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Chronic atmospheric reactive N deposition has breached the N sink capacity of a northern ombrotrophic peatbog increasing the gaseous and fluvial N losses

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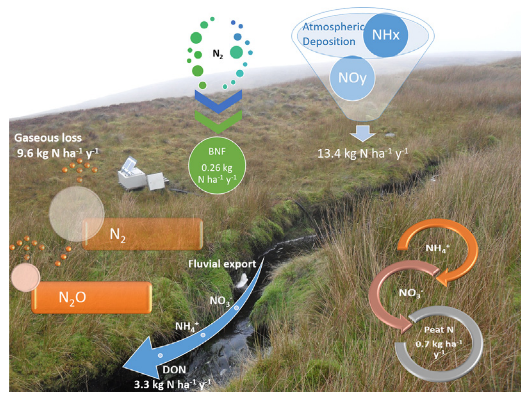
HIGHLIGHTS

- The mean annual N mass balance cannot account for the long-term peat N accumulation.
- BNF is suppressed and has only minor contribution to the N inputs in the bog.
- Denitrification removes 70% of the excess N in the form of the inert N_2 gas.
- A high-resolution DON record was used to estimate fluvial N export with low uncertainty.

GRAPHICAL ABSTRACT



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ABSTRACT

Peatlands play an important role in modulating the climate, mainly through sequestration of carbon dioxide into peat carbon, which depends on the availability of reactive nitrogen (Nr) to mosses. Atmospheric Nr deposition in the UK has been above the critical load for functional and structural changes to peatland mosses, thus threatening to accelerate their succession by vascular plants and increasing the possibility of Nr export to downstream ecosystems. The N balance of peatlands has received comparatively little attention, mainly due to the difficulty in measuring gaseous N losses as well as the Nr inputs due to biological nitrogen fixation (BNF). In this study we have estimated the mean annual N balance of an ombrotrophic bog (Migneint, North Wales) by measuring in situ $N_2 + N_2O$ gaseous fluxes and also BNF in peat and mosses. Fluvial N export was monitored through a continuous record of DON flux, while atmospheric N deposition was modelled on a 5×5 km grid. The mean annual N mass balance was slightly positive (0.7 ± 4.1 kg N ha^{-1} y^{-1}) and varied interannually indicating the fragile status of this bog ecosystem that has reached N saturation and is prone to becoming a net N source. Gaseous N losses were a major N output term accounting for 70% of the N inputs, mainly in the form of the inert N_2 gas, thus providing partial mitigation to the adverse effects of chronic Nr enrichment. BNF was suppressed by 69%, compared

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Peatbog
^{15}N isotopes

to rates in pristine bogs, but was still active, contributing ~2% of the N inputs. The long-term peat N storage rate (8.4 ± 0.8 kg N ha^{-1} y^{-1}) cannot be met by the measured N mass balance, showing that the bog catchment is losing more N than it can store due its saturated status.

1. Introduction

Despite covering about 3 % of the earth's surface (or 4,000,000 km^2), northern peatlands are globally significant sinks of carbon (C), accumulating an estimated ~500 Gt C (Loisel et al., 2014), much of which occurred during the Holocene. In addition to sequestering C, it is estimated that northern peatlands store up to 12–21% of the world's soil N (Limpens et al., 2006). While human activities have more than doubled the supply of reactive nitrogen (Nr) to the biosphere from ~110 to 286 Tg N y^{-1} from 1860 to 2005, the respective change to the global C cycle has only been in the range of 5–7% (Scheer et al., 2020). The impetus for the doubling of Nr in the biosphere has been agricultural intensification and the fixation of twice as much N via the Haber-Bosch (120 Tg N y^{-1}) process than natural terrestrial N fixation (63 Tg N y^{-1})(Fowler et al., 2013). Increased inputs of Nr have serious environmental consequences for all ecosystems such as biodiversity loss, eutrophication, and acidification (Erisman et al., 2013; Galloway et al., 2003).

In ombrotrophic peat bogs, which gain much, if not all of their nutrients from atmospheric sources, chronic Nr deposition can lead to significant ecological damage, including; the replacement of *Sphagnum* moss cover in favour of vascular plant growth (Juutinen et al., 2010; Juutinen et al., 2016), reduced tolerance of moorland vegetation to natural stressors (Pilkington et al., 2007), loss of *Sphagnum* N filtering capacity and enhanced peat decomposition (Moore et al., 2019), an increase in gaseous N losses (Tipping et al., 2017) and ecosystem respiration (Larmola et al., 2013) and increased loss of DIN and DON to downstream ecosystems (Bragazza and Limpens, 2004; Edokpa et al., 2015). Global atmospheric N deposition increased from 86.6 to 93.6 Tg N y^{-1} between 1984 and 2016, an increase of 8% (Ackerman et al., 2019). However, against this backdrop of increasing global N deposition, due to extensive regulation targeting oxidised N compounds (Fowler et al., 2007), Europe has experienced in the last three decades a steady decline in deposition rates. Despite this reduction, the United Kingdom, still receives Nr deposition in the region of <6 - >25 kg N ha^{-1} y^{-1}, which is considerably more than background deposition of ~2 kg N ha^{-1} y^{-1} (Payne, 2014).

Assessing nitrogen budgets at the ecosystem scale can be an indicator of environmental pressures, with the determination of stock quantities and dynamics of Nr fluxes between air, soil and water, providing important information for designing effective environmental regulations for mitigating environmental pressures (Vogt et al., 2013). Although complete C budgets for bogs are now common in the literature (Billett et al., 2010; Moody et al., 2018; Nilsson et al., 2008; Worrall et al., 2018), comprehensive N budgets have received comparatively little attention. Worrall et al. (2012) conducted a multi-annual nitrogen budget (1993–2009) for a peat covered catchment in the north east of England. Despite a reduction in atmospheric N deposition from 35 to 7 kg N ha^{-1} y^{-1} over the period of study, a long-term decline in the peat N storage capacity was observed. While overall the system was found to be a sink of 1.9 kg N ha^{-1} y^{-1}, for 4 years the system acted as a net source of N, suggesting a transition from net N sink to net source. Similarly, Vogt et al. (2013) and Drewer et al. (2010) concluded that a moorland catchment in southern Scotland is showing signs of nitrogen saturation, defined as ecosystem N losses being equal or exceeding N inputs (Butterbach-Bahl et al., 2011), with a negative N balance of −1.6 to −2.4 kg N ha^{-1} y^{-1}. Despite a relatively low atmospheric N deposition rate (3.3 kg N ha^{-1} y^{-1}) in a northern Minnesota bog, it was found that more than twice as much N was exported than received (Hill et al., 2016). However, N inputs may have been underestimated since biological N_2 fixation (BNF) was not measured but a literature value of 0.5 kg N ha^{-1} y^{-1} (Urban and Eisenreich, 1988) was used instead, while denitrification N losses were estimated under laboratory conditions with the unreliable acetylene inhibition technique (Felber et al., 2012; Sgouridis et al., 2016). Due to a scarcity of reliable data, this is true for all recent N budget studies in bogs, which commonly rely on literature estimates of BNF (Vogt et al., 2013). In addition, uncertainty estimations of the N mass balance are often increased as in-situ measurements of gaseous N losses are commonly substituted for either literature estimates (Worrall et al., 2012) or calculated using highly uncertain emission factors (Vogt et al., 2013).

