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The formation of peat—Decreasing density with depth in UK peats

Fred Worrall[1] | **Gareth D. Clay**[2] | **Katherine Heckman**[3] | **Jonathan Ritson**[2] | **Martin Evans**[2] | **Julian Small**[4]

[1]Science Laboratories, Department of Earth Sciences, Durham University, Durham, UK

[2]Department of Geography, School of Environment, Education and Development, University of Manchester, Manchester, UK

[3]USDA Forest Service, Northern Research Station, Houghton, Michigan, USA

[4]Natural England, Humberhead Peatlands National Nature Reserve, Doncaster, UK

Correspondence
Fred Worrall, Science Laboratories, Department of Earth Sciences, Durham University, South Road, Durham DH1 3LE, UK.
Email: fred.worrall@durham.ac.uk

Abstract

Increasing bulk density with depth in a peat profile has been seen as key to the formation of peat. Increasing bulk density with depth causing the changes in porosity and permeability of peat soils has been proposed as a mechanism to explain how waterlogged, stagnant conditions persist in peat bog soils. However, a previous study (Clay & Worrall, 2015; *Soil Use & Management*, 31, 77) observed, in passing, that this was not always the case, but this previous study could not test the nature of the peat bulk density profile. Thus, this present study examined 22 peat cores from 13 locations across climatic gradients of the UK, including valley fens, blanket and raised bogs, and both intact peatlands and former peat extraction sites. At none of the 13 locations was there a significant increase in dry bulk density with depth in the peat profile. The oxidation state of the organic carbon (C_{ox}) in the peat profile showed no common pattern of change with depth. The only measured property that showed a consistent change down the peat profile among all 13 locations was an increase in the degree of unsaturation of C bonds. The change in degree of unsaturation shows a trend away from vegetation biomass composition and toward lignin-like compositions with an average rate of change of 0.2 π-bonds/ka. The measured pattern of bulk density between locations and types of peat shows that peat density reflects the contemporary peat environment, rather than the nature of peat formation. The bulk density profile likely reflects average water table position, as determined by topographic and land-management factors, with peat compaction and accelerated decomposition within the aerobic zone. The presence of gas bubbles may also contribute to low bulk density at depth. The common bulk density profile found across the UK for peat ecosystems shows that peat formation is not controlled by porosity change but more specifically by water flow and hydraulic conductivity.

KEYWORDS

degree of unsaturation, dry bulk density, oxidation state, peat

1 | INTRODUCTION

Globally, 415±150 Gtonnes C are stored in peatlands (Hugelius et al., 2020), which is approximately a third of the global soil carbon yet concentrated in only 3% of the Earth's terrestrial land surface (Turunen et al., 2002). Under suitable conditions, peat soils can carry on growing and accumulating organic carbon for millennia (Turunen et al., 2001) and so represent an ongoing sink of atmospheric carbon that has been fixed via primary productivity. The very existence of peat soils relies on the rate of organic matter decomposition being slower than the rate of input from primary production (Rydin & Jeglum, 2006). The relative slow rate of decomposition of organic matter in the peat profile can be ascribed to waterlogged stagnant conditions, which limits ingress of oxygen into the sub-surface. As oxygen is the most energetically-favourable terminal electron acceptor (TEA) for the decomposition of litter from primary production (LaRowe & Van Cappellan, 2011), restrictions on oxygen diffusion by waterlogging strongly limits decomposition. However, stagnant conditions are also required alongside the waterlogging. Water tables could remain high (i.e., close to the soil surface), but if that water table were maintained with water flushing through the pore space, then that water could bring in oxygenated water, or water rich in other terminal electron acceptors (e.g., nitrate, iron or sulphate), allowing the rate of decomposition to also remain relatively high. A continuous flow of water through the peat also flushes out reaction products, which allows the soil pore spaces to remain thermodynamically open, thus driving further organic matter reactions (Beer & Blodau, 2007).

Waterlogged and stagnant conditions can occur due to the topographic context of the peatland (e.g., within a landscape hollow such as peat formed in a kettlehole) but also because of the decrease in porosity, permeability and hydraulic conductivity down the peat profile produced by the process of peat formation itself. Clymo (1984) proposed that as the plant elements collapse the bulk density increases, the porosity decreases and the radius of curvature of water meniscus increases leading to an increase in thickness of the capillary fringe, thus maintaining waterlogged conditions. Clymo (1992) gives a model of peat growth that shows increase in bulk density with depth in the peat profile. Several authors have related increasing bulk density of peat with decreasing hydraulic conductivity of the peat (Boelter, 1972; Braekke, 1983; Holden et al., 2001). Given the Clymo model (Clymo, 1992), collapse of the porosity means that hydraulic conductivity is highest in near surface layers of the peat, which in turn means that any excess water is more likely to flow laterally and so preserving a stagnant water table lower in the soil profile. Baird et al. (2008) showed that although there was change in hydraulic conductivity with depth, the lower, permanently saturated 'catotelm' layer was not necessarily impermeable. These mechanisms mean that with an ongoing supply of plant material from primary production the water table will continue to rise as the organic matter accumulates. These processes enable peat to accumulate on shallow slopes (as blanket bogs) and to form shallow domes (i.e., raised bogs).

The process by which bulk density increases has been assumed to