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Long-term macronutrient stoichiometry of UK ombrotrophic peatlands

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HIGHLIGHTS

- C, N and P concentrations and long-term burial rates in UK peat are of similar magnitude to published values elsewhere.
- The long-term burial flux in UK peat of P is broadly consistent with atmospheric deposition rates; N burial exceeds atmospheric deposition, consistent with substantial N fixation by peat bogs.
- N and P concentrations in peat are strongly associated in both UK and sites elsewhere in the world, consistent with a key role for P in biological fixation of N and C.

GRAPHICAL ABSTRACT

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ABSTRACT

In this paper we report new data on peat carbon (C), nitrogen (N) and phosphorus (P) concentrations and accumulation rates for 15 sites in the UK. Concentrations of C, N and P measured in peat from five ombrotrophic blanket mires, spanning 4000–10,000 years to present were combined with existing nutrient data from ten Scottish ombrotrophic peat bogs to provide the first UK perspective on millennial scale macronutrient concentrations in ombrotrophic peats. Long-term average C, N and P concentrations (0–1.25 m) for the UK are 54.8, 1.56 and 0.039 wt%, of similar magnitude to the few published comparable sites worldwide. The uppermost peat (0–0.2 m) is enriched in P and N (51.0, 1.86, and 0.070 wt%) relative to the deeper peat (0.5–1.25 m, 56.3, 1.39, and 0.027 wt%). Long-term average (whole core) accumulation rates of C, N and P are $25.3 \pm 2.2 \text{ gC m}^{-2} \text{ year}^{-1}$ (mean $\pm$ SE), $0.70 \pm 0.09 \text{ gN m}^{-2} \text{ year}^{-1}$ and $0.018 \pm 0.004 \text{ gP m}^{-2} \text{ year}^{-1}$, again similar to values reported elsewhere in the world. The two most significant findings are: 1) that a regression model of N concentration on P concentration and mean annual precipitation, based on global meta data for surface peat samples, can explain 54% of variance in N concentration in these UK peat profiles; and 2) budget calculations for the UK peat

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Stoichiometry
Holocene

cores yield an estimate for long-term average N-fixation of $0.8 \text{ g m}^{-2} \text{ year}^{-1}$. Our UK results, and comparison with others sites, corroborate published estimates of N storage in northern boreal peatlands through the Holocene as ranging between 8 and 15 Pg N. However, the observed correlation of N% with both mean annual precipitation and P concentration allows a potential bias in global estimates that do not take this into account. The peat sampling data set has been deposited at the NERC Data Centre (Toberman et al., 2016).

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1. Introduction

Peatlands represent a globally-important store for carbon (C) (530–694 Pg C: Yu et al., 2010) and nitrogen (N) (8–15 Pg N: Limpens et al., 2006) through the Holocene, and ombrotrophic peats across northern latitudes make an especially significant contribution (436 Pg C: Loisel et al., 2014; 9.7–18.5 Pg N: Loisel et al., 2014; Wang et al., 2015; 0.34 Pg P: Wang et al., 2015). A key characteristic of ombrotrophic bogs is that N, P and other elements (e.g., Ca, K, Mg) vital to their biogeochemical functioning (Bridgman et al., 1998; Bubier et al., 2007; Damman, 1986) and plant assemblage structure (Baker and Boatman, 1990; Fritz et al., 2012; Gotelli et al., 2008) are almost exclusively supplied via the atmosphere (Damman, 1990; Kellogg and Bridgman, 2003; Malmer, 1988). Such inputs of N and P are estimated to be low (Tipping et al., 2014; Turunen et al., 2004), suggesting that their availability should limit peat bog primary production (Schlesinger and Bernhardt, 2013), an effect that has been demonstrated experimentally (Aerts et al., 1992; Aerts et al., 2001; Olid et al., 2014). Although they are both supplied from the atmosphere, N and P differ in the mechanisms by which this supply takes place. P is supplied solely by deposition processes, while for N biological fixation is an important additional pathway (Knorr et al., 2015). Despite the apparent role of these nutrients in controlling both bog functioning and C burial, limited attention has been paid to investigating the patterns of, and controls over, their long-term accumulation, cycling and stoichiometry in ombrotrophic peatlands. Although consideration has been given to the C:N ratio as an indicator of peat decay (Malmer and Holm, 1984), interpreted in terms of changing hydrological conditions (Malmer and Wallén, 2004; Silamiş et al., 2010), few studies have considered C, N and P in combination. Published case studies that do consider all three nutrients have examined peatlands in North America (Gorham and Janssens, 2005; Wang et al., 2015, 2014), tropical settings (Rwanda: Pajunen, 1997; Indonesia: Weiss et al., 2002) and Patagonia (Knorr et al., 2015). Other than work in Sweden (Damman, 1978), there is a dearth of stoichiometric data from Europe and the UK in particular despite decades of peatland research for various purposes, including reconstructing palaeoclimate variability through the Holocene (e.g., Charman et al., 2006), assessing carbon storage (e.g., Billett et al., 2010) and investigating ecosystem functioning (e.g., Holden et al., 2004).

Long-term peat records have revealed changes in nutrient element concentration with depth. In the case of P a consistent pattern is observed, with enrichment in the aerobic surface layer (acrotelm) containing living vegetation: typically the upper 20–40 cm in temperate peatlands, extending to 2 m depth in tropical settings, and has been interpreted as evidence of biological P recycling (Damman, 1978; Craft and Richardson, 1993; Weiss et al., 2002; Wang et al., 2015). In the case of N, changes in concentration through the peat profile are also observed (Malmer and Holm, 1984; Craft and Richardson, 1993; Kuhry and Vitt, 1996; Malmer and Wallén, 2004; Gorham and Janssens, 2005; Wang et al., 2015), but the direction of change varies between sites, such that generalisation is uncertain. Furthermore, there is conflicting evidence about the possible role of recent (20th Century) anthropogenically-driven atmospheric nutrient enrichment (Galloway et al., 2004; Vitousek et al., 1997). Malmer (1988) observed a latitudinal gradient of bog surface N concentrations that reflected the deposition rates across Sweden and Norway (Malmer, 1988), while Gorham and Janssens (2005) found no recent increase at sites across North America despite high N deposition (Turunen et al., 2004). Where