Biological nitrogen fixation (BNF) by diazotrophic microbes is an energy demanding metabolic process that serves as an additional source of nitrogen (N) in moss-dominated, nutrient-poor peatlands (Knorr et al., 2015; Moore et al., 2005). High rates of atmospherically deposited Nr could potentially negate the need for a 'costly' investment on BNF. Experimental studies with N additions above ambient levels have shown an inconsistent change of BNF activity with the added N (Kox et al., 2016; van den Elzen et al., 2018), while BNF rates under a natural gradient of Nr deposition in the UK have been shown to reduce but not completely shut down (Saiz et al., 2021). This can potentially have important implications when estimating the N economy of peatlands and should be quantitatively accounted for in N budget studies. Another elusive term of existing N budgets is denitrification, the dissimilatory reduction of nitrate to nitrous oxide and dinitrogen gases under sub-oxic conditions, that constitutes the main N removal pathway in terrestrial soils (Houlton and Bai, 2009). Denitrification and particularly its main product N_2, is notoriously difficult to measure under field conditions against the huge atmospheric N_2 background (Groffman et al., 2006). Field denitrification measurements based on the acetylene inhibition technique are no longer considered reliable (Scheer et al., 2020) and as such, there are only a handful of studies that have measured N losses via denitrification in peatlands using either the He/O_2 soil core flow method (Roobroeck et al., 2010; Wray and Bayley, 2007) or the ^{15}N gas flux method (Sgouridis and Ullah, 2015; Tauchnitz et al., 2015). These studies show that despite the low nitrate availability and low pH, gaseous N losses via denitrification are quantitatively important and spatiotemporally variable and are responsible for up to 66% of N input removal in ombrotrophic bogs (Hill et al., 2016).

Despite a rise in the number of studies starting to investigate N budgets in peat dominated catchments, many of these studies are reliant on, to at least some degree, modelled or literature data of key biological processes such as BNF and denitrification, while denitrification is often the 'missing' term in N budgets. The aim of this research was to calculate the N budget of an ombrotrophic peatland catchment in order to determine the effect of chronic N deposition on its N storage capacity using a complete set of field measurements of key biological processes. To the best of the authors' knowledge this is the first study to combine in-field measurements of BNF, $N_2 + N_2O$ gaseous fluxes, and fluvial export to derive a robust catchment N budget estimate with associated uncertainty boundaries.

2. Methods

2.1. Study site

The study catchment is located on the Migneint moors (Fig. 1), the largest area of blanket bog in north Wales (52°59′59" N 3°48′13" W). Located in the headwaters of the Afon Conwy and covering an area of 1.3 km^2, the study site is part of a larger protected area covering 2750 ha of land designated as a Site of Special Scientific Interest (SSSI)

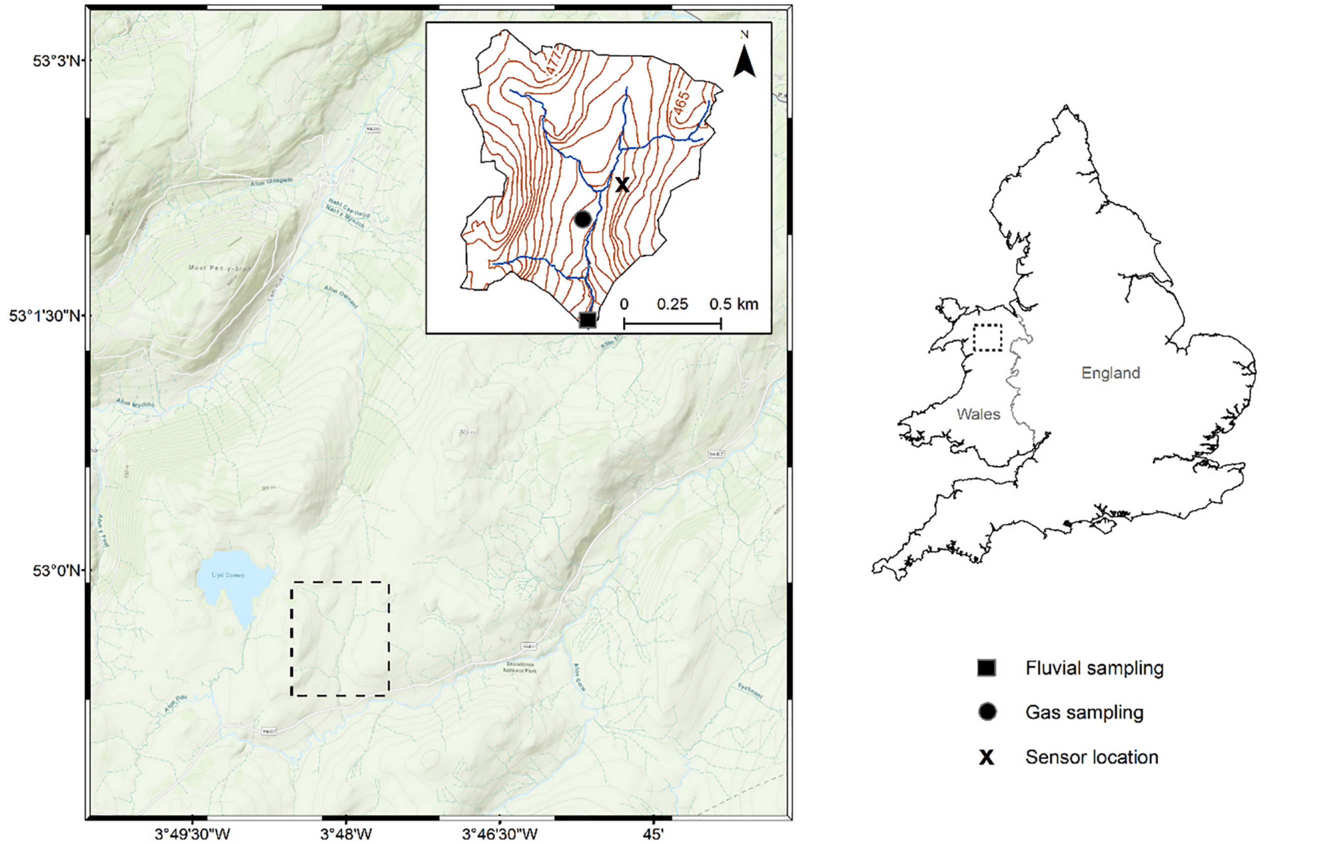

Fig. 1. Location of the study site within the United Kingdom.

within the National Trust's Ysbyty Ifan Estate. Land cover classification is dominated by peat bog (80 %), with acid grassland and dwarf shrub and heath covering 17 % and 3 % respectively (data supplied by the UK Centre for Ecology & Hydrology, UK). Vegetation is dominated by *Sphagnum spp.*, *Calluna vulgaris - Eriophorum vaginatum* with localised areas of *Erica tetralix* (Sgouridis and Ullah, 2014). Snowdonia is the wettest area in north Wales with annual rainfall totals exceeding 3000 mm/yr^{-1}. Underlying geology is dominated by Cambrian mudstones and siltstones (Lynas, 1973). While there are no major agricultural processes impacting the catchment, light animal grazing does occur seasonally.

2.2. N inputs

2.2.1. Atmospheric deposition

Developed to model atmospheric deposition of reduced nitrogen (Singles et al., 1998), and subsequently adapted to include oxidised nitrogen species (Fournier et al., 2005), the Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME) model (version 4.17) was used in this study to generate an annual estimate of wet and dry N deposition. Briefly, FRAME is a Lagrangian model, simulating air columns moving along strait line trajectories. Emissions of ammonia were estimated using data on animal numbers and fertiliser applications, including crops and non-agricultural emissions (Dragosits et al., 1998), with NOx emissions taken from the National Atmospheric Emissions Inventory for the UK (Salway et al., 1999). Point source emissions of NOx are treated individually in the model. Wet and dry deposition output was modelled at 5 km × 5 km grid resolution covering the period of study and providing an annual value per deposition element. For a detailed description of the FRAME model see Singles et al. (1998).

