996).

Atmospheric deposition was measured as precipitation, with samples, combining both wet and dry deposition, taken on a weekly basis from January 1993 to December 2015, while the rain gauge in the catchment recorded the amount of rainfall on an hourly basis. With relevance to this study, precipitation samples over the entire period of record had been analyzed for dissolved organic carbon (DOC), SO_4 -S, and Fe. Note that it was DOC that was monitored and no samples of precipitation DOM were available for organic S analysis.

As part of the ECN, water samples were collected weekly from CHS and TB (Figure 2) until August 2012, from then on these were sampled fortnightly. Peat soil water was sampled biweekly from six soil water sites within the catchment (Figure 2). Soil water was sampled at two depths-10 and 50 cm below the surface; in this study the six samples from each depth were averaged. With relevance to this study, samples were analyzed for SO_4 -S, DOC and Fe. The DOC values were converted to dissolved organic sulfur (DOS) by reference to the C:S measurements for the relevant samples described above. Particulate concentrations of any form are not routinely measured at the study site. It was possible to calculate fluxes of dissolved and particulate components using hourly flow records from the gauging station at the catchment outlet, TB, that have been recorded since October 1992.

Monthly water chemistry was used to determine annual precipitation input, and the flux of S and Fe from the shallow soil pore water, at CHS and TB. When calculating a catchment S, or Fe, budget, this study follows the methods of Worrall, Moody, et al. (2016).

Atmospheric deposition incorporated concentrations of DOC, Fe and SO_4 -S combined with the rainfall data to determine a weekly precipitation flux. Annual deposition input fluxes of DOC, Fe and SO_4 were obtained from the weekly fluxes. Flux was calculated as:

$$F = K \sum_i^n C_i R_i \quad (5)$$

where R_i = total precipitation during period i (mm); C_i = concentration in period i (mg/L); and K = unit conversion constant. It was possible to derive an estimated DOS content by converting the DOC concentration using the C:S ratio. No precipitation DOM samples were collected in this study, so the C:S ratio of 216 from CHS DOM samples was used to derive precipitation DOS content. It is difficult to identify measurable sources of uncertainty within estimates of atmospheric inputs. Any error in this estimate would be due to the representativeness of the measurement of the rainfall volume from the rain gauge or the estimate of the C:S ratio of the precipitation DOM.

The export of S leaving the catchment was determined at three spatial scales-from soil profile; from CHS; and from TB. The initial source of water leaving the catchment was from soil water. For an ombrotrophic peatland, precipitation is the only input of water to the catchment and the interaction with peat soil provides the water exported to the stream network, through subsurface throughflow or surface runoff. Therefore, the first flux estimate was based on the average of the six, biweekly shallow soil water samples and applying it to the flow recorded on the day of sampling at TB. The DOC flux was converted to the DOS flux

based on a mean C:S ratio of 223 from shallow pore water DOM samples. The export of Fe was only considered for CHS.

The fluvial flux from the first order stream (CHS) was based upon the ECN's weekly and subsequently bi-weekly sampling of CHS for Fe, SO₄-S and DOC. The stream water at CHS can be thought of as integrating the flowpaths through and over the peat soils of the catchment. The final flux of S was calculated at TB based on the weekly sampling of SO₄-S and DOC there. The difference between the shallow soil water, CHS and TB shows in-stream processing of S and C across the catchment to TB.

The fluvial S budget was calculated from the flux of SO₄-S, dissolved organic S (DOS) and particulate organic S (POS). Of the three components of the S budget, only SO₄-S was measured from ECN monitoring. Dissolved organic S was derived from the DOC concentration, using the mean C:S ratio from the elemental analysis of DOM. The C:S ratio for shallow soil water was derived from peat pore water DOM, while the stream water sites of CHS and TB, used the C:S ratio of CHS DOM. Having calculated the flux of POC, POS was determined from the C:S ratios of POM sampled from CHS.

For fluvial fluxes of S, hourly flow records from TB were used, from which SO₄-S, DOS and POS were derived. To calculate the flux of POS, the flux of POC was first calculated by an extrapolation method based on a suspended sediment rating curve for TB (Worrall et al., 2003) adjusted to the carbon content of sampled POM and POS calculated from the measured C:S ratio of the sampled POM.

Fluvial fluxes of SO₄, DOS and Fe fluxes were calculated by an interpolation method:

$$F = KE(C_i)Q_{\text{total}} \quad (6)$$

where Q_{total} = total flow in a year (m³/yr); $E(C_i)$ = the expected value of sampled concentrations (mg/L); and K = unit conversion constant (0.000001 for flux in tons).

For interpolation methods of flux estimation, that is, Equation 6, the major sources of error are the sampling frequency and the inherent error in the method used. Worrall et al. (2013) showed that for weekly sampling interpolation has a very low bias (6% for sampling frequency of one per week, 9% for sampling frequency of one per fortnight) and a high accuracy (1% at frequency of one per week and 2% for fortnightly). For extrapolation methods, the error analysis depends on the fit of the equation between the determinand and the driving variable; error in the estimate of the POC was calculated by Worrall et al. (2009) as $\pm 86\%$. The other source in the estimates of DOS and POS fluxes are the variation in the C:S ratio of both DOM and POM.

2.5. Internal Transfers

Alongside analyzing the composition of organic matter and the input and output fluxes of S, this study also considered the internal transfer of S and the processes involved in its cycling in the peat profile. Previous studies have investigated the internal transfer of nitrogen (Worrall et al., 2012) and phosphorous (Worrall, Moody, et al., 2016) by understanding the change in C:N and C:P ratios and the relationship of the nutrients to the carbon budget. If C is sequestered and accumulates as organic matter into the peat profile then the other elements in the composition of the organic matter are also being sequestered. Change in the C:S ratio can be used to assess whether there is release or uptake of S as organic matter is transferred down the profile. The dry matter budget were taken from Forrest (1971) and the C budget was taken from Worrall et al. (2009, 2012). Over a 13 years study, the C budget for the Moor House peat soils varied from net sink of -20 to -93 t C/km²/yr, with an average of -56 t C/km²/yr with an average primary productivity a net sink of -178 t C/km²/yr. At Moor House for every 100 C atoms sequestered via primary productivity, 31 C atoms are stored in the peat soil at 1 m depth

2.6. Statistical Analysis

Four analyses of variance (ANOVA) were considered. First, to assess the difference in C:S ratio between organic matter types, a one-way ANOVA was conducted between the C:S ratio of the different vegetation types, peat, DOM and POM. Second, the change down the peat profile was considered, ANOVAs were performed on the ρ_{bd} , CHNOS, C:S and C:N ratios, C_{OX} and degree of unsaturation of the peat cores. Results

from C, S and C:S are presented in the manuscript, with others in the SI. Two factors were included in the analysis: (a) core, with two factor levels; and (b) depth, which had 22 factor levels.