observed, increases in N concentration with depth have been attributed primarily to preferential decay and loss of C during progressive decomposition of the plant-derived organic matter (Malmer and Holm, 1984; Craft and Richardson, 1993; Kuhry and Vitt, 1996; Malmer and Wallén, 2004; Wang et al., 2015). That the extent of decay, varying as it does with bog wetness (Aaby and Tauber, 1975), is a factor in governing the relative concentrations of N and C, does not preclude alternative processes. Thus, Charman et al. (2013) considering both stratigraphic variation through cooler episodes of the Medieval Climate Anomaly, and inter-site variation across the globe, find that C accumulation is better predicted by indicators of Net Primary Productivity (NPP) than by indicators of decay, pointing away from preferential decay as the dominating factor. This conclusion is consistent with the interpretation of Toberman et al. (2015) that an observed association between N and P in surface peat is explained by P supply regulation of biological N-fixation. Equally, an association of N with P is an expected consequence of recycling and retention of nutrients. Uncertainty about which factors are most important in driving bog nutrient content and productivity means that any prediction of environmental change impacts on the peat C stores is also uncertain.

Ombrotrophic peats that have accumulated during the Holocene are an important wetland ecosystem in Britain, covering approximately 6.5% of the terrestrial surface area (15,728 km²; BGS 1:650,000 Superficial Deposits, Geological Map Data, British Geological Survey) (Taylor, 1983). Therefore, investigating the factors that control nutrient concentrations and fluxes in these peats is essential if we are to fully understand nutrient dynamics in the British landscape. This paper, reporting research undertaken as part of the LTLs Project (NERC Macronutrient Cycles Programme, project *Analysis and Simulation of the Long-Term, Large-Scale Interactions of C, N and P in UK land, freshwater and atmosphere*) aims to contribute the first millennial-scale reconstruction of C, N and P content in British ombrotrophic peat sequences to redress the paucity of data and compare long-term nutrient dynamics across the boreal peatlands. To provide a comprehensive picture, we combine existing data from ten sites across Scotland with five new dated peat sequences that lie along an extended latitudinal gradient spanning England and Scotland. We also compare our data with existing studies elsewhere in the world, and address the extent of systematic variation.

2. Data and methods

2.1. Five new peat cores

New cores were collected from five upland ombrotrophic blanket bogs selected to represent a latitudinal gradients through Britain (Fig. 1). Triplicate adjacent cores were extracted in 2014 using both a box corer (to recover the surface vegetation and uppermost 1 m of peat) and a Russian-type corer (for peat deeper than 1 m). The sites were: Great Gnat's Head on Dartmoor (DM), Migneint (Mg) in northwest Wales, Moor House (MH) in northern England, Glensaugh (G) near the north eastern Scottish coast and Forsinard Flows (F) in the far north of mainland Scotland. Physiographical information for each site is summarised in Table 1. All cores extended down to the underlying mineral substrate, ranging in length from 95 cm (Glensaugh) to 417 cm (Forsinard).

The new cores were carefully extruded, sliced at 10 cm intervals, air-dried for one week, manually sieved to 2 mm to remove large particles and roots, oven-dried at 60 °C to remove residual moisture and ball-

Fig. 1. Sample locations in relation to the distribution of peat, including fen peat (BGS 1:650,000 Superficial Deposits, Geological Map Data, British Geological Survey).

milled to a fine, homogenous powder. Bulk densities of all samples were calculated prior to milling by dividing the dry matter mass by the original volume of wet material. Phosphorus content was measured colorimetrically using a Seal Analytical AQ2 discrete analyser after digestion in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$. After drying at 105°C , carbon and nitrogen were determined on an Elementar Vario-EL analyser using an ISO17025 accredited method.

2.2. Existing data from Scotland

The National Soil Inventory of Scotland (NSIS2) (Lilly et al., 2011) contains 721 soil profiles sampled between 2007 and 2009 for which C, N, and P concentrations have been measured. Here we consider ten of these sites, those classified as deep blanket peat. Details for all methods are given in Chapman et al. (2013). In brief, the selected peat

profiles were 90–120 cm in thickness and samples taken at between three and five depths, often based on observed changes in humification in the peat profile. Bulk density was measured in triplicate on subsamples collected in 7.3 cm internal diameter stainless steel cylinders, adjusted to correct for removal of the >2 mm fraction. Around 2 kg of sample were taken at each site for elemental analysis, returned to the laboratory where they were air-dried at 30°C and sieved (<2 mm), further dried at 50°C prior to milling. Carbon and nitrogen were determined using a Flash EA 1112 Series Elemental Analyser connected via a ConFlo III to a DeltaPlus XPisotope ratio mass spectrometer (all Thermo Finnigan, Bremen, Germany). The C contents were calculated from the area output of the mass spectrometer calibrated against a standard reference material which was analysed with every batch of ten samples). Total P was measured colorimetrically following fusion with NaOH (Smith and Bain, 1982).

Table 1
Physiographical information for the five LTLS sites.