2.2.2. Biological nitrogen fixation

Measurements of BNF derived in situ are rare in the literature. While BNF was not measured during the 2013–14 study period, for the purpose of constructing our N budget without relying on literature values from elsewhere, we have used in situ measurements of BNF from the Migneint from 2016 - 17 reported in Saiz et al. (2021). BNF was measured in 4 *Sphagnum* spp. (*S. cuspidatum*, *S. fallax*, *S. papillosum* and *S. capillifolium*) as well as in peat (5–10 cm depth) from hollows and hummocks using the $^{15}N_2$ direct assimilation method (Saiz et al., 2019). For each species and peat, four out of five replicates were incubated with $^{15}N_2$ (98 atom% Cambridge Isotope Laboratories Inc., USA), with the fifth being the control (incubated using ambient air). Each replicate consisted of 20 live moss shoots (~ upper 5 cm) of the selected moss species or 10 g of peat. Shoots and peat were placed in 50 ml serum vials which were capped with airtight rubber septa and placed ‘upside down’ (avoiding cap shade) in the same area where the samples were taken from and incubated for 24 h. Following the incubation, the vials were opened and aerated and the moss and peat samples were dried, weighed and subsequently pulverised (<2 mm). The pulverised samples were analysed for ^{15}N content using a Carlo Erba NA1500 (Italy) elemental analyser coupled to a Dennis Leigh Technologies (UK) isotope ratio mass spectrometer and BNF rates were calculated as per Saiz et al. (2019). Two sampling campaigns were performed per growing season (May – September 2016 & 2017). Mean annual rates were estimated for 255 days of growing season and adjusted for 45% areal coverage of the selected *Sphagnum spp.*, while for asymbiotic BNF in peat the areal coverage was 100 % assuming that nitrogen fixation in peat is occurring under the moss carpet as well as among heather roots. The BNF in mosses and asymbiotic peat BNF were summed to estimate a total annual BNF rate.

2.3. N outputs

2.3.1. N_2 and N_2O emissions

The fluxes of both N_2 and N_2O gases were measured monthly in situ using an adapted ^{15}N Gas-Flux method (Sgouridis et al., 2016), between

April 2013 and October 2014, with the exception of November 2013 and January 2014. Five plots were randomly established in March 2013 within the main body of the ombrotrophic bog covering all habitats. In each plot a round PVC collar (basal area 0.05 m^2; chamber volume 4 l) was inserted into the soil at c. 15 cm depth 2–4 weeks before the measurement date. The collars were open at the bottom to maintain natural drainage and root growth during the measurements. The natural vegetation cover at the soil surface of each installed collar remained unchanged. The PVC collars were fitted with a circular groove of 25 mm depth to fit in an acrylic cylindrical cover (chamber) providing a gas-tight seal when filled with water. Labelled $K^{15}NO_3^-$ (98 at. % ^{15}N, Sigma-Aldrich) was applied in each plot via ten injections of equal volume through a grid (4×6 cm) using custom-made 15 cm long lumber needles attached to a plastic syringe. The average tracer application rate reflected current daily estimates of atmospheric Nr deposition in the UK (0.05 kg N ha^{-1} d^{-1}). Following the tracer application, the collars were covered with an opaque chamber and duplicate gas samples (20 and 5 ml each) were collected with a gas tight syringe (SGE Analytical science) through the septum of the chamber cover at $T = 1$ h, $T = 2$ h and $T = 20$ h after the tracer injection, while a $T = 0$ h sample was collected immediately after tracer injection above the plot surface before fitting the chamber cover. The duplicate gas samples were transferred into pre-evacuated (<100 Pa) 12 ml and 3.5 ml, respectively borosilicate glass vials with butyl rubber septa (Exetainer vial; Labco Ltd., High Wycombe, United Kingdom) for storage under positive pressure and were analysed within 8 weeks from collection. The collars were moved to new random plots within the study site every three months to minimise any priming effects from repeated tracer application in the same plots.

The ^{15}N content of the N_2 in each 12 ml vial was determined using a Continuous Flow Isotope Ratio Mass Spectrometer (Isoprime Ltd., UK) and the total N_2 flux from the uniformly labelled soil nitrate pool was calculated using the 'non-equilibrium' equations as described in Sgouridis et al. (2016) and linear regression between sampling intervals and expressed as μg N m^{-2} h^{-1}. The limit of detection for the N_2 flux was 4 μg N m^{-2} h^{-1}. The second set of gas samples (3.5 ml vials) was analysed for total N_2O ($^{14+15}N$-N_2O) on a GC-μECD (7890A GC Agilent Technologies Ltd., Cheshire, UK). Flux rates were determined by linear regression of gas concentrations in the chamber headspace (adjusted for standard temperature and pressure) between 0 and 2 h, multiplied by the chamber volume and divided by the chamber area and time of incubation. The minimum detectable flux was 0.34 μg N_2O-N m^{-2} h^{-1}. Annual fluxes were estimated by interpolating monthly measurements for each year and calculating the average between the two monitoring years. The measurement uncertainty associated with the gas flux determination was assessed by examining the accuracy and precision of the measurement of a range of analytical gas standards. The analysis showed that over the range of concentrations observed in this study the errors were homoscedastic and given that the field samples were run in a random order, there was no temporal correlation. Given this, the largest source of observational uncertainty was deemed to be derived from in-field spatio-temporal variations and therefore the measurement uncertainty stated below is derived from the standard deviation of the replicate field measurements.

2.3.2. Fluvial export

All riverine sampling and analysis of chemical variables used in this study were collected and analysed by staff from UKCEH and Bangor University (Cooper et al., 2017). River stage was recorded at the Nant-y-Brwyn stream (lat: 52.990162; long: −3.8018288) at 15 min intervals using a Druck PDCR 1830 type pressure transducer, installed and maintained by staff from UKCEH Bangor (Marshall and Cooper, 2016). Chemical variables used in our analysis include: Total Oxidised Nitrogen (TON), Total Dissolved Nitrogen (TDN), Total Nitrogen (TN), and Dissolved Organic Carbon (DOC). Samples were collected across base and storm flow conditions using a combination of manual and automatic water samplers, with sampling frequency varying from weekly to bi-monthly between April 2013 and November 2015. Where available, Dissolved Organic Nitrogen (DON) concentrations were calculated using this dataset as the difference between TDN and inorganic N species (DON = TDN - TON - NH_4^+-N).

In order to minimise error in the estimation of fluvial loading, high resolution DON concentrations were generated using the novel method described here. High resolution (fifteen-minute) DOC concentration data were generated instream using a Spectrolyser optical sensor (s::can, Messtechnik GmbH), operated and maintained by staff at UKCEH Bangor. Following bias correction using paired laboratory measurements, regression analysis between instream sensor DOC concentrations and spot measurements demonstrated a significant relationship (Fig. 2a; $p < 0.0001$, $r^2 = 0.77$). DOC and DON concentrations at this site also demonstrated a significant linear relationship (Fig. 2b; $p < 0.0001$, $r^2 = 0.80$) with minimal seasonal variation in DOC:DON ratio observed over the study period. This predictive relationship was then used to generate a high-resolution record of DON concentrations. Modelled vs. observed DON data demonstrated a strong, significant relationship (Fig. 2c; $p < 0.0001$, $r^2 = 0.71$). Annual DON loading was estimated by combining concentration data with high resolution level data, converted into a measurement of discharge using a ratings curve, produced and supplied by CEH Bangor (Marshall and Cooper, 2016). Missing data were infilled with seasonal averages to factor in biological processing of material and produce a robust load estimate. DON loading was then scaled up to account for additional oxidised N species to generate a loading of TN.

Uncertainty estimates were generated for each part of the annual fluvial load calculation and the errors propagated through the process to provide a robust estimate of the annual load. The uncertainty associated with the stage-discharge relationship used to derive the river flow was assessed using a non-parametric local weighted scatterplot smoothing regression (LOWESS) approach described in detail in Coxon et al. (2015) and Lloyd et al. (2016). This approach allowed the standard deviation of residuals to be examined at every value of stage height and thus enabling heteroscedasticity to be represented (supplementary information Fig. S1). These data along with an assessment of autocorrelation were then included in a simple 1st order autoregressive model (Evensen, 2003; García-Pintado et al., 2013; Lloyd et al., 2016) to generate 100 iterations of the error series which could be added to the calculated discharge dataset. The analysis showed that the errors in the stage-discharge derived values were not temporally correlated but were heteroscedastic, with larger absolute uncertainties existing at higher stage values. The standard deviation of residuals ranged from ~0 to 0.0274 m^3 s^{-1}, resulting in up to 22.5% error. The discharge timeseries with 10th to 90th percentile uncertainty estimates can be seen in supplementary information Fig. S2.