To understand the changes in elemental composition as DOM transfers from soil pore water to the fluvial network, a third ANOVA was conducted on CHNOS content of DOM, using source as the factor in the model. Source had four factor levels: shallow soil water, deep soil water, bulk soil water and first-order stream DOM—as such, any change in the composition of soil pore water with depth could be determined alongside the transformation of DOM in the stream network. To increase the sample size of CHS DOM in the ANOVA, samples collected exclusively for this study were further supplemented with additional samples of CHS DOM as referred to in Section 2.2 (Worrall, Moody, et al., 2016). As with the peat core analysis, results focus on C, S and C:S ratios of DOM, with further analysis of additional variables in the SI.

Finally, a two-way ANOVA was conducted on the ECN 23 years long-term water chemistry data set. The first factor was to assess the differences between the S budget and net S budget (atmospheric inputs minus fluvial exports) of shallow soil water, CHS, and TB in comparison to the second factor, which is the difference between years.

Prior to any ANOVA, the Anderson-Darling test was applied to check the normality of data set distribution, while Levene's test assessed homogeneity of variances. If a data set failed one or both of these tests, it was transformed and the data set re-tested. Natural-log and Box-Cox transformations were applied. Outlying values were classified as those beyond three standard deviations of the mean, and were removed from the data set prior to ANOVA. For the ANOVA of organic matter type 1 sample in a total of 81 samples was removed; for the core analysis, C_{ox} was the only ANOVA to have an outlier removed (1/44); for DOM analysis, no outliers were removed from any ANOVA; for the two fluvial budget ANOVAs: one in 67 samples were removed. Significant differences between factor levels were determined using the Tukey post-hoc test. Results are viewed as the least squares means (marginal means) as the best representation of each level within each factor. For multi-factor ANOVA analysis, the percentage variance explained by each factor was determined using the generalised omega-squared statistic— ω^2 (Olejnik & Algina, 2003).

To help understand groupings of data and show how organic matter transforms from vegetation to litter, from litter to peat, and from terrestrial sources to fluvial DOM and POM, principal components analysis (PCA) was conducted on CHNOS content, C_{ox} , OR and Ω . The additional CHS DOM samples, POM samples, and above and below-ground biomass samples (Worrall, Moody, et al., 2016) were included in the PCA to increase the sample size and improve understanding of different organic matter sources and pathways. Standards of cellulose, protein, humic acid, and lignin were included in the PCA. All variables were Z-transformed prior to analysis to allow standardization of variables with different measurement units. Principal components (PCs) were selected as all PCs with an eigenvalue >1 and the first PC with an eigenvalue <1 (Chatfield & Collins, 1980). All statistical analysis was conducted in Minitab v.17.

3. Results

The elemental composition of the organic matter sampled in this study is summarized in Table 2 with detailed data in Table S1. The lowest C:S ratios were observed for the DOM (both peat soil water and stream water DOM) while the highest C:S ratios were for *Sphagnum* and other vegetation. The ANOVA of C:S ratio ($R^2 = 53.65\%$, $p < 0.0005$) indicated that DOM, particularly CHS DOM, had a significantly lower C:S (Figure 3) ratio than other organic matter types, while increases in S content during degradation of vegetation was only significant between peat and *Sphagnum*.

3.1. Peat Soil Cores

Summary statistics of dry bulk density, CHNOS, C:S, C:N, C_{ox} and degree of unsaturation for peat soil cores and DOM are provided in Table S1. Sulfur content in the peat cores had a range of 0.31%–0.61% in core 1, and a range of 0.29%–0.58% in core 2 (Figure 4). ANOVA (Table 3) indicated there were no significant differences in the % S content with depth, with only the significant difference being between the cores ($R^2 = 10.31\%$, $p = 0.034$). Core 1 had a fitted mean of 0.419%, significantly higher than core 2 with a sulfur content of 0.365%. Across five sites in Western and Central Europe, including the UK, Novak et al. (2005)

Table 2
Median: Elemental Composition (mol/100g), C:S Ratio (mol/mol), C_{OX} , OR and Degree of Unsaturation (Ω)

Source	C	H	N	O	S	C:S	C_{OX}	OR	Ω	Stoichiometry
Peat	4.19	5.95	0.09	2.32	0.0117	354	-0.25	1.08	2.28	$C_{359}H_{509}N_8O_{199}S$
CHS DOM	2.95	3.45	0.11	2.40	0.0168	179	0.53	0.90	2.29	$C_{176}H_{206}N_6O_{143}S$
CHS POM	3.39	5.62	0.24	1.96	0.0106	326	-0.29	1.13	1.70	$C_{319}H_{529}N_{23}O_{185}S$
Soil DOM	4.17	5.60	0.14	2.03	0.0184	227	-0.26	1.09	2.41	$C_{227}H_{305}N_8O_{111}S$
Soil POM	4.34	5.57	0.09	2.16	0.0140	310	-0.23	1.07	2.60	$C_{310}H_{398}N_6O_{154}S$
AG-BM	4.15	6.40	0.07	2.55	0.0055	760	-0.27	1.08	1.99	$C_{760}H_{1171}N_{13}O_{466}S$
BG-BM	4.23	6.30	0.09	2.48	0.0057	736	-0.26	1.08	2.12	$C_{736}H_{1096}N_{15}O_{432}S$
Eriophorum	3.91	6.14	0.09	2.58	0.0055	713	-0.19	1.06	1.88	$C_{713}H_{1121}N_{16}O_{472}S$
Litter	4.08	5.92	0.14	2.48	0.0072	578	-0.14	1.06	2.19	$C_{564}H_{818}N_{19}O_{342}S$
Sphagnum	3.73	6.13	0.07	2.71	0.0041	921	-0.14	1.05	1.69	$C_{910}H_{1497}N_{16}O_{661}S$
Lignin	5.14	6.03	0.06	1.81	0.00		-0.43	1.12	3.15	$C_{87}H_{103}NO_{31}$
Cellulose	3.60	6.25	0.00	3.21	0.00		0.05	0.99	1.47	CH_2O
Humic acid	2.99	3.68	0.06	2.03	0.00		0.19	0.97	2.18	$C_{49}H_{60}NO_{33}$
Protein	3.88	6.79	0.97	1.97	0.00		0.03	1.18	2.01	$C_4H_7NO_2$

Note. Median stoichiometry of samples relative to sulfur (note difference between C:S ratio and C values in stoichiometry due to rounding process). Median stoichiometry of standards relative to nitrogen, bar cellulose (carbon). AG-BM = above ground biomass; BG-BM = below ground biomass. DOM, dissolved organic matter; POM, particulate organic matter.

reported S content (for three cores at 0–45 cm depth at each site) of ~0.1–1.5%, with the change down-profile depending upon site history. For instance, Thorne Moors in the UK showed an increase in S content up profile from the base of the core to ~10 cm, when peak S content occurred in 1945 and was associated with industrial pollution (Novak et al., 2005). Accumulating data from three different studies, Tipping et al. (2016) reported concentrations of S in temperate peatlands ranging 0.060%–0.859% in topsoil.