Site name (code)	Lat., long.	Alt. (m)	MAT (°C)	MAP (mm)	Geology	Dominant surface vegetation
Great Gnat's Head, Dartmoor, England (DM)	50.495, –3.950	469	8.8	1800	Carboniferous–Permian granite	Grasses, <i>Eriophorum</i> , <i>Sphagnum</i> , <i>Calluna</i>
Migneint, Wales (Mg)	52.994, –3.803	432	7.3	2236	Ordovician sandstone	<i>Eriophorum</i> , <i>Calluna</i> , <i>Vaccinium</i> , <i>Sphagnum</i>
Moor House, England (MH)	54.694, –2.389	575	6.4	1478	Carboniferous limestone	<i>Calluna</i> , <i>Erica</i> , <i>Vaccinium</i> , <i>Eriophorum</i> , moss (various), <i>Cladonia</i>
Glensaugh, Scotland (G)	56.917, –2.512	439	7.0	916	Cambrian metamorphic pelite	<i>Calluna</i> , <i>Vaccinium</i> , <i>Nardus</i> , <i>Eriophorum</i> (Other grasses, various), <i>Sphagnum</i> (Other mosses, various) <i>Cladonia</i>
Forsinard, Scotland (F)	56.917, –2.562	215	6.9	1104	Neoproterozoic metamorphosed (various)	<i>Sphagnum</i> , <i>Racomitrium</i> , <i>Calluna</i> , <i>Erica</i> , <i>Myrica gale</i> , <i>Eriophorum</i> , grass (various), <i>Cladonia</i> .
Creag Dubh, Sutherland	58.147, –4.380	330	5.7	1182	Neoproterozoic metamorphosed psammite	Data unavailable
Rubha Mor, Lewis	58.080, –6.752	35	8.1	2241	Archaen–Proterozoic gneiss	<i>Sphagnum papulosum</i> , <i>Racomitrium lanuginosum</i> , <i>Calluna</i> , <i>Erica tetralix</i>
Meall Chrombaig, Cairngorms	56.900, –3.643	567	4.6	1287	Neoproterozoic pelite	<i>Sphagnum papulosum</i> , <i>Racomitrium lanuginosum</i> , <i>Calluna</i> , <i>Erica tetralix</i>
Queensberry, Lowther Hills	55.284, –3.576	472	5.6	2000	Silurian metasandstone & metasiltstone	<i>Sphagnum papulosum</i> , <i>Racomitrium lanuginosum</i> , <i>Calluna</i> , <i>Erica tetralix</i>
Sheilhope Hill, Lowther Hills	55.467, –3.267	480	6.0	1787	Silurian metasandstone & metasiltstone	<i>Sphagnum papulosum</i> , <i>Racomitrium lanuginosum</i> , <i>Calluna</i> , <i>Erica tetralix</i>
Tom Roiseneabhat, Lewis	58.271, –6.437	105	7.5	1626	Archaen–Proterozoic gneiss	<i>Sphagnum</i> (various species), <i>Erica tetralix</i>
Garbh Leachtir, Loch Lomond Hills	56.526, –4.604	372	5.9	2976	Neoproterozoic quartzite & psammite	<i>Sphagnum papulosum</i> , <i>Erica tetralix</i> , <i>Calluna</i> , <i>Eriophorum angustifolium</i> , <i>Potentilla erecta</i>
Cock Hill, Cairngorms	56.910, –2.658	417	6.4	1093	Neoproterozoic semipelite and mica psammite	<i>Sphagnum papulosum</i> , <i>Erica tetralix</i> , <i>Calluna</i> , <i>Eriophorum angustifolium</i> , <i>Potentilla erecta</i>
Carn nan Aighean, Easter Ross	57.781, –4.692	496	5.3	1787	Neoproterozoic amphibolite	<i>Calluna vulgaris</i> , <i>Eriophorum vaginatum</i> , <i>Sphagnum</i> (various), <i>Rhytidiadelphus loreus</i>
Dun Mount, Cairngorms	57.267, –2.996	520	5.7	1051	Neoproterozoic metamorphosed psammite	<i>Calluna vulgaris</i> , <i>Eriophorum vaginatum</i> , <i>Sphagnum</i> (various), <i>Rhytidiadelphus loreus</i>

Table 2

Radiocarbon data for horizons at Dartmoor (DM), Migneint (Mg), Moor House (MH), Glensaugh (G) and Forsinard (F). The IntCal13 curve was used for calibration (Reimer et al., 2013) using the calibration programme CLAM. The 14C % modern absolute are reported for use in soil modelling.

Laboratory number	Site identifier and sample depth (cm)	14C % modern absolute ($\pm 1\sigma$)	Conventional 14C age (year BP $\pm 1\sigma$)	2 σ calibrated age range (mean) cal year BP	$\delta^{13}\text{C}_{\text{VPDB}}\text{‰} \pm 0.1$
SUERC-58230	DM 20–30	84.54 $\pm$ 0.40	1286 $\pm$ 37	1092–1295 (1225)	–27.6
SUERC-58231	DM 90–100	69.57 $\pm$ 0.33	2852 $\pm$ 38	2859–3075 (2969)	–27.6
SUERC-58232	DM 180–190	64.26 $\pm$ 0.30	3489 $\pm$ 38	3644–3859 (3762)	–27.9
SUERC-58233	Mg 20–30	98.03 $\pm$ 0.46	96 $\pm$ 37	12–270 (131)	–27.2
SUERC-58234	Mg 50–60	90.18 $\pm$ 0.42	767 $\pm$ 37	661–759 (701)	–27.1
SUERC-58235	Mg 110–120	54.82 $\pm$ 0.26	4766 $\pm$ 38	5330–5590 (5503)	–27.5
SUERC-58219	MH 20–30	97.33 $\pm$ 0.46	154 $\pm$ 37	42–285 (150)	–26.3
SUERC-58220	MH 100–110	75.42 $\pm$ 0.35	2203 $\pm$ 37	2130–2325 (2226)	–27.2
SUERC-58221	MH 190–200	52.54 $\pm$ 0.25	5107 $\pm$ 39	5746–5926 (5834)	–27.6
SUERC-58225	G 20–30	90.28 $\pm$ 0.40	759 $\pm$ 35	661–737 (696)	–27.8
SUERC-58226	G 50–60	80.18 $\pm$ 0.36	1711 $\pm$ 36	1550–1705 (1624)	–27.9
SUERC-58229	G 110–120	63.28 $\pm$ 0.28	3613 $\pm$ 36	3835–4071 (3927)	–27.8
SUERC-58252	F 20–30	97.17 $\pm$ 0.43	167 $\pm$ 35	37–290 (156)	–27.2
SUERC-58223	F 200–210	55.46 $\pm$ 0.27	4672 $\pm$ 38	5313–5575 (5409)	–27.5
SUERC-58224	F 400–410	31.76 $\pm$ 0.17	9151 $\pm$ 42	10,229–10,477 (10,318)	–27.3

2.3. Environmental data

For the new cores, details of vegetation type were recorded in situ and equivalent information was obtained from the JHI database following the key of Robertson (1984). Altitude (Landmap UK), underlying geology (DiGMapGB) and local 1971–2000 mean annual precipitation (MAP) and temperature (MAT) were determined for all sites from the 5 $\times$ 5 km gridded UKCP2009 dataset (Perry and Hollis, 2005).