The uncertainty associated with the modelled DON data was assessed by comparing the modelled DON values with the concurrent laboratory derived values, the modelled values were matched with the closest laboratory time points (within 10 min, $n = 147$). The residuals were examined, and the error found to be temporally independent but heteroscedastic, with larger errors at higher concentrations of DON (supplementary information Fig. S3). The standard deviation of the residuals varied from 0.03–0.11 mg L^{-1} representing up to 38 % error. The statistical information derived from the residuals were then used as input to the 1st order autoregressive model and 100 iterations of the possible error series were generated and subsequently added to the modelled DON data. Following this, the 100 iterations of both the discharge and DON timeseries were combined to produce 10,000 iterations of the possible DON load timeseries (supplementary information Fig. S4) and therefore estimates of annual DON load. The results presented in this study represent the mean annual load based on these 10,000 estimates and the uncertainty represented by the standard deviation of the estimates.

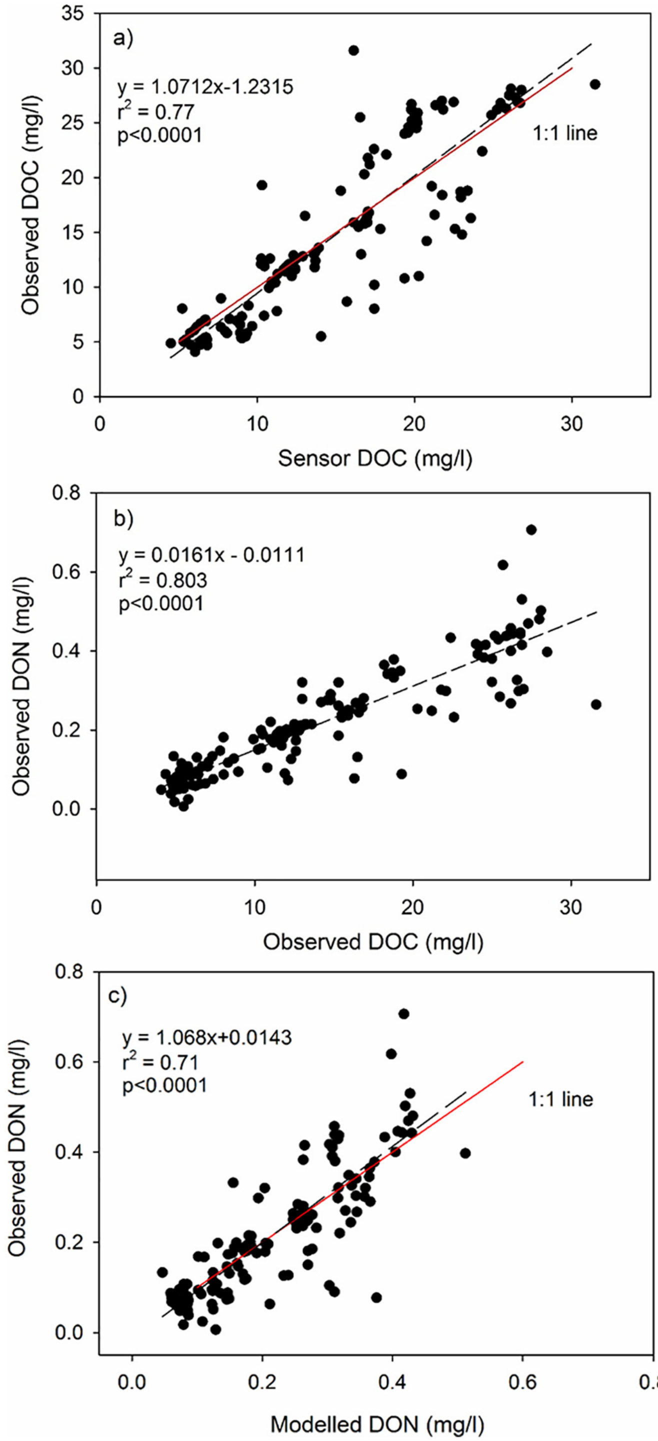

Fig. 2. (a) Relationship between observed DOC concentration data and sensor derived DOC concentrations following bias correction, (b) the relationship between laboratory generated DOC and DON concentrations for data across the period 04/2013–10/2015 and (c) relationship between observed and modelled DON concentrations. Dashed lines represent the linear relationship between variables and the solid red lines represent a 1:1 relationship.

The hydrological balance of the catchment area (supplementary information Table S1), for each monitoring year was slightly negative, with river discharge and evapotranspiration losses exceeding precipitation inputs. This was attributed to the below average precipitation (1674 mm/yr) observed during the study years, effectively draining the bog. Moreover, the hydrological balance indicated no groundwater recharge, which is in agreement with the hydrological investigation of the same bog by Holden et al. (2017), which showed predominantly overland flows and subsurface flows into the stream draining the bog. Consequently, N loss through groundwater re-charge was considered zero.

2.3.3. N storage

Long-term mass accumulation rates for N were calculated by Schillereff et al. (2016) for the Migneint during a study of UK ombrotrophic peatlands in 2014. Briefly, cores were extracted in triplicate using both a box corer (for peat shallower than 1 m), and Russian-type corer (peat deeper than 1 m). The core was sliced to 10 cm intervals with samples air dried, manually sieved to 2 mm to exclude large roots and dried at 60 °C before being ball-milled to a homogenous powder. After drying at 105 °C, carbon and nitrogen were determined using an Elementar Vario-EL analyser. Bulk sub-samples of the upper (20–30 cm), mid and base of the core were then submitted to the NERC Radiocarbon Facility at East Kilbride for ^{14}C analysis. These data were used to estimate down core patterns in accumulation rates utilised in this study.

3. Results

3.1. Atmospheric deposition

Total input of N from atmospheric deposition is 13.4 kg N ha^{-1} yr^{-1}. Wet deposition dominates this flux with NH_x and NO_y accounting for 49 % and 32 % of total deposition, respectively. Dry deposition contributes on average an additional 2.5 kg N ha^{-1} yr^{-1}. A complete breakdown of modelled atmospheric deposition can be seen in Table 1. Even though the model itself does not produce uncertainty boundaries, the relatively fine-scale resolution modelling applied to local land cover data produces fairly robust Nr deposition estimates with typical uncertainties reported at ±20% (Vogt et al., 2013).

3.2. Biological nitrogen fixation

BNF rates were highly variable across the different *Sphagnum spp* with *Sphagnum fallax* displaying the highest rates (Median: 0.72 ± median absolute deviation 0.650 μg N g^{-1} d^{-1}), while BNF in peat hollows was on average twice as much that in peat hummocks (Fig. 3). Daily BNF rates were extrapolated per 255 days of average growth season in 2016–2017 and adjusted to ~45% areal coverage for *Sphagnum* spp. to give an average annual rate of 0.053 kg N ha^{-1} yr^{-1}. Asymbiotic BNF in peat was estimated from the incubated peat samples from hummocks and hollows and scaled up to 100% coverage over the 255 days of average growth season resulting to a mean annual rate of 0.21 kg N ha^{-1} yr^{-1}. Therefore, the mean annual total BNF activity (including mosses and peat) was 0.26 kg N ha^{-1} yr^{-1}. Unfortunately, areal coverage per species was not available to be able to adjust uncertainty per species and therefore the uncertainty of the BNF rate is based on the standard deviation of the median, for all moss species and peat respectively, and amounts to ±0.261 kg N ha^{-1} yr^{-1}.