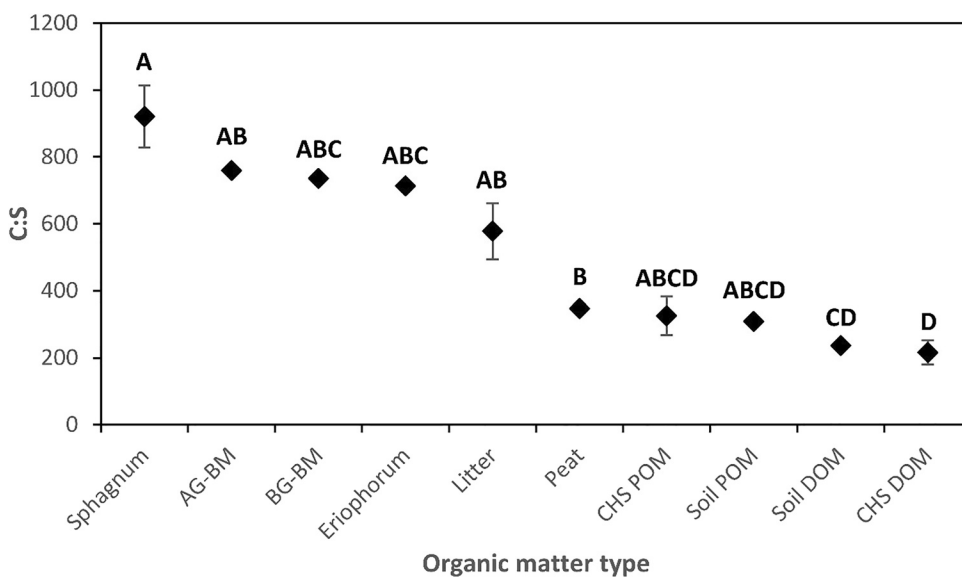


Figure 3. Mean \pm standard error (where visible) of C:S ratio for all organic matter types. Significant similarities (i.e., no significant difference) between organic matter types from four analyses of variance is denoted by organic matter types having a shared letter. AG-BM = above ground biomass; BG-BM = below ground biomass.

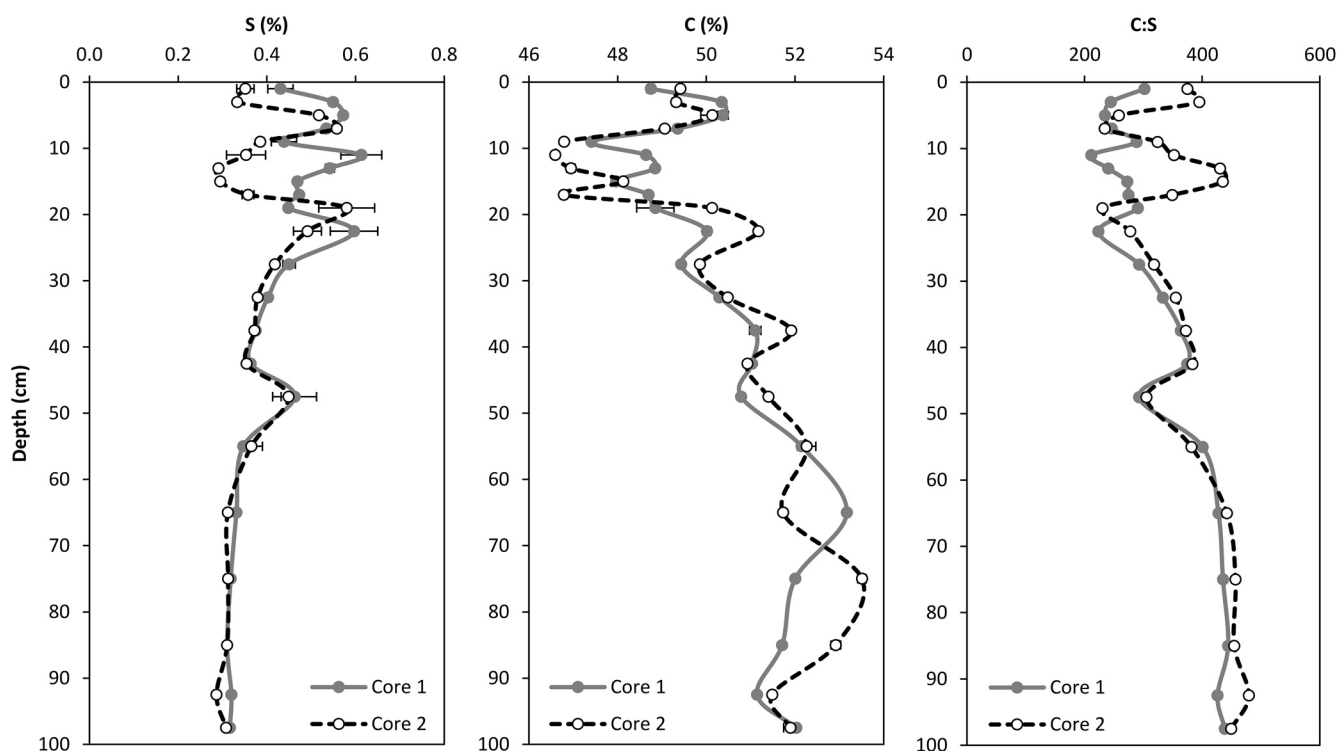


Figure 4. S and C content; and C:S ratio for peat soil cores. Error bars show standard error (where visible) for duplicate analysis (S) and triplicate analysis (C). Element profiles presented as percentage weight, conversion factors for moles/100g are: ÷ by 12 for C and 32 for S.

Carbon content in core 1 varied between $47.41 \pm 0.02\%$ (mean of triplicate analysis \pm standard error) and $53.17 \pm 0.04\%$; in core 2, the range was 46.59 ± 0.02 and $53.5 \pm 0.1\%$. The difference between cores (Core factor) was not significant, but there was a significant change with depth ($p < 0.0005$, $R^2 = 91.43\%$). Deep layers were generally, but not exclusively, significantly different to near-surface layers (8–18 cm was significantly different to 35–100 cm). Schillereff et al. (2016) analyzed C and N content from UK ombrotrophic bogs, including Moor House. Carbon content was at its maximum at or near the base of the cores, ranging from 55%–61% in cores deeper than 1 m, while minimum values occurred at the top of the core, ranging

Table 3

Minimum and Maximum Values, Four Analyses of Variance Factors, P-values and R^2 for Significant Variables by Peat Soil Core and Dissolved Organic Matter

Variable	Core (N = 44)				DOM (N = 27)			
	Min	Max	Factor	P-value	Min	Max	Factor	P-value
C (%)	46.59	53.51	Core	0.806	26.68	51.64		
			Depth	<0.0005			Source	<0.0005
				R^2 91.43%				R^2 80.69%
S (%)	0.29	0.61	Core	0.034	0.26	1.82		
			Depth	0.006 ^a			Source	0.945
				R^2 10.31%				
C:S	212	479	Core	0.003	39	412		
			Depth	<0.0005			Source	0.863
				R^2 67.96%				

Note. P-values included for insignificant factors but final ANOVA models only include significant factors.