2.4. Age-depth models

14C data have not been measured for the JHI peat cores. For the five new cores, ball-milled sub-samples of bulk peat from the upper section (20–30 cm), mid-profile and base of one core from each of the five LTLS sites ($n = 15$; Table 2) were submitted to the NERC Radiocarbon Facility at East Kilbride for determination of its 14C signature by accelerator mass spectrometry (AMS). CO₂ released by combustion (in an oxygen-filled high-pressure bomb) of the sieved soil was separated cryogenically, graphitised by iron-zinc reduction (Slota et al., 1987) and analysed using the Scottish Universities Environmental Research

Centre (SUERC) AMS (5MV NEC, National Electrostatics Corporation, Wisconsin, US) (Xu et al., 2004). Stable carbon isotope ratios were measured on sub-samples of CO₂ using a dual-inlet mass spectrometer with a multiple ion beam collection facility (Thermo Fisher Delta V) in order to normalise 14C data to $-25\text{‰} \delta^{13}\text{C}_{\text{VPDB}}$. Data are reported as conventional radiocarbon ages (relative to 1950 CE) and absolute % modern (for use in on-going associated nutrient modelling), adjusted to reflect on-going radioactive decay of the international reference standard (oxalic acid) since 1950 CE (Stuiver and Polach, 1977). All 14C measurements were given the mid-point depth and a vertical error of ± 5 cm and used to estimate the down-core pattern in accumulation rate. The calibration of 14C measurements ages was part of this process and used the IntCal13 curve (Reimer et al., 2013).

2.5. Statistical analysis

Normality tests (Anderson-Darling statistic), one-way ANOVA, 2-sample *t*-tests, correlation tests and regression were performed using MINITAB17.

Fig. 2. Spatial variation in N and P concentrations in the UK (average values for depth interval 0–125 cm).

3. Results

3.1. Chronology

Peat 14C concentrations were measured on sieved (<2 mm) bulk fractions, and these data have been used to establish age models for the peat profiles. Though plant macrofossils are commonly preferred for dating purposes (Nilsson et al., 2001), we consider the average age of the 10 cm peat subsamples sufficient for our low-resolution analysis. The 2 sigma calibrated 14C age ranges for samples from the five new cores are presented in Table 2. The uppermost dates at Migneint, Moor House and Forsinard fall within the time interval during which fossil fuel emissions and thermonuclear bomb testing have perturbed the atmospheric 14C curve (last 200 years). The five sequences exhibit variable basal ages (quoted in the text as median modelled age). The peats at Dartmoor and Glensauagh have accumulated since ca. 4000 years before present (year BP), the Moor House peats since ca. 5700 year BP the Migneint sequence since ca. 6200 year BP while the Forsinard Flow record spans most of the Holocene (since ca. 10,580 year BP).

3.2. UK between-site differences in nutrient composition

The site mean concentrations (JHI data in S1 and 5 new sites, Table 4) show statistically significant between-site differences in element concentrations (one-way ANOVA between-group $df = 14$, and $F = 27.7$, 11.7 and 19.1 for C, N and P respectively). There is a slight tendency for N to increase westwards (Fig. 2), however there are no statistically significant associations of element concentration with either latitude or longitude. A statistically significant positive association is found of N (but not P) concentration with mean annual precipitation ($r = 0.65$, $p = 0.008$).

To calculate the UK mean element concentrations we have averaged six site means (Table 4), the five latitudinally distributed new coring sites, and mean of the ten JHI sites from Scotland. The JHI sites were treated as a single site to 1) avoid over-sampling Scotland, and 2) reflect the low number of samples in each of the ten cores.

3.3. Depth profiles

The C concentration is maximal at or near the base of the profile at all sites (Fig. 3) that have recovered peat sequences thicker than 1 m, with maximum values in the range 55 to 61 wt%, and at a minimum at the top of the profile, with minimum values in the range 44 to 52 wt% C. Some shallow sites from the JHI data set exhibit slightly greater C near the peat surface. Three of the five new cores contain a mineral-enriched basal section with low C concentrations (e.g., Dartmoor C = 10%), presumably reflecting the soil/fen peat on which ombrotrophic peat bog developed (basal peat at Moor House and Forsinard). A similar mid-depth layer in Migneint has previously been interpreted in terms of water table drawdown and erosion (Ellis and Tallis, 2001). These sections are ignored in subsequent analysis of nutrient cycling under ombrotrophic conditions. In contrast to C, the trend in N concentration is more variable. N rises in concentration up through the peat profile at four of the five new cores, increasing by up to a factor of two in the upper 40 to 100 cm. However, at Migneint a decline in N concentration occurs above a mid-profile peak (55–65 cm), while six of the ten JHI data set profiles show either an up-profile decline or no change. Maximum N was measured at the surface at four of the five new sites (Migneint being the exception).

In contrast with N, surface enrichment of P is observed at all fifteen sites, with concentrations at 0–20 cm being greater by a factor of 1.5 to 3.3 (mean 2.4) than in the interval 20–125 cm at the five new peat cores (Table 4). In most cases, the highest P concentration was measured in the uppermost sample (Fig. 3). Maximum near-surface P concentrations vary between the new sites to some extent: surface peat

at Migneint is most enriched in P (maximum = 0.11 wt%), followed by Glensauagh (0.093 wt%) and surface P maximum is lowest at Forsinard (0.068 wt%). Alongside near-surface maxima, N and P concentrations appear related at depth: an earlier phase of elevated P at Migneint corresponds with maximum N content, while at Forsinard N rises at a constant rate from 125 cm depth, corresponding to an interval of higher P concentrations (95–125 cm). However, except at these specific depths the concentrations of N and P show less variation in the deeper parts of the profile depth (below 50 cm, N typically ranges 1.0 to 1.5 wt%, and P 0.02 to 0.03 wt%) (Fig. 3). A statistically significant correlation is found between N and P concentration for peat deeper than 50 cm for all sites except Forsinard.

3.4. Long-term accumulation rates of C, N and P

Whole core long-term accumulation rates (Table 3) of C, N and P for the UK (calculated from the five dated LTL sites) are $25.3 \pm 2.2 \text{ gC m}^{-2} \text{ year}^{-1}$ (mean $\pm$ SE), $0.70 \pm 0.09 \text{ gN m}^{-2} \text{ year}^{-1}$ and $0.018 \pm 0.004 \text{ gP m}^{-2} \text{ year}^{-1}$, respectively. Some geographic variability is observed: C and N accumulation was 0.6–0.7 times the average at Glensauagh (least) and 1.3 times at Dartmoor (greatest), while P accumulation ranged from 0.6 times the average at Forsinard to 1.8 times at Migneint.