3.3. N_2 and N_2O emissions

The flux of N_2 dominated the gaseous N export (range: 2.9–746.5 μg N m^{-2} h^{-1}, $n = 58$), whilst the N_2O flux was 3 orders of magnitude

Table 1
Modelled wet and dry atmospheric N deposition on the Migneint bog catchment in kg N ha^{-1} yr^{-1}.

Year	NH_x dry	NO_y dry	NH_x wet	NO_y wet	Total
2013	1.8	0.9	6.6	3.8	13.1
2014	1.6	0.6	6.5	5.0	13.7
Mean	1.7	0.8	6.5	4.4	13.4

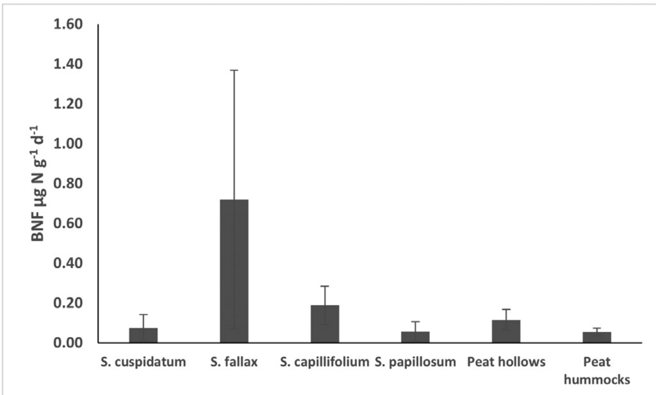

Fig. 3. Median ($\pm$ median absolute deviation) BNF rates per *Sphagnum* species and peat hummocks and hollows during the 2016–2017 growth seasons in the Migneint bog.

lower (range: -0.65 - 2.46 µg N m^{-2} h^{-1}, $n = 76$). N_2O consumption (significant negative flux) was measured in plots throughout the studied period, but only in September 2013 was the monthly average flux negative. N_2 fluxes tended to be higher in winter and spring months (Fig. 4a), but due to the high spatiotemporal variability the differences were not statistically significant. Conversely, N_2O fluxes peaked in summer and winter months, but again the differences were not significant (Fig. 4b). The annual total ($N_2 + N_2O$) gaseous N export for the first year (April 2013–March 2014) was 10.7 $\pm$ 4.45 kg N ha^{-1} y^{-1} and for the second year (December 2013–October 2014) was lower at 8.6 $\pm$ 1.81 kg N ha^{-1} y^{-1} with the average across the two years being 9.6 $\pm$ 3.1 kg N ha^{-1} y^{-1}. The contribution of N_2O to the total gaseous N export (as indicated by the ratio $N_2O/N_2 + N_2O$) increased from 0.18% in the first year to 0.29% in the second year.

3.4. Fluvial export

The annual fluvial flux of N calculated during the first year was 3.97 $\pm$ 0.01 kg N ha^{-1} y^{-1}. Loading during the second year studied, was lower at 2.71 $\pm$ 0.02 kg N ha^{-1} y^{-1}, with the average across both years being 3.34 $\pm$ 0.01 kg N ha^{-1} y^{-1}. Based on observed nutrient speciation data, 71% of this export was in the form of DON, with the remaining split evenly between NO_3^--N and NH_4^+-N. Temporal variability in both DON concentrations and discharge can be seen in Fig. 5. Particulate N concentrations were largely below limits of detection. Observed nutrient speciation is largely constant between years. Intra-annual variation in N export is also noted. During the first year, N loading is highest during the autumn when elevated instream concentrations coincide with a high density of rainfall events. While N loading during autumn in year 2 is also elevated, changes in seasonal rainfall result in highest loading during the spring.

The complete sensor record used for load estimation was 94.7% complete with the largest number of missing data points occurring during the autumn during year 1 (13 days). Due to large variations in both missing sensor measurements between seasons and the observed intra-annual variation in the data, missing load estimates were scaled up using seasonal, rather than annual mean export.

3.5. N storage

The peat accumulation rate of nitrogen and carbon was estimated by Schillereff et al. (2016) in three cores up to 105 cm depth collected in the Migneint in 2014. Radiocarbon dating was used to estimate the age range in depth increments along the core with the 0–20 cm representing ~100 years before present (BP), 20–30 cm ~ 200–300 years BP, 50–60 cm ~700 years BP and 105 cm ~5000 years BP. The C and N accumulation rates largely covaried along the core depth (Fig. 6), both displaying a decreasing trend in the upper layers, while

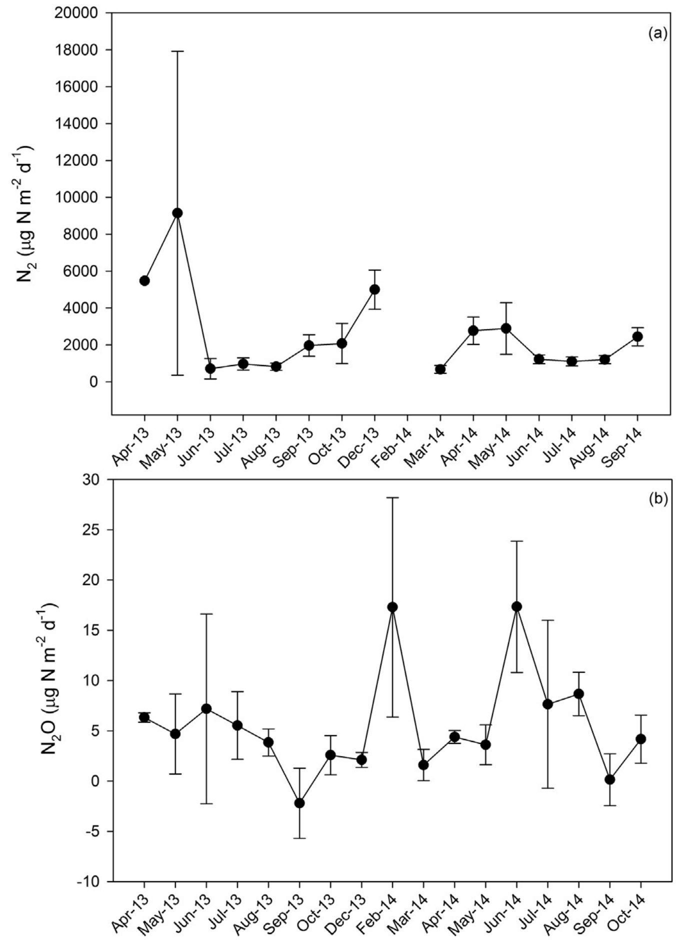

Fig. 4. a) N_2 and b) N_2O fluxes between April 2013 and October 2014 ($n = 5$ per month).

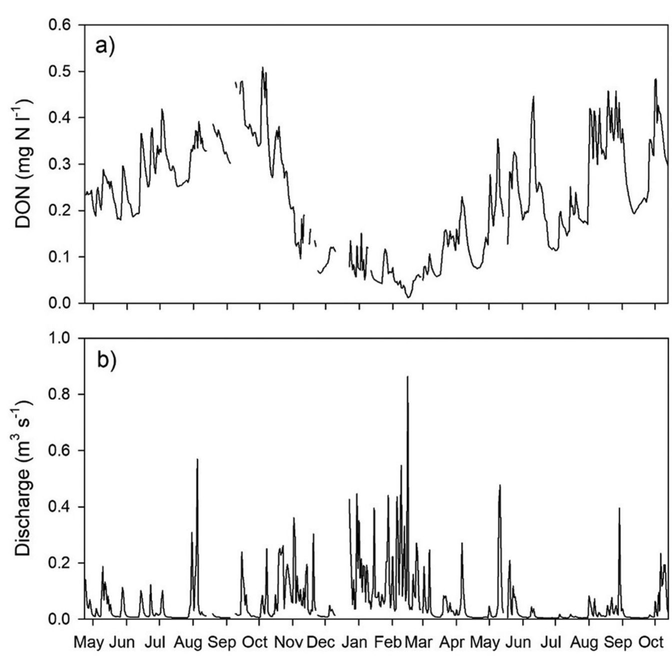

Fig. 5. Mean daily (a) modelled DON concentrations and (b) discharge for the study catchment covering the period April 2013–October 2014.