^adepth significant in initial ANOVA model but no significant differences in Tukey post-hoc test.

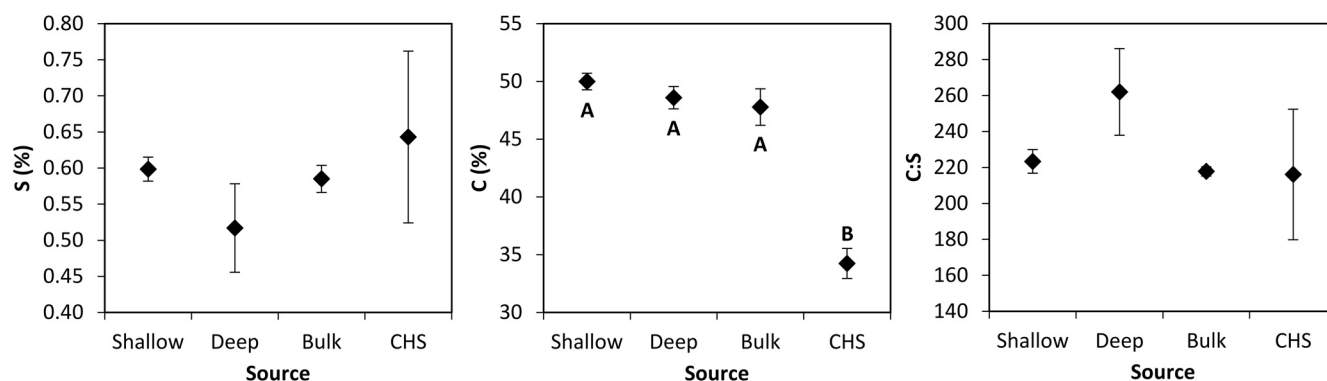


Figure 5. Mean \pm standard error (where visible) elemental composition and C:S ratio of dissolved organic matter (DOM). Four analyses of variance significant differences denoted where letters not shared between DOM source.

from 44%–52% C. The Moor House cores of Schillereff et al. (2016) went to 2 m depth as opposed to the 1 m cores of this study, yet C content exceeded 50% in all samples.

The C:S ratio of core one ranged between 212 and 444 and for core two the range was between 231 and 479. Both core ($p = 0.003$) and depth ($p < 0.0005$) were significant in the ANOVA model ($R^2 = 67.96\%$). Core 1 (C:S 366) had a significantly higher ratio than core 2 (C:S 321). The C:S ratio in peat increased with depth as the bottom 70–100 cm had a significantly higher C:S ratio than 4–8 cm and 18–25 cm depths. The C:S ratio of 60–70 cm was also significantly higher than 4–8 cm and 20–25 cm depths. Consequently, the base of the cores had significantly higher C:S ratios than some near-surface peat layers.

3.2. DOM

Mean S content of DOM was $0.60 \pm 0.06\%$ weight percent (standard error in the mean, not of the triplicate analysis) and the range of S values was 0.26%–1.82%. Analysis of variance (Table 3) indicated that there were no significant differences in S content between the different DOM sources, that is, between peat soil water and CHS stream water.

Carbon content (Figure 5) was highest in shallow soil pore water DOM, with a mean of $50.0 \pm 0.7\%$. Carbon decreased in deeper soil pore water ($49 \pm 1\%$) but was within standard error of shallow DOM. Bulk DOM had a C content of $48 \pm 2\%$, within standard error of the shallow and deep DOM. There was a decrease in C content in CHS DOM, with the mean $34 \pm 1\%$. ANOVA results ($R^2 80.69\%$, $p < 0.0005$) indicated that there was a significantly lower C content in CHS DOM compared to soil pore water DOM, but no significant difference between soil pore water types.

The C:S molar ratio of DOM had a mean of 226 ± 19 with a range of 39–412. There were no significant ($p = 0.863$) differences between DOM source types. However, as noted above (Figure 3) the C:S ratio of DOM was significantly lower than any other organic matter type measured in this study suggesting the S is fractionated into DOM.

3.3. Internal Transfers

The peat core data shows that there is accumulation of S into the peatland (Figure 4). The presence of S in the organic matter of the deepest peat soils shows that as C is accumulating than some S is also being passed in to long term storage. Given the long-term C budget for the study site as between -20 and -93 t C/km²/yr and the C:S ratio at 1 m depth of 442, then between 45 and 210 kg S/km²/yr is being accumulated—an average of 127 kg S/km²/yr.

Second, the C:S ratio significantly changes from the vegetation into the peat soil profile and down the peat profile. The surface peat has an average C:S ratio of 239 compared to an average C:S ratio of 810 in vegetation, 578 in litter; and an average C:S ratio of the deepest peat of 442. Therefore, S is being fixed in to the organic matter at shallow depths in the peat profile between 5 and 10 cm below the surface. Primary

Table 4
Loading of Principal Components

Variable	PC1	PC2	PC3	PC4
N	0.11	0.13	-0.76	-0.24
C	0.47	0.12	0.28	-0.15
H	0.50	-0.11	-0.04	0.11
O	0.08	-0.71	0.28	-0.14
S	-0.28	0.34	0.18	0.63
C _{ox}	-0.46	-0.13	-0.20	-0.30
OR	0.47	0.19	-0.18	0.18
Unsat	-0.02	0.53	0.39	-0.61
Eigenvalue	3.86	1.55	1.41	0.90
Proportion	0.48	0.19	0.18	0.11
Cumulative	0.48	0.68	0.85	0.96

Note. Unsat = degree of unsaturation.

productivity at the study site would represent a sink of 230 kg S/km²/yr. As such, despite peat soils showing a relative increase in S over C as organic matter is transported into the peat profile, the overall loss of the organic matter with peat formation means that the process is a net release of S of 103 kg S/km²/yr. The soil water DOM (average C:S ratio = 237) and CHS DOM (average C:S ratio = 216) have C:S ratios close to or lower than the lowest values of the peat profile (C:S ratio = 239) and are significantly different from the peat implying a fractionation of S in to the DOM. The creation of DOM absorbs S, at the average C:S ratio of DOM and assuming it is created from the point in the peat profile with the lowest C:S ratio then 1.4 kg S absorbed for every 1,000 kg of C as DOM.

3.4. Principal Component Analysis

Three principal components (PC, Table 4) had eigenvalues >1, explaining 85% of variance in the data set. The fourth PC had an eigenvalue of 0.90 and explained 11% of variance in the data set. Principal component one (PC1) had high positive loadings for C, H and OR and a high negative loading for C_{ox}. Principal component two (PC2) was dominated by O with a high negative loading, while degree of unsaturation and S had strong positive loadings. Principal component three (PC3) was dominated by a negative loading of N, with degree of unsaturation the strongest positive loading. The final component, PC4, was characterized by a positive loading for S and negative loading for degree of unsaturation.