3.5. Comparison with other sites

A comprehensive comparison with other studies is restricted by the lack of sites for which C, N and P have all been measured. Although lacking chronological information, the most comprehensively studied region is Ontario (Wang et al., 2015, $N = 400$), where values differ from those recorded in the UK (Table 5, Fig. 4, values presented as ratios, C concentrations not being reported in Wang et al., 2015). In Fig. 4 we display these ratios in the form N:C and P:C, reversing the conventional approach in order to place greater emphasis on changes in N and P. However, for the comparisons in Table 5 we show C:N and C:P, as this is the only form in which some of the data are available.

In the upper 40–50 cm of the profile the Minnesota and Ontario data have lower N:C and N:P ratios (and thus lower N concentrations) compared with the UK data (Fig. 4). The Patagonia peat sample (Knorr et al., 2015) is the most contrasting with much higher C:N and C:P (lower N:C and P:C), though with similar N:P (Table 5).

The full-core data (Table 5) also reveal differences when compared with sites elsewhere in the world. The Ontario (Wang et al., 2015) and Québec (Wang et al., 2014) data are similar to the UK, but the C:N ratios are far lower (thus, N:C higher) than the five North America sites of Gorham and Janssens (2005). More strikingly, the Ontario data set shows falling N:C ratios up core (Fig. 4), in strong contrast with the UK and two complete records of Gorham and Janssens (2005) from North America (despite their different mean values).

The full-core site mean values for C:N, C:P, and N:P are normally distributed (Anderson-Darling test, all p values > 0.16). A 2-sample t -test finds no significant difference between the UK and non-UK site mean values for C:P and N:P, but finds UK C:N to be significantly ($p = 0.027$) lower than the non-UK sites, showing that UK peats are relatively N enriched (though less so than Ontario peats, Wang et al., 2015).

4. Discussion

4.1. Long-term average C, N and P concentrations in UK peats

We have measured the concentrations of C, N and P in newly sampled peat profiles at 5 sites spanning the length of the UK, supplemented by new analysis of the geochemical composition of 10 existing peat cores from Scotland (Figs. 2 & 3, Table 4). The data reveals some spatial variability across the UK (Fig. 2, Table 4) that is associated in part with variations in climate, specifically with mean annual precipitation. This

Fig. 3. Depth profiles (cm) of C, N and P concentrations. For the 5 new coring sites, triplicate cores were measured.

probably explains the greater range of C and N values reported from the JHI sites, especially the west to east precipitation gradient across Scotland (Perry and Hollis, 2005). However, climatic associations with C, N

and P concentrations are relatively weak, and our results suggest that ombrotrophic peats in the Britain are fairly uniform in their macronutrient concentrations.

Table 3
Apparent long-term mass accumulation rates for the new cores ($\text{g m}^{-2} \text{ year}^{-1}$).

	Peat accumulation rate mm year^{-1}	C	N	P
Forsinard	0.43	23.6	0.64	0.011
Glensnagh	0.29	18.7	0.42	0.012
Moor House	0.42	26.0	0.68	0.019
Migneint	0.47	26.0	0.94	0.032
Dartmoor	0.79	32.2	0.82	0.015
Mean	0.48	25.3	0.70	0.018
SE	0.08	2.2	0.09	0.004

4.2. N & P enrichment in surface peat

In most of the UK peat profiles, N and P concentrations are elevated in the uppermost peat layers (Fig. 3). However, the two elements show rather different patterns of variation, and the enrichments have been explained rather differently. Consequently, N and P are here discussed separately.

The surface P enrichment at the UK sites (Fig. 3), present in all 15 cores, is also seen at sites elsewhere in the world (Fig. 4, expressed as P:C ratio). The UK average P:C ratio decreases down profile from 0.00125–0.00156 in the interval 0–20 cm to 0.00049–0.00067 in the interval 50–125 cm, similar in form and magnitude to profiles in Minnesota (Gorham and Janssens, 2005) and Ontario (Wang et al., 2015). At the Newfoundland site of Gorham and Janssens (2005) a similar surface enrichment is seen, but with a far lower P:C ratio, attributed by the authors to limited deposition of wind-blown dust sourced from the continental interior. Such surface P enrichments are also reported from the Everglades (Craft and Richardson, 1993, 2008), Sweden (Damman, 1978) and Indonesia (Weiss et al., 2002).

Surface P enrichment is generally attributed to nutrient cycling. Damman (1978) and Malmer (1988), observing that P uptake by the contemporary bog flora greatly exceeds annual atmospheric receipts, propose a biologically-driven process whereby upward translocation of nutrients through the roots of surface vegetation sustains new growth. Such a mechanism, essential to maintaining productivity in ombrotrophic peatlands, is certainly in operation but may not be the only factor since human activities have increased the throughput of

both N and P at regional and global scales since industrialisation (Neff et al., 2008). Gorham and Janssens (2005) observed progressive depletion of P (and N) content with distance from the cultivated Midwest, and attribute this to transport of nutrients as a component of wind-blown dust (Neff et al., 2008; Ravi et al., 2011; Van Pelt and Zobeck, 2007). Cheesman et al. (2012) demonstrate that P availability decreases along a transect from a swamp-rimmed ombrotrophic wetland in Panama towards its centre, consistent with declining lateral supply (Tipping et al., 2014) with distance from neighbouring forest ecosystems. In the UK, increased inputs of P via dust and biological debris may be especially prevalent, due both to the proximity of many of its bogs to agricultural land, and to the magnitude of agricultural intensification over recent centuries. Additional work with other element concentrations, including dust proxies for example, is needed before any generalisations may be confidently deduced.