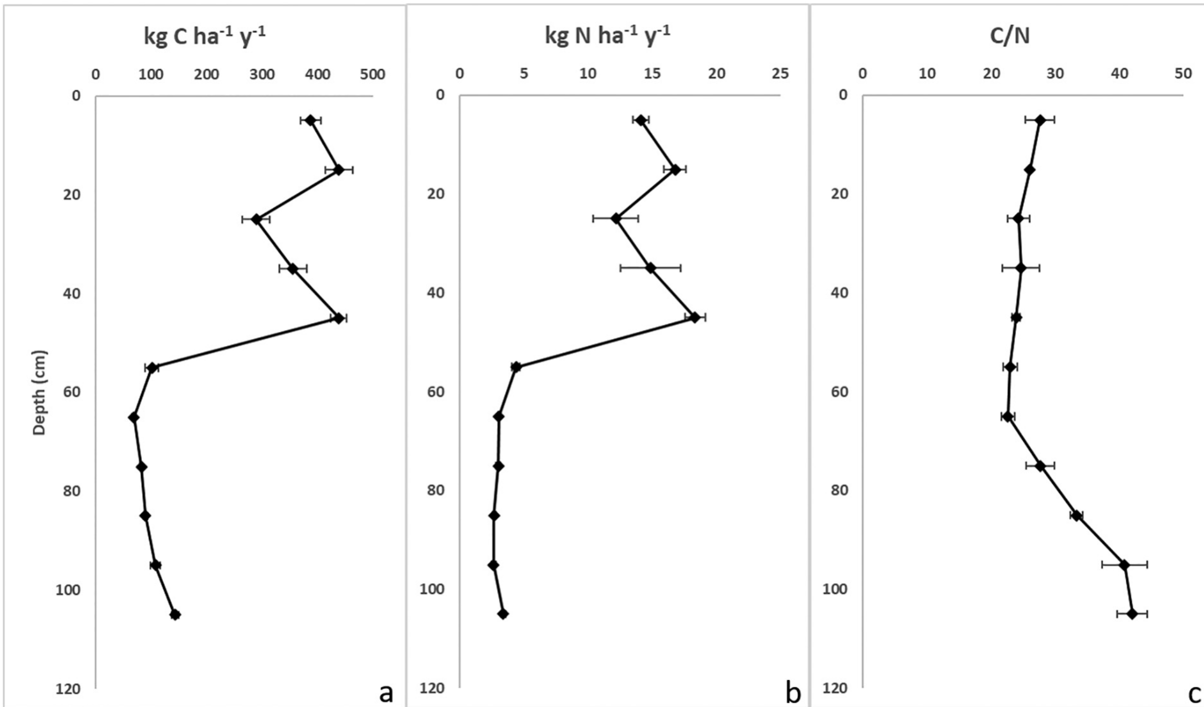

Fig. 6. a) Mean C accumulation rate, b) mean N accumulation rate and c) the mean C/N ratio from the three peat cores collected in the Migneint bog in 2014. Error bars represent standard error.

the C/N ratio has been relatively constant between 0 and 65 cm depth with the average for the top 50 cm at 25.3. The long-term average N accumulation rate based on the whole core was 8.4 ± 0.8 kg N ha^{-1} y^{-1}, whereas the most recent (top 0–5 cm layer) N accumulation rate was 14.1 ± 0.6 kg N ha^{-1} y^{-1}. As the N accumulation rate is not constant overtime and across depth (Fig. 6), in order to estimate uncertainty, each core was treated separately in calculating an average rate across the whole depth and then the range between the three cores was used as the uncertainty value.

3.6. Total N budget

The yearly N budgets and the average annual N mass balance for the Migneint bog catchment are shown in Table 2. Our N budgeting approach is similar to the one used by Vogt et al. (2013), where all N entering and subsequently leaving the peat catchment has been accounted for. Since all input and output processes are natural (grazing was not accounted for as it is considered minimal), they are directly linked to peat cycling processes and the downstream flux. Therefore, the mass balance between input and output processes represents changes in N storage within the peat over time. Each input and output process was assigned an error boundary depending on the accuracy of the data source. The overall uncertainty of the N mass balance, in individual years and also for the annual mean, was propagated and calculated as the square root of the sum of the error squares (Vogt et al., 2013).

Table 2
Summary of N inputs, outputs, and mass balance for each studied year in the Migneint bog. All budget terms and associated errors expressed in kg N ha^{-1} y^{-1}.

	2013	Error	2014	Error	Annual Mean	Error
N inputs						
Atmospheric deposition	13.1	±2.62	13.7	±2.74	13.4	±2.68
Biological Nitrogen Fixation	0.26	±0.261	0.26	±0.261	0.26	±0.261
N outputs						
Fluvial export	4.0	±0.01	2.7	±0.02	3.3	±0.01
Gaseous export	10.7	±4.45	8.6	±1.81	9.6	±3.10
Mass balance	−1.3	±5.17	2.6	±3.29	0.7	±4.10

The mean total inputs (atmospheric deposition + BNF) are 13.7 kg N ha^{-1} y^{-1}, while the total outputs (fluvial and gaseous export) are 12.9 kg N ha^{-1} y^{-1}, with the mean annual mass balance being slightly positive at 0.7 kg N ha^{-1} y^{-1}. However, when the propagated uncertainty (± 4.10 kg N ha^{-1} y^{-1}) is taken into account it becomes apparent that the ecosystem N balance is at a fragile equilibrium that can tip from a net sink to a net N source interannually. The positive mean annual mass balance can only account for a fraction of the measured long term peat N storage rate (8.4 kg N ha^{-1} y^{-1}), which is a further indication that the Migneint bog catchment is approaching N saturation. Gaseous export is responsible for the removal of 70% of N inputs, while fluvial export of N is much lower at 24% of N inputs when N retention accounts for only 5% of the inputs.

4. Discussion

In this study, we have estimated a complete annual N budget for an ombrotrophic bog catchment in North Wales, UK, using, for the first time in the literature, a combination of comprehensive field measurements of N input via biological nitrogen fixation, gaseous N losses via denitrification and a high-resolution record of fluvial N export. Although a mean positive N mass balance was found annually, the significant propagated uncertainty of the mass balance points towards a fragile bog ecosystem where the current N sequestration capacity is threatened by the legacy of chronic elevated atmospheric Nr deposition. This finding is broadly in line with a recent spatially distributed nitrogen budget for the whole of Great Britain, which indicated that 34% of areas, located predominantly in the western part of the country, are identified as N sinks (see Fig. 4 in (Fan et al., 2020). However, it also corroborates the few recent N budget studies in peatland catchments (Hill et al., 2016; Vogt et al., 2013; Worrall et al., 2012) that have shown that these northern peatlands can often behave as N sources, although a common conclusion has been the high uncertainty of estimates regarding key N cycle processes such as biological nitrogen fixation and soil denitrification that are difficult to measure and for which there is scarcity of available field data.

Atmospheric nitrogen deposition has been steadily declining in the UK since the 1990s (Tipping et al., 2017), mainly as a result of a reduction in NOx emissions from industrial processes (Payne, 2014). The modelled atmospheric deposition for the Migneint bog catchment (Table 1) falls in the middle of the range reported for the UK (7.6–27.6 kg N ha^{-1} y^{-1};(Fan et al., 2020), while the uncertainty typically associated with the UK FRAME model is between 20 and 30% (Tipping et al., 2017; Vogt et al., 2013). Catchment inputs from NHx wet deposition were dominant reflecting the rural setting of the bog, surrounded by grazing land and being far from any significant industry, as well as its high annual precipitation, which could explain the mid-range N deposition rate (Fan et al., 2020). Taking the lowest uncertainty estimate into account, the atmospheric deposition rate of the Migneint bog (13.4 ± 2.68 kg N ha^{-1} y^{-1}) remains equal to or above the critical load limit stipulated for blanket bog communities (5–10 kg N ha^{-1} y^{-1}; (Payne, 2014), posing a real threat for the future of the N sink capacity of this fragile ecosystem especially since N deposition decline is projected to plateau in the decade between 2020 and 2030 (Payne, 2014). However, the effects of the high Nr loading may not be 'visible' in the short-term due to significant hysteresis between increases in N stocks in soil and plant tissues and response of the vegetation community composition and more long-term approaches of thirty-year cumulative deposition metrics have been proposed as more appropriate for assessing ecosystem impacts (Payne et al., 2019).