The loading plot of PC1 against PC2 (Figure 6) distinguished DOM from peat pore water and the DOM from the stream water (CHS). Cottage Hill Sike (CHS) DOM was distinct from the other organic matter analyzed, and plotted relatively close to humic acid. Samples of CHS DOM were separated by S content, with the highest S values having a positive PC2 score. Peat pore water DOM plotted close to near-surface peat, suggesting the DOM evolved from peat rather than vegetation. The soil pore water DOM end-member was from deep

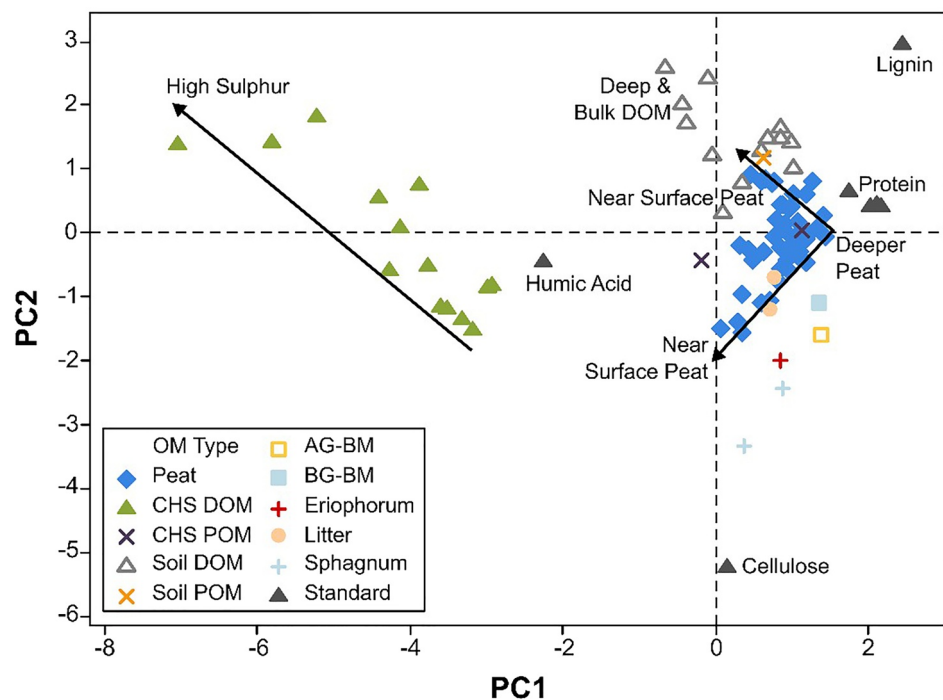


Figure 6. Principal components analysis of organic matter. PC1 versus PC2. AG-BM = above ground biomass; BG-BM = below ground biomass.

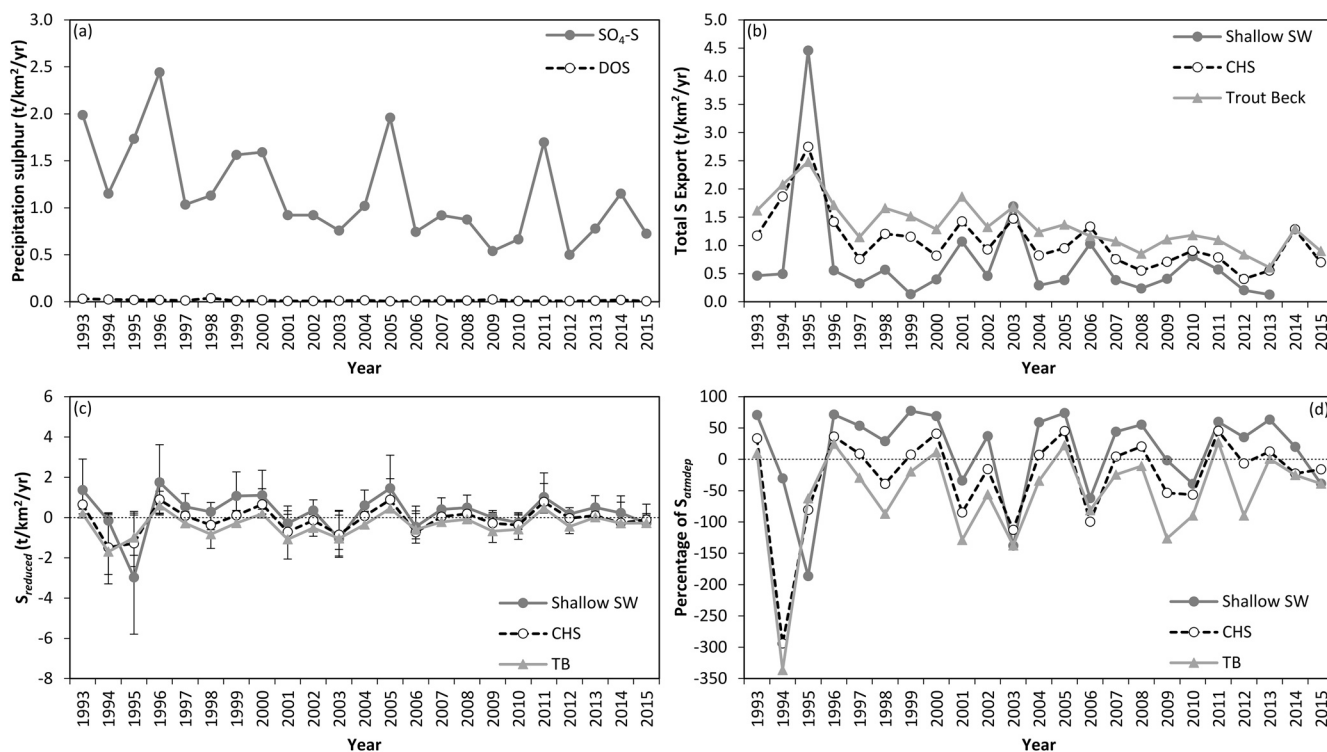


Figure 7. Fluvial sulfur budget: (a) atmospheric deposition of SO₄-S and dissolved organic sulphur (DOS) through precipitation; (b) total S export budgets (SO₄-S, DOS, POS) for shallow soil water, Cottage Hill Sike and Trout Beck—note, no SO₄-S data for shallow soil water was available for 2014 and 2015; (c) net S_{reduced} budget ± 95% confidence intervals; and (d) percentage of S_{atmdep} exported to a given fluvial flux.

and bulk peat DOM, and was characterized by a high degree of unsaturation, with the highest degree of unsaturation after the lignin standard. Peat samples had two near-surface end-members; one peat end-member plotted next to soil DOM, with the second plotting close to vegetation and representing samples with a high O content of >40% and lower degree of unsaturation than the other group of peat compositions that plotted adjacent to the soil DOM. The near-surface peat samples plotting close to vegetation evolved along a vegetation trend line parallel and close to the line joining the standards (cellulose, protein and lignin), and toward deep peat, and toward lignin. Principal component 3 was dominated by the protein standard due to its high N content and is consequently unshown. However, near-surface and deep peat samples could be separated by their degree of unsaturation.