The situation with N is more complex. Nine of the 15 UK sites show increased N (and N:C ratios) in the surface peat, N:C on average increasing from 0.015–0.029 in the interval 50–125 cm to 0.035–0.045 in the interval 0–20 cm. This accords with some previous studies. Thus, long records from Minnesota and Newfoundland (Gorham and Janssens, 2005), though with higher mean N:C than our peats, show the same tendency to increase towards the peat surface. Malmer and Wallén (2004) report an increase in N:C ratio over the last 1000 years of peat accumulation at Store Mosse (Sweden). However, our results contrast with those of Wang et al. (2015) who find an average decrease in N:C from 0.034 to 0.035 in deeper peat to 0.023 to 0.025 at 0–50 cm in a study of >400 peat profiles from Ontario. At another site in Canada (Alberta), Kuhry and Vitt (1996) report a still larger reduction, with N:C falling below 0.01 in the upper 50 cm, but exceeding 0.03 below 50 cm.

The more variable character of the N enrichment reflects a greater number of driving factors. As with P, plant cycling has been shown to transport mineralised N to the bog surface (Vile et al., 2014) contributing to surface enrichment. However, it is generally regarded that differences in decay rates of C and N in peat have a greater influence over the N concentration. Thus, Malmer and Wallén (2004) attributed a strong increase in N:C in recent peat at a Swedish bog to preferential decay of C (exported as CO_2) following a recent change in the peat hydrology that increased the oxygenation of the acrotelm. However, this site appears to be unusual. In the absence of recent disturbance, the extent

Fig. 4. Comparison of N:C, P:C and N:P depth profiles for average UK peat cores (Black squares, with SE bars), average Ontario peat (Wang et al., 2014, diamonds), and two North America peats of Gorham and Janssens (2005) (dashed line, Minnesota; solid line, Newfoundland).

Table 4

Variation in N, P and C concentration (wt%) with depth in UK ombrotrophic peat sequences. The JHI data has been averaged because of the low number of samples at each site, and the over-representation of Scottish peats had each of the 10 sites been included. Full data for JHI sites in S1. The italics were to distinguish N (nitrogen) from N (the number of observations).

		0–125 cm		0–20 cm		20–50 cm		50–125 cm		125 cm - base	
		Mean	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range
Dartmoor	N	1.53 ± 0.06	0.80–2.33	2.13 ± 0.07	1.89–2.33	1.71 ± 0.07	1.27–2.03	1.31 ± 0.06	0.80–1.67		
	P	0.027 ± 0.002	0.014–0.080	0.051 ± 0.009	0.024–0.080	0.030 ± 0.001	0.021–0.033	0.021 ± 0.001	0.014–0.027		
	C	56.9 ± 0.3	52.3–58.9	55.0 ± 1.0	52.3–58.6	57.3 ± 0.2	56.4–58.4	57.2 ± 0.3	54.3–58.9		
	N	39		6		9		24			
Migneint	N	1.99 ± 0.07	1.29–2.67	1.89 ± 0.08	1.57–2.09	2.25 ± 0.09	1.79–2.67	1.90 ± 0.10	1.29–2.64		
	P	0.059 ± 0.004	0.026–0.113	0.094 ± 0.006	0.082–0.113	0.060 ± 0.005	0.042–0.083	0.044 ± 0.005	0.026–0.077		
	C	55.8 ± 0.6	49.0–61.4	50.4 ± 0.4	49.0–51.5	53.9 ± 0.4	52.3–55.2	58.3 ± 0.5	53.2–61.4		
	N	35		6		9		20			
Moor House	N	1.37 ± 0.03	0.97–1.91	1.63 ± 0.06	1.48–1.91	1.51 ± 0.04	1.32–1.68	1.26 ± 0.03	0.97–1.55	1.21 ± 0.02	1.00–1.38
	P	0.033 ± 0.002	0.016–0.078	0.062 ± 0.004	0.047–0.078	0.033 ± 0.001	0.028–0.038	0.025 ± 0.001	0.016–0.035	0.022 ± 0.002	0.018–0.040
	C	54.9 ± 0.4	50.6–58.5	52.0 ± 0.2	51.1–52.4	53.0 ± 0.4	50.6–54.2	56.3 ± 0.2	54.1–58.5	59.1 ± 0.2	57.3–60.3
	N	39		6		9		24		18	
Glensauagh	N	1.25 ± 0.06	0.94–2.06	1.81 ± 0.09	1.50–2.06	1.25 ± 0.07	1.04–1.65	1.06 ± 0.02	0.94–1.25		
	P	0.035 ± 0.004	0.019–0.093	0.077 ± 0.007	0.053–0.093	0.030 ± 0.003	0.021–0.047	0.020 ± 0.002	0.019–0.025		
	C	55.5 ± 0.3	51.8–57.7	52.8 ± 0.4	51.8–54.5	55.3 ± 0.2	54.4–56.5	56.6 ± 0.2	55.0–57.7		
	N	32		6		9		17			
Forsinard	N	1.58 ± 0.07	0.93–2.40	2.00 ± 0.17	1.25–2.39	1.91 ± 0.10	1.50–2.40	1.35 ± 0.06	0.93–1.98	1.12 ± 0.02	0.95–1.45
	P	0.023 ± 0.002	0.010–0.068	0.048 ± 0.006	0.032–0.068	0.025 ± 0.003	0.014–0.045	0.017 ± 0.001	0.010–0.029	0.020 ± 0.001	0.012–0.025
	C	57.0 ± 0.3	49.8–59.5	52.9 ± 1.0	49.8–57.0	57.1 ± 0.4	54.6–58.2	58.0 ± 0.1	56.8–59.5	59.0 ± 0.1	57.4–60.6
	N	39		6		9		24		43	
JHI	N	1.66 ± 0.08	0.88–2.87	1.78 ± 0.11	1.11–2.42	1.82 ± 0.21	1.17–2.87	1.45 ± 0.12	0.88–2.23		
	P	0.058 ± 0.005	0.018–0.130	0.080 ± 0.009	0.032–0.130	0.058 ± 0.009	0.024–0.108	0.036 ± 0.004	0.018–0.058		
	C	48.8 ± 0.5	44.3–57.1	46.8 ± 0.4	44.7–49.6	47.9 ± 0.8	44.3–52.1	51.5 ± 0.9	47.0–57.1		
	N	32		12		9		11			
UK	N	1.56 ± 0.10		1.87 ± 0.07		1.74 ± 0.14		1.39 ± 0.12			
	P	0.039 ± 0.006		0.069 ± 0.007		0.039 ± 0.006		0.027 ± 0.004			
	C	54.8 ± 1.2		51.7 ± 1.1		54.1 ± 1.4		56.3 ± 1.0			
	N	6		6		6		6			

of peat decay generally increases with depth such that preferential decay is more commonly invoked to explain surface depletion in N rather than surface enrichment. To a first order, the intensity of peat decay varies with the duration that peat remains within the periodically oxygenated acrotelm (Malmer and Wallén (2004), and thus is expected to show periodic fluctuations in response to changing climate (Barber et al., 1994) and peat drainage (Blackford and Chambers, 1991). It is on this basis that Wang et al. (2015) attribute their observed increase in N concentration with depth in the peat to preferential loss of C during peat decomposition. The relative importance of decay processes and supply factors in governing the N concentration and N:C ratios in UK peats cannot be readily estimated. Hydrologically moderated peat decay (Clymo, 1984; Malmer and Wallén, 2004) will have played a role that varies from site to site, and certainly our findings are not consistent with the effect reported by Wang et al. (2015) for their large Ontario data set.