Despite the relatively high atmospheric deposition of Nr above the critical load of 10 kg N ha^{-1} y^{-1} that in the long-term could favour the dominance of vascular plants over *Sphagnum* mosses (Dore et al., 2012), biological nitrogen fixation associated with mosses and in bulk surface peat (asymbiotic) has not completely shut down but accounted for ~2% of the N inputs in the Migneint bog. Saiz et al. (2021) have shown that BNF activity in the Migneint is suppressed by 69% compared to the more pristine Swedish Degerö Stormyr peatland receiving ~2 kg N ha^{-1} y^{-1} of background Nr atmospheric deposition. This suppression was found to be close to the reduction in BNF (by 64%) caused by experimental fertilisation treatments in plots of Degerö Stormyr receiving 30 kg N ha^{-1} y^{-1} of Nr for more than 20 years. The magnitude of the suppression in BNF activity was shown to be higher in more pristine peatlands rather than bogs that have been exposed to long-term elevated Nr deposition (Saiz et al., 2021), as in the Migneint, and this could be ascribed to adaptations of the physiological response of the mosses to inorganic N supply. Specifically, it has been shown that *Sphagnum* is capable of regulating its uptake of ammonium, in a way that maximises N use efficiency while avoiding intoxication (Fritz et al., 2014). Conversely, nitrate uptake can be 8 times slower than ammonium (Fritz et al., 2014) and it is more likely to leach into deeper peat layers where it could be denitrified to N_2 and N_2O, raise the porewater pH and increase organic N mineralisation (van den Elzen et al., 2018). Moreover, Schillereff et al. (2016) have shown a sustained increase in phosphorus (P) concentration along the Migneint peat cores towards the surface layers, which was attributed to both an increase in aeolian P deposition by agricultural intensification, but also a biologically-driven upward translocation of P by the roots of surface vegetation to sustain new growth partly fuelled by the presence of additional Nr. The increase in surface P concentration has been correlated with fixed N across surface peats from around the world (Toberman et al., 2015) and likely further contributes to the sustenance of BNF.

The combined BNF rate (both moss symbiotic and peat asymbiotic) estimated in this study (0.26 ± 0.261 kg N ha^{-1} y^{-1}) was lower than the literature BNF rates of 0.5 and 1 kg N ha^{-1} y^{-1} used in Hill et al. (2016) and Vogt et al. (2013), respectively which are likely underestimated considering the median atmospheric Nr deposition measured in both studies (3.3 and 8.2 kg N ha^{-1} y^{-1}, respectively). It should be noted that the BNF measurements used in this study were conducted twice in only 2 growth seasons (2016–2017), 2 years later than the data collection for all other budget parameters and that due to high variability between the measured moss species and low number of replicates, uncertainty was estimated at ~100%. Nevertheless, they represent the closest estimate of BNF based on the most robust method available for the studied bog catchment and highlight the need for more high resolution field measurements of BNF in natural peatlands, where N_2 fixing activity is sustained and is likely to increase its quantitative importance as Nr deposition declines, but thus far has been omitted from country-wide N budgets (Fan et al., 2020; Tipping et al., 2017).

Enrichment of the UK's natural and semi-natural ecosystems by Nr deposition over the period 1750–2010 was estimated to increase total denitrification by approximately 25% (Tipping et al., 2017). The average annual gaseous N export was measured at 9.6 ± 3.1 kg N ha^{-1} y^{-1}, which accounts for 70% of the N inputs and is by far the most significant N output pathway in this bog catchment. Although considered in many studies, due to the acidic pH of the Migneint peat (~ 4) and the lack of significant grazing activity and therefore animal excreta or any other form of fertilisation, NH_3 volatilisation is unlikely to be an important output pathway in this catchment. Literature values for NH_3 volatilisation in peatlands with no agricultural activity are often low. Hill et al. (2016) used a modelled input value of 0.1 kg N ha^{-1} y^{-1} for NH_3 volatilisation, well within the estimated uncertainty (32%) of our measured gas emissions and therefore would not have a significant effect on the N budget outcome.

It is rare in the literature of N budget studies in peatlands to include measured fluxes of N_2 and N_2O due to denitrification. Our measured rates constitute the closest and the most temporally intensive estimates of true field fluxes for bogs using the more reliable ^{15}N Gas Flux technique (Scheer et al., 2020). In comparison to the rates reported by Vogt et al. (2013) and Hill et al. (2016) our measured rates are significantly higher, but apart from the fact that denitrification tends to be highly spatiotemporally variable, the lower atmospheric N deposition in these studies may be one reason why gaseous N losses were also lower. Other confounding factors include the use of emission factors based on land surface N inputs, soil type and precipitation patterns (Vogt et al., 2013), which tend to overestimate N_2O (Sgouridis and Ullah, 2017) and are highly uncertain for N_2 fluxes (Vogt et al., 2013). Also, the use of the acetylene inhibition technique in lab incubations for measuring peat denitrification (Hill et al., 2016), has been shown to seriously underestimate N_2 fluxes and overestimate the $N_2O/N_2 + N_2O$ ratio (Groffman et al., 2006; Scheer et al., 2020; Sgouridis et al., 2016). Our N_2O fluxes were 3 orders of magnitude lower than the N_2 and consequently the $N_2O/N_2 + N_2O$ product ratio was on average 0.23%, much lower than the similar range fluxes of N_2 and N_2O reported by (Vogt et al., 2013) and the global terrestrial denitrification product ratio of 8% recently estimated by Scheer et al. (2020). It should be noted that all potential sources of N_2O were considered in our budget (i.e both denitrification and nitrification) and our results corroborate the notion that ombrotrophic peatlands in the UK are minimal sources of N_2O (Curtis et al., 2006; Dinsmore et al., 2009; Drewer et al., 2010) due mainly to the prevalence of more complete denitrification. At the same time, we highlight the quantitative importance of the N_2 flux as a major N output pathway in Nr enriched bog catchments, which at present appears to counteract much of the deposited Nr and contribute to the alleviation of the severity of chronic N saturation of this bog.

Increased fluvial loss of N due to elevated atmospheric Nr deposition has been stipulated in peatland catchments either via direct leaching of surplus supply of inorganic N, under N saturation conditions (Curtis et al., 2004; Edokpa et al., 2015), indirectly via stimulation of microbial decomposition of organic matter with consequent leaching of DOC and DON (Bragazza et al., 2006; Moore et al., 2019), or direct DON leaching from *Sphagnum* tissue (Bragazza and Limpens, 2004). The TN loss from the Migneint bog catchment was 3.34 ± 0.01 kg N ha^{-1} y^{-1} representing 25% of the N inputs. While this is similar or lower than the fluvial N losses reported from peat catchments that were identified as N sources (22% in Worrall et al. (2012); 41% in Vogt et al. (2013) our

N loading data falls within the range reported by Chapman and Edwards (2001) for upland areas of the UK receiving a similar degree of atmospheric loading (10–15 kg ha^{-1} yr^{-1}) and a high percentage contribution of DON to TN loading. Concentrations of DON accounted for 71% of TN, consistent with a wide range of studies investigating DON dynamics in natural/semi-natural peatland systems (Chapman and Edwards, 2001; McKenzie et al., 2016; Vogt et al., 2013; Yates et al., 2019). Marked seasonal differences in TN speciation (higher DON contribution in summer and autumn vs. DIN being higher in winter and spring) suggest active seasonal vegetation growth in the surface peat layer and consequently DIN uptake, potentially enhanced by the additional supply of Nr and also P from deeper peat layers as shown earlier (Edokpa et al., 2015; Reynolds and Edwards, 1995; Schillereff et al., 2016). The contribution of DON to TN in rainwater is understudied, and as a result data are sparce and highly uncertain. It has been estimated that rainwater contributions to the TN pool in atmospheric deposition can be as high as 25 % across a European gradient (Cornell, 2011). However, McKenzie et al. (2016) while studying a Scottish peat bog receiving lower total atmospheric N deposition showed that DON accounted for less than 10 % of the deposited N. It could even be assumed that under higher Nr deposition levels, as in the Migneint, the relative contribution of deposited DON would be even lower. Due to the low contribution of rainwater DON, it is likely that DON in the Migneint catchment is of biological origin.