3.5. Atmospheric Deposition

Deposition of SO₄-S dominated the precipitation inputs (Figure 7a) with annual budgets ranging between 0.5 and 2.4 t SO₄-S/km²/yr, with a mean of 1.17 ± 0.11 t SO₄-S/km²/yr (±SE mean). Previous literature indicated SO₄-S deposition rates between 1994 and 1996 at Moor House to be 0.898 t SO₄-S/km²/yr, with a UK wide deposition rate of 0.798 t SO₄-S/km²/yr (Adamson et al., 2001); and between 1993 and 2002 at Moor House a mean deposition of 0.934 t SO₄-S/km²/yr (Clark et al., 2005). The atmospheric deposition of DOS ranged between 0.006 and 0.040 t S/km²/yr, with a mean of 0.0154 ± 0.0018 t S/km²/yr. Total S inputs ranged between 0.51 and 2.46 t S/km²/yr with a mean of 1.18 ± 0.11 t S/km²/yr. There was a significant negative correlation (R² 31.8%, p = 0.005) between precipitation inputs and year, indicating that deposition decreased over the 23 years data set at an average rate 0.03 t S/km²/yr². Sulfur budgets at other sites include 3.6 t S/km²/yr at Thorne Moors, UK; 4.2 t S/km²/yr at Connemara, Ireland; and 4.4 t S/km²/yr on Mull, UK (Novak et al., 2005).

3.6. Fluvial Exports

Exports from the system included $\text{SO}_4\text{-S}$, DOS and particulate organic sulfur (POS), estimated based upon the shallow soil water, CHS and TB concentrations (Figure 7b shows combined total flux). The export budget was dominated by $\text{SO}_4\text{-S}$. Mean fluxes of $\text{SO}_4\text{-S}$ based upon $\text{SO}_4\text{-S}$ concentrations was highest for TB ($1.23 \pm 0.09 \text{ t SO}_4\text{-S/km}^2\text{/yr}$ —where \pm SE mean), followed by that from CHS ($0.91 \pm 0.11 \text{ t SO}_4\text{-S/km}^2\text{/yr}$), with the lowest based on $\text{SO}_4\text{-S}$ concentrations measured in the shallow soil water ($0.52 \pm 0.20 \text{ t SO}_4\text{-S/km}^2\text{/yr}$). For the majority of years, TB had the largest flux, yet the maximum flux estimated was of $\text{SO}_4\text{-S}$ was from shallow soil water in 1995. For 1995, the flux of $\text{SO}_4\text{-S}$ from CHS was also larger than that of TB and the higher fluxes from shallow soil water and CHS could be ascribed to drought conditions experienced in the United Kingdom during that year. Worrall and Burt (2008) estimated that the 1995 drought had a 27 years return period and was the severest drought during the period of record available at Moor House. The 1995 drought led to water table drawdown and increased $\text{SO}_4\text{-S}$ concentrations in soil pore water from oxidation of reduced organic and inorganic sulfur (Clark et al., 2005).

Fluxes of DOS were typically higher when based upon DOC concentrations measured in shallow soil water than those estimated for DOC concentrations measured in CHS and TB, though not exclusively so. Mean flux of DOS decreased from shallow soil water to CHS and to TB, with means \pm SE mean of 0.15 ± 0.01 , 0.120 ± 0.007 , and $0.085 \pm 0.004 \text{ t S/km}^2\text{/yr}$ for shallow soil water, CHS and TB respectively. Likewise, POS decreased from shallow soil water to TB, with mean fluxes of 0.050 ± 0.005 , 0.042 ± 0.002 , and $0.038 \pm 0.002 \text{ t S/km}^2\text{/yr}$, for shallow soil water, CHS and TB respectively. Despite generally giving the highest POS flux estimates, estimates based on shallow soil water had the lowest flux in 1994, 1999, 2008, and 2013. The POS flux of CHS and TB was less variable than the flux observed for DOS or $\text{SO}_4\text{-S}$, though in some years such as 2006, there was a noticeable difference in flux ($0.64 \text{ t S/km}^2\text{/yr}$ CHS and $0.25 \text{ t/km}^2\text{/yr}$ TB).

The maximum observed total fluvial flux of sulfur was based upon estimates from shallow soil water concentrations in 1995 ($4.6 \text{ t S/km}^2\text{/yr}$, Figure 7b). For fluxes based upon shallow soil water concentrations, the mean flux was $0.7 \pm 0.2 \text{ t S/km}^2\text{/yr}$, with the flux increasing to a mean of $1.1 \pm 0.1 \text{ t S/km}^2\text{/yr}$ when based on concentrations from CHS and a mean of $1.35 \pm 0.09 \text{ t S/km}^2\text{/yr}$ when based on concentrations measured at TB. ANOVA (R^2 82.99%) showed that all three water sources ($p < 0.0005$, $\omega^2 = 43.92\%$) were significantly different from one another, with a significant increase in total S from shallow soil water to TB. Year ($p < 0.0005$, $\omega^2 = 38.85\%$) was significant, with total S in 1995 significantly higher than all years other than 1994, 1996, 2001, 2003, and 2006—which also had significant differences to other years.

3.7. S Budget

Based upon Equation 1 and results above it was possible to estimate S_{reduced} , that is, the precipitation inputs (S_{atmdep}) minus fluvial exports (S_{fluvial}) and the accumulation in to the peat (S_{peat}) (Figure 7c). When S_{fluvial} is based on the shallow soil water concentration then the value of S_{reduced} was positive 15 out of 23 years, which indicates atmospheric deposition inputs exceeded that exported to the fluvial network, and therefore there is net reduction of atmospheric inputs to either H_2S or mineral sulphide. For estimates based upon concentrations measured in CHS, 14 out of 23 years the atmospheric deposition exceeded fluvial export of S, and the value S_{reduced} was positive. For estimates based upon TB concentrations, only eight out of 23 years did atmospheric deposition exceed the fluvial export. Consequently, for 15 out of 23 years the value of S_{reduced} was negative and the export of sulfur at TB exceeded that deposited from precipitation.

Based on concentrations values from the shallow soil water, values of S_{reduced} ranged between -3.0 and $1.75 \text{ t S/km}^2\text{/yr}$ with a mean of $0.25 \text{ t S/km}^2\text{/yr}$ —a positive value would indicate a net gain in S storage, while a negative value would imply net loss of S from accumulated stores of S leading to export of S to the streams of the catchment. The maximum value of S_{reduced} (i.e., $1.75 \text{ t S/km}^2\text{/yr}$) must represent the capacity of the peatland to reduce S inputs. The minimum value of S_{reduced} $-3.0 \text{ t S/km}^2\text{/yr}$ occurred during the drought year of 1995 when water tables were at their lowest and oxidation of mineral sulphide potential high (Clark et al., 2005). There was no significant trend over the study period on this budget. Based on concentrations measured in CHS, the value of S_{reduced} ranged between -1.49 and $0.89 \text{ t S/km}^2\text{/yr}$, with a mean of $-0.09 \text{ t S/km}^2\text{/yr}$: again there was no significant trend on this value. For concentrations measured at TB, the values of S_{reduced} ranged from -1.70 to 0.99 with a mean of $-0.37 \pm 0.10 \text{ t S/km}^2\text{/yr}$, and no significant trend on these

budget estimates. Analysis of variance (R^2 88.75%) indicated that year ($p < 0.0005$, ω^2 67.84%) and source ($p < 0.0005$, ω^2 20.76%) significantly explained variation in the value of S_{reduced} .