In addition to recycling and preferential decay, recent human-induced increases in the external inputs of both N and P (Neff et al., 2008) may also have impacted peat N. Malmer (1988) showed an association between N deposition and N content of *Sphagnum* mosses, and by inference in the peat too, and it is reasonable to expect that this signal may be present in the peat record. However, a straightforward addition of enhanced N supply to the peat need not occur, as evidence exists (DeLuca et al., 2008) that N deposition may substitute for rather than add to existing N fixation. Toberman et al. (2015) found no association of N concentration with N deposition flux in a meta study of surface peats across the world. Instead, they found a statistically significant association of N concentration with mean annual precipitation and P concentration, which they interpret as indicating a role for P in N fixation, and consequently, C fixation.

An association of N concentration with MAP and P concentration is also observed in our UK peat cores (log transformed, $r = 0.72$ and 0.49 for P and MAP, respectively, $p < 0.005$ in both cases). A multiple regression analysis confirms independent contributions from both P and MAP ($r^2 = 0.55$, $p < 0.005$, and $t = 13.7$ and 4.6 for log P and log MAP,

respectively). Applying the multiple regression model of Toberman et al. (2015) (simplified model, $\log N = 0.35 \log P + 0.44 \log \text{MAP} + 0.59$) to predict N% yields good agreement with the observed values (Fig. 5). The Ontario data of Wang et al. (2014, 2015) plot close to the UK data, with slightly low predicted N. The five North American

Fig. 5. Prediction of N concentration from the peat P concentration and climate (MAP) using the empirical model of Toberman et al. (2015) shows good agreement with the new peat profile sites (5 new UK cores, JHI combined as in Table 4, filled diamonds). Five peat profiles from North America (Gorham and Janssens, 2005, open diamonds), and the Ontario data of Wang et al. (2014, 2015), also agree well with the model. For the data of Wang et al. (2014, 2015) N and P concentrations were calculated from the reported N:C and P:C data assuming C = 55%. Linear regression of observed N on modelled N for all 12 sites is statistically significant ($F = 12.9$, $p = 0.004$, and $R^2 = 0.54$), with slope not significantly different from 1.

sites of [Gorham and Janssens \(2005\)](#) also show good agreement with the [Toberman et al. \(2015\)](#) model, but with higher predicted N. This association between N and P could arise from the elements have a common source, such as biological supply in the form of bird faeces or plant debris, or because P plays a key role for N fixation as concluded by [Toberman et al. \(2015\)](#) for surface peat.

4.3. Long-term peat nutrient budgets

[Wang et al. \(2015\)](#) reported that the long-term rate of accumulation of P in peat bogs is similar to atmospheric receipts in their Ontario bogs. At our 5 new LTLS sites the long-term rate of P accumulation ($0.018 \text{ gP m}^{-2} \text{ year}^{-1}$; [Table 3](#)) is slightly lower than the median UK value for atmospheric deposition over the last few decades as estimated from deposition collectors ($0.027 \text{ gP m}^{-2} \text{ year}^{-1}$, [Tipping et al., 2014](#)) whereas the apparent surface accumulation rate, which is presumably enhanced by plant recycling of nutrients, is rather higher ($0.047 \text{ gP m}^{-2} \text{ year}^{-1}$). However, this comparison does not take into account leaching of P from peat. Peats are known to lose DOC in runoff, and though not measured, must also be losing DON and DOP. Typical export rates of DOC from UK peatlands lie in the range of 5 to $30 \text{ gC m}^{-2} \text{ year}^{-1}$, with a mean value of 20 ([Buckingham et al., 2008](#); [Gibson et al., 2009](#)), which when combined with a rounded estimate of 1000 for the C:P ratio of dissolved organic matter ([Tipping et al., 2016](#)) yields P loss in the range $0.02 \text{ g m}^{-2} \text{ year}^{-1}$. Long-term P export via this pathway would thus slightly exceed our long-term burial rate estimate. Combined, these yield a long-term P loading in Britain in the order of $0.038 \text{ gP m}^{-2} \text{ year}^{-1}$, a value similar to the estimated recent P deposition. This result is consistent with the conclusion of [Wang et al. \(2015\)](#) that in the long term peat bogs are in balance with their atmospheric receipts. At present such a conclusion rests on uncertain information, not just of the peat burial fluxes and losses, but also with regard to the atmospheric P loading. The atmospheric supply estimate of [Tipping et al. \(2014\)](#) is based on deposition samplers that purposefully exclude P supplied from some biological macro-aerosols such as bird faeces, a contribution of unknown magnitude. Lateral exchange of P from neighbouring more enriched landscape will certainly be taking place ([Tipping et al., 2014](#)), but at rates that are not known. Although difficult to quantify, future efforts to measure contemporary P deposition that account for these sources and losses should be a priority for the community, including estimation of short range atmospheric transfer of P from agricultural to natural ecosystems.