The importance of DON in exporting labile N to downstream ecosystems from generally N-limited peatland catchments has only recently been acknowledged with DON dominating N loading from a wide variety of catchments (Durand et al., 2011; Edokpa et al., 2018; Edokpa et al., 2015; McKenzie et al., 2016). The use of instream optical sensors in this study to estimate DON concentrations at a high temporal resolution ensures a robust load estimate, reducing uncertainties in the overall N budget in relation to fluvial N loss. The effect of sampling frequency on load estimation has long been recognised as a potential cause of error (Johnes, 2007; Kronvang and Bruhn, 1996). Studies in similar peatland catchments have found the potential to underestimate DOC by 7–9% when relying on bi-weekly measurements, with this uncertainly increasing to between 13 and 19% when relying on monthly sample collection alone (Büttner and Tittel, 2013). The potential for load underestimation is high, particularly in catchments where hydrological response to rainfall is rapid, such as those draining the Migneint (Austnes et al., 2010), as manual sampling campaigns often miss high flow events.

The method of DON estimation employed in this study aimed at minimising the errors caused by under sampling of high flow events. However, although modelled and observed data correlated well in this study, it does not mean this method is appropriate in all catchments. There are two main factors that enable this approach to be undertaken, (1) minimal anthropogenic input, and (2) a low baseflow index. Minimal anthropogenic interference is important as the inclusion of additional nutrient source areas such as sewage treatment systems, agricultural processes or large areas of wetland may cause a significant, and prolonged de-coupling of catchment DOC:DON ratios (Inamdar and Mitchell, 2007), with pulses of N-rich DOM entering the river. Secondly, a flow regime with a high degree of seasonality will result in water entering the stream from stored sources (i.e. aquifers). Microbial processing of DOM has been shown to alter fluorescence-based indices of DOM composition, with increases in both humification and fluorescence index, indicative of continued microbial decomposition of DOM (Tye and Lapworth, 2016). Given the strong regression observed between lab DOC and DON concentrations and subsequently, between observed and modelled DON we are confident that the load estimation is robust, covering all flow conditions experienced across the period of study.

The mean annual N mass balance for the Migneint bog estimated in this study was slightly positive (0.7 ± 4.10 kg N ha^{-1} y^{-1}), albeit with a considerable propagated uncertainty, which indicates that the current N sink status of the bog may be easily reversed into a N source interannually. Interannual variability in N budgets of ombrotrophic peatlands that rely on natural N input processes affected by climatic variability is to be expected as shown by the multi-annual budget of a peatland catchment in Worrall et al. (2012). The mass balance between N inputs and outputs represents the internal peat N storage and our estimate can only account for a fraction of the long-term N storage term (8.4 ± 0.8 kg N ha^{-1} y^{-1}) measured by Schillereff et al. (2016) in the Migneint peat cores in 2014, giving a strong indication that the N saturation capacity of the bog has been reached (Butterbach-Bahl et al., 2011). Additionally, the long-term N storage, based on whole peat cores ranging back thousands of years into the Holocene, is likely masking the more recent effects of chronic Nr deposition and the N accumulation rates almost double (~ 14 kg N ha^{-1} y^{-1}) when the acrotelm or surface peat (0–30 cm) is considered. A recent biogeochemical ecosystem model (N14CP; Tipping et al. (2017) has shown that soil organic carbon stocks, and therefore organic N too, have increased over the period 1750–2010 as a consequence of increased primary productivity of British semi-natural ecosystems (including moorlands) fuelled by ecosystem fertilisation by atmospheric nitrogen deposition. A comparison of the Migneint nutrient stoichiometry in Schillereff et al. (2016) with other peatbogs in the UK, along an east to west gradient of increasing Nr deposition, and with more pristine bogs in Canada, the U.S. and South America is quite revealing of the status of nutrient enrichment in this bog. The C/N ratio in the top 50 cm of peat in the Migneint is 25.3 (UK mean 31.7), the lowest of all the UK and global bogs considered (see Table 5 in Schillereff et al. (2016). It has been suggested, in forested ecosystems, that a C/N ratio of <25 is an indicator of N saturation and therefore increased risk of leaching (Gundersen et al., 1998). Moreover, the Migneint has by far the lowest C/P ratio (794 versus 1468 of the UK mean) among the UK and global bogs considered by Schillereff et al. (2016), highlighting a concurrent increase in both essential nutrients for plant growth and posing a real threat to the future of peatland moss communities that could be overtaken by vascular plants (Juutinen et al., 2010; Juutinen et al., 2016) if these conditions persist in the long-term.

5. Conclusions

Our synthesis study has revealed the fragile status of a UK ombrotrophic bog with respect to its N sequestration capacity and consequently future C sequestration ability. Our novel field measurements broadly confirm model predictions (N14CP; Tipping et al. (2017) of increased N stocks and increased gaseous N export as a result of long-term Nr enrichment, which parallels the fertilisation effects observed in bog experimental studies (Moore et al., 2019). Long-term enrichment with Nr via atmospheric deposition has suppressed biological nitrogen fixation by up to 69%, compared to pristine northern peatlands. However, BNF is still active with minor contribution to the bog N inputs, albeit the measurement uncertainty remains high and highlights the need for more comprehensive measurements of this key process for the N economy of peatlands, especially as Nr deposition continues to recede. A major proportion (70%) of the N inputs is lost via denitrification and in particular the inert N_2 gas makes up the majority of the gaseous flux. This finding, shown for the first time in this study, is quantitatively crucially important for the abatement of the adverse effects of chronic Nr enrichment. However, the benefits of complete denitrification could be reversed by future climate change as an increased frequency of droughts could alter the denitrification product ratio in favour of the potent greenhouse gas N_2O, potentially turning peatlands into significant sources of this gas (Pärn et al., 2018). An increased frequency of flash floods, also triggered by climate change, could lead to a significant increase in fluvial DON export causing a downstream fertilisation effect. This is a plausible scenario since organic C and N stocks have increased considerably in the last few centuries (14 kg N ha^{-1} y^{-1} in the Migneint vs. 3.4 kg N ha^{-1} y^{-1} for global northern peatlands; (Loisel et al., 2014) by increased primary productivity fuelled by primarily external Nr supply and to a lesser extent also P. There appears to be a fine balance between the receding atmospheric Nr deposition in recent decades and the significant hysteresis between increases in N stocks in soil and plant tissues and response of the vegetation community composition and longer-term monitoring of these fragile ecosystem is warranted to be able to assess future impacts.

CRediT authorship contribution statement

Fotis Sgouridis: Conceptualization, Methodology, Formal analysis, Writing – original draft. **Christopher A. Yates:** Formal analysis, Writing – review & editing. **Charlotte E.M. Lloyd:** Formal analysis, Writing – review & editing. **Ernesto Saiz:** Investigation. **Daniel N. Schillereff:** Investigation, Writing – review & editing. **Sam Tomlinson:** Investigation. **Jennifer Williamson:** Investigation, Resources. **Sami Ullah:** Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.147552.

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