As a percentage of atmospheric deposition (Figure 7d), the rate of removal by S_{reduced} peaked at 71% but conversely the export based on values from TB was up to 136% higher than the atmospheric deposition.

3.8. Fe Budget

The concentration of Fe in precipitation had a median value of 0.02 mg/l in 1992 but declined to a median 0.00 mg/l by 2012. The atmospheric deposition flux of Fe to the peatland varied from 8.7 to 129 kg Fe/km²/yr with a significant decline in flux over the period. The concentration of Fe in the soil water is given in Table 1 and is an order of magnitude higher than the concentration in the precipitation. The average concentration of Fe in CHS was 0.52 mg/l. The flux of Fe from CHS was between 0.38 and 1.39 t Fe/km²/yr with no significant trend on that flux over the study period.

4. Discussion

The purpose of this study was to understand the S budget as a means of understanding its constraints on the C and greenhouse gas budget of a peatland. The importance of S is through its role as a terminal electron acceptor (TEA). Simple bacterial sulfate reduction (BSR) should produce two moles of CO₂ for every mole of SO₄²⁻ consumed by bacteria, while CH₄ production could be out-competed and inhibited by the process of BSR (Watson et al., 1997). This postulation is based on:



Equation 7 works because S changes in oxidation state from +6 to -2 while C changes from 0 to +4. However, it is wrong to assume that the oxidation state of the organic carbon is zero and it is in fact more reduced (Worrall, Clay, et al., 2016). Furthermore, it is not possible to transfer 100% of the energy content of the complete oxidation of organic matter, or any other substrate. Therefore, it matters by which biochemical pathway the oxidation occurs. Complete oxidation of glucose can produce 12 nucleotides (NADH) or 36 ATP molecules based on the release of 24 electrons per glucose molecule. The heat of combustion of glucose is 15.6 MJ/kg (2.8 MJ/mol) whereas for each nucleotide the value is 0.22 MJ/mol and for each ATP molecule it is 0.053 MJ/mol, that is, glucose energy conversion via NADH is 94% efficient and that via ATP is 68% efficient. Therefore, there is not a direct link between the energy content of the substrate and the energy expended to make the product. Therefore, the ratio of CO₂ to SO₄²⁻ reduced would be:

$$\frac{[CO_2]}{[SO_4^{2-}]} = \frac{\phi(8 - C_{\text{ox}}^{\text{sub}})}{C_{\text{ox}}^{\text{CO}_2}} \quad (8)$$

where: [CO₂] = the moles of CO₂ produced; [SO₄²⁻] = moles of SO₄²⁻ S consumed; C_{ox}^y = the oxidation state of the carbon with y as CO₂ or sub substrate; and ϕ = the efficiency of energy transfer. Lafitte and Loomis (1988) showed that the efficiency in plant processes varied between 0.84 and 0.89 and that range was used here. The value of $C_{\text{ox}}^{\text{sub}}$ could be thought of as value for the substrate measured in this study (average C_{ox} peat soil = -0.25). This would therefore mean that 1.79 moles of CO₂ were produced for every mole of SO₄²⁻ reduced. However, the peat soil samples as measured in this study would be the residual of the oxidation of the organic matter and would not represent the component of the organic matter that had actually reacted. Worrall et al. (2017) showed that the component that had reacted had an average C_{ox} of 0.18. In this case this would mean that 1.69 moles of CO₂ were produced for every mole of SO₄²⁻ reduced. This study would suggest a capacity of the peat soils at this location to remove 1.74 t S/km²/yr, or 23.1 kmoles S/km²/yr, which would equate to 0.47 t C/km²/yr. The estimated CH₄ flux of this catchment is between 5.6 and 6.9 t C/km²/yr (Worrall et al., 2009, 2012), that is, between 6% and 7% of possible CH₄ flux is diverted by S deposition. Gauci et al. (2004) found, in experimental peat mesocosms, that an addition of 1.5 t S/km²/yr led to 30% suppression of CH₄ flux.

The value of S_{reduced} did vary from positive to negative values and had a long term average of 0.25 t S/km²/yr. Over the 23 years of the data available to this study, there was net reduction of SO₄²⁻. The fate of this S

could be either stored as mineral sulphides or lost as hydrogen sulphide. If the S is reduced and stored as mineral sulphide then it is available to be oxidized in a subsequent year and released as SO_4^{2-} . The large values of $\text{S}_{\text{reduced}}$ observed in 1995 can be ascribed to mineral sulphide oxidation during a period of sustained drought in the catchment (Clark et al., 2005). The atmospheric deposition of S declined over the study period implying high values existed prior to the period of study. If there were periods of higher deposition in the past, then there could be a legacy of mineral sulphide accumulated into the peat profile that is, only now being lost as atmospheric deposition of S declines. Curtis and Simpson (2014) considered S deposition at 12 upland sites across the UK and found that between 1988 and 2007, 11 of the 12 sites considered showed significant declines over that period with S deposition typically decreasing by a factor of two. RoTAP (2012) concluded that atmospheric deposition of S peaked in the 1970s with S emissions having peaked in the UK in 1969 (Zhao et al., 1998). Therefore, it is probable that the study was receiving atmospheric S deposition loads of perhaps $5 \text{ t S/km}^2/\text{yr}$ and that mineral sulphides accumulated during a period of high S deposition may now be oxidized and released into the streams of the catchment. Adamson et al. (2001) found that SO_4^{2-} concentrations in peat pore waters had a peak correlation to water table depth three weeks prior at 10 cm depth with a five week lag at 50 cm depth indicating SO_4^{2-} found deeper in the peat profile was from diffusion of SO_4^{2-} oxidized from reduced H_2S in aerobic conditions higher in the peat profile. Increases in SO_4^{2-} associated with dry periods and oxidation of reduced sulfur species have also been observed in peatlands in the North York Moors, UK (Evans et al., 2014) and fen peatlands in Canada close to industrial pollution sources that have experienced high levels of historical S deposition (Szkokan-Emilson et al., 2013). Oxidation of S to SO_4^{2-} may not only be a short-term response to drought periods and can also be related to gully erosion causing water table drawdown in degraded peatlands, such as in blanket bog peatlands in the southern Pennines (Daniels et al., 2008, 2012). Enhanced concentrations of SO_4^{2-} in peat soil water and enhanced SO_4^{2-} leaching have been shown to inhibit DOC solubility through increased ionic strength and acidity leading to reduced DOC concentrations in peat soil water (Clark et al., 2011). Given declining atmospheric deposition of S observed in this study, the slow long-term release of historically deposited S from peat soils may constitute an additional source of S at both CHS and TB, yet the influence of groundwater contributions to baseflow (Worrall et al., 2003) at the catchment outlet may suggest a geological source for TB as well.