A similar approach may be taken with N burial in the peat profile. Our UK average long-term N burial is $0.7 \text{ g m}^{-2} \text{ year}^{-1}$, and N export via DON in runoff will be of the same order (0.5 based on N:C being 41:1, range 0.1 to $0.7 \text{ g m}^{-2} \text{ year}^{-1}$). If we assume that N:P for pre-industrial atmospheric deposition is 10:1 (rounded average of dust - [Lawrence and Neff, 2009](#); vegetation and litter - [Wang et al., 2015](#); forest fire smoke - [Zhang et al., 2002](#)), then based on the long-term mean atmospheric P loading calculated above we can expect $0.38 \text{ gN m}^{-2} \text{ year}^{-1}$ from atmosphere. This leaves $0.8 \text{ g m}^{-2} \text{ year}^{-1}$ to be supplied through biological N fixation, rather lower than has been measured in Alberta peat bogs ([Vile et al., 2014](#); 1.7 to $3.4 \text{ g m}^{-2} \text{ year}^{-1}$). If denitrification was active in peat bogs prior to modern N deposition, then our estimate for average long-term N fixation would be proportionately higher. The budget calculations thus concur with the interpretation of [Toberman et al. \(2015\)](#) that correlation of N and P in peat is indicative of long-term N-fixation.

4.4. A global perspective

The long-term C, N and P burial rates ([Table 3](#)) are similar to comparable studies elsewhere in the world. [Clvmo et al. \(1998\)](#) reported a global average for carbon accumulated in the catotelm of $25 \text{ g C m}^{-2} \text{ year}^{-1}$. [Wang et al. \(2014\)](#) reported $29.5 \pm 2.1 \text{ gC m}^{-2} \text{ year}^{-1}$ (mean $\pm$ SE), $0.87 \pm 0.01 \text{ gN m}^{-2} \text{ year}^{-1}$ and $0.017 \pm 0.002 \text{ gP m}^{-2} \text{ year}^{-1}$ for the long-term apparent accumulation rates at Mer Bleue (Ottawa), and

Table 5

Nutrient stoichiometric ratios in UK peats compared to other ombrotrophic bogs worldwide.

	Location	C:N	C:P	N:P
Top 50 cm	UK mean	31.7	1468	45.4
	<i>Forsinard</i>	29.4	2060	67.3
	<i>Glensaugh</i>	38.9	1471	35.4
	<i>Moorhouse</i>	34.1	1317	38.3
	<i>Migneint</i>	25.3	794	31.7
	<i>Dartmoor</i>	30.8	1700	54.1
	Global surface peat (0–25 cm) ^a			27.1
	Ontario, average ^b	42.0	892	24.5
	Minnesota (0–25 cm) ^c	38.1	913	24.0
	Patagonia ^d	61.1	1695	36.0
	Mean	37.5	1355	37.6
	SE	3.9	162	4.8
Full core	UK mean	41.2	2160	50.9
	<i>Forsinard</i>	46.3	3091	67.8
	<i>Glensaugh</i>	46.8	2067	42.3
	<i>Moorhouse</i>	43.5	2103	47.5
	<i>Migneint</i>	29.5	1129	37.2
	<i>Dartmoor</i>	40.1	2411	59.7
	Mer Bleu, Ontario ^e	38.8	1942	50.0
	Ontario, average ^b	33.0	1338	46.4
	RLP Minnesota ^f	64.9	2000	30.8
	LPR Québec ^f	57.0	2208	38.8
	GSH Maine ^f	58.9	2947	50.0
	CMV Newfoundland ^f	81.3	4727	58.2
	EGR Labrador ^f	65.4	2944	45.0
	Mean	50.5	2409	47.8
	SE	4.4	273	3.0

^a [Toberman et al. \(2015\)](#) (Average of country means).

^b [Wang et al. \(2015\)](#).

^c [Bridgman et al. \(1998\)](#).

^d [Knorr et al. \(2015\)](#).

^e [Wang et al. \(2014\)](#).

^f [Gorham and Janssens \(2005\)](#).

[Wang et al. \(2015\)](#) propose similar rate for N and P from their large Ontario data set. Applying the Ontario C:N ratio to an assumed C storage of 500 Pg in northern peatlands (based on [Yu et al., 2010](#); [Loisel et al., 2014](#)), [Wang et al. \(2015\)](#) estimate N storage to be 18.5 Pg. Applying the same reasoning but using our higher C:N ratio (the average of all site values, [Table 5](#)), we find 8 to 12 Pg N, values more in line with the 8 to 15 Pg range estimated by [Limpens et al. \(2006\)](#) and [Loisel et al. \(2014\)](#). However, our observation that N concentration is associated with both P concentration and MAP suggests that estimation of global average N fluxes should take both climate and P supply into account. Applying the same approach to P, we find 0.21 Pg P in northern peatlands, very much lower than the 0.34 Pg estimated from Ontario stoichiometry ([Wang et al., 2015](#)).

The broad similarity in these estimates of long-term rates is encouraging in the context of global modelling, and suggests that a biogeochemical model of long-term (centuries to millennia) nutrient accumulation based on UK data may be applicable to boreal peatlands across northern latitudes. However, our results also suggest that spatial and temporal variations in external P supply to peatlands might lead to systematic variation in N and C fixation. In particular, recently enhanced atmospheric supply of nutrients may impact C uptake and burial by peat bogs, though parallel changes in the species composition of bog in response to nutrient pollution complicates this picture. Biogeochemical modelling is needed to further interpret these data; most importantly to resolve the issue of nutrient impacts on C accumulation.

5. Conclusions

- Long-term C accumulation in UK ombrotrophic peat estimated to be $25.3 \pm 2.2 \text{ g C m}^{-2} \text{ year}^{-1}$, similar in magnitude to values reported from elsewhere in the world.

- We report the first estimates for UK peat of long-term accumulation rates of N ($0.70 \pm 0.09 \text{ g m}^{-2} \text{ year}^{-1}$) and P ($0.018 \pm 0.004 \text{ g m}^{-2} \text{ year}^{-1}$), the value for N being rather lower than reported in the large Ontario dataset of Wang et al. (2014, 2015).
- N and P concentration profiles show higher values in the surface peat, consistent with biological recycling of nutrients. More work is needed to ascertain whether recent increases in atmospheric nutrient loading have also contributed.
- N and P concentrations in peat are strongly associated. A published regression model of N concentration on P concentration and mean annual precipitation, based on a global data set of surface peat samples, yields good agreement with peat cores sites in the UK and North America. This is consistent with a key role for P in N and C fixation.
- The long-term average N:P ratio of UK peat (51:1) is considerably higher than in both bog vegetation and unpolluted atmospheric deposition, also consistent with substantial role for biological N fixation in peat bogs.

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