The estimate of the capacity for the peat profile of the study site to use SO_4^{2-} as an alternative TEA does assume that there is no role for the reduction of S into the organic matter. This study has shown that in the long-term $127 \text{ kg S/km}^2/\text{yr}$ is sequestered and stored in to deep peat, approximately 10% of the incoming atmospheric SO_4 -S deposition. The significant change in C:S ratio with depth was not caused by a change in S content, as the only significant differences associated with S concentration were between peat cores and not peat depths. The increase in C:S ratio was caused by an increase in C content with depth, as more labile compounds were preferentially removed leaving more aromatic, recalcitrant C to accumulate at depth (Drollinger et al., 2019, 2020), as supported by the higher degree of unsaturation at the base of the cores. The S in naturally occurring organic compounds can have varying oxidation states between +6 (sulfone functional groups) and -2 (sulphide functional groups). Incorporation of S into organic matter in a reduced form would have the electron acceptor effect but the size of the effect would depend on the proportions of the various functional groups and their oxidation states. Chapman and Davidson (2001) measured the ester-S in peats compared to total organic sulfur and found that between 99% and 19% of the organic-S was in the highly oxidized functional groups with this proportion highest in the surface layers of the peat. Therefore, we must conclude that additional SO_4^{2-} reduction is occurring leading to additional oxidation of organic matter and diversion of C away from CH_4 production. Despite the lack of change in S content with depth here, use of S isotopes could elucidate oxidation-reduction processes, with bacterial SO_4^{2-} reduction preferentially utilizing ^{32}S over ^{34}S (Bartlett et al., 2005; Thompson & Bottrell, 1998).

Bartlett et al. (2005), working raised bogs, found that sulfur was incorporated into peat via plant uptake, direct from the atmosphere and from surface waters. Organic S content in vegetation such as *Eriophorum* and *Sphagnum* was found to be substantially lower than that preserved within the peat profile, yet sulfur in near-surface peat layers shared similar isotopic composition to the sulfur found in vegetation. Concentrations of sulfur were also lower in vegetation than peat in this study and showed how there is an accumulation of S and decrease in C:S ratio as organic matter is incorporated into the peat profile. Bartlett et al. (2005) found that between 22 and 30 cm depth S content decreased and C:S ratios increased in organic matter,

representing a loss of S from the organic fraction relative to carbon during the mineralization process. The mineralization process also saw an enrichment in $\delta^{34}\text{S}$ as the lighter isotope was preferentially removed. Despite this, organic S increased and C:S ratios decreased from 30 cm to the base of the core at 43 cm as bacterial SO_4^{2-} reduction-derived sulphide was added to organic and inorganic S pools (Bartlett et al., 2005). At an oligotrophic fen in Finland, S content increased with depth across microforms of hummocks, hollows and lawns with a concomitant decrease in C:S ratios at depth (Parvin et al., 2018). However, the decrease in C:S ratio occurred between 15 and 50 cm depth, with no change between 50 and 200 cm. This study did not show a decrease in C:S ratio with depth to the base of the peat profile, rather there was a significant increase between the upper 25 cm and bottom 30–40 cm to the base of the core and unlike the other studies reflected the relative decrease in S compared to carbon.

To help understand the potential for sequestration of $\text{S}_{\text{reduced}}$ as mineral sulphides the Fe budget was considered. The simple comparison between atmospheric deposition and stream losses shows a considerable net gain in Fe across the catchment which implies that there is another source of Fe within the catchment. The geology of the catchment is a sequence of Carboniferous age limestones with sand and shale bands within (Johnson & Dunham, 1963) where the shale strata contain pyrite. Furthermore, the area was mineralized by sulphide depositing fluids. The presence of a weathering source of Fe and SO_4^{2-} not only explains the net gain in Fe across the catchment but also the apparent increase in SO_4^{2-} flux in the streams across the catchment, given the increase in SO_4^{2-} concentrations in CHS and TB compared to shallow soil water.

If there is a weathering source of Fe and S within catchment could be elucidated by a better understanding of the hydrological pathways operating within the catchment. Equally, there is the possibility that rainwater SO_4^{2-} is directly transferred to the streams of the study catchment via flowpaths (e.g., surface runoff) that bypass the peat profile's capacity to reduce SO_4^{2-} . Worrall et al. (2003) used geochemical analysis to determine hydrological flow paths at Moor House and found soil waters evolved from precipitation inputs with little compositional differentiation between samples taken at 10 and 50 cm depths. However, the evolution of soil water from precipitation inputs was due to cation exchange reactions and differences between 10 and 50 cm soil water samples were due to residence time. The composition of CHS stream water was predominantly sourced from soil water; however, the higher order stream of TB had different compositions dependent upon whether baseflow conditions evolved from groundwater or storm runoff conditions dominated that sampled near-surface peat layers. Despite the hydrological connection between soil water and streams observed by Worrall et al. (2003), Clark et al. (2005) found that peat soils at Moor House were only the main source of SO_4^{2-} to streams during drought periods, with atmospheric inputs otherwise dominant. Boothroyd et al. (2015) used 10 cm depth traps and surface water runoff traps to observe the hydrological response and mixing of water sources as dissolved organic carbon transferred across hillslopes to stream networks in an upland blanket peat catchment in the Peak District, UK. Such an approach here could further elucidate S cycling in near-surface peat layers to the stream network. The presence of weathering sources of Fe or S in the study catchment also means that the catchment is not truly ombrotrophic and further that caution should be applied when transferring these results to other peatlands setting or peatland types (e.g., fens) where different sources S will exist.

5. Conclusions

By reconstructing the 23-years long S budget of an upland peat catchment this study has shown that: despite significantly declining atmospheric deposition of total S (from 2.4 to 0.5 t S/km²/yr) there was no significant change in the total fluvial flux of S through the streams in the catchment. On average the 0.25 t S/km²/yr were reduced though this varied from 1.74 to −3.0 t S/km²/yr. In 34% of the years of the study the catchment was a net exporter of total S as oxidation of mineral sulphide released S to the streams. Allowing for the efficiency of energy transfer in the redox process and the oxidation state of peat organic matter means that every mole of SO_4^{2-} reduced 1.69 moles of CO_2 were produced and not 2 moles normally assumed. In this catchment an average of 0.47 t C/km²/yr are diverted from methanogenesis.

Data Availability Statement

The long term monitoring data for Moor House is available from <http://www.ecn.ac.uk/>. Data are available in the manuscript, in the supplementary information and from University of Durham data repository (<https://collections.durham.ac.uk/>; and <http://doi.org/10.15128/r2pk02c9794>). The compositional data used are given in the Supplementary Material.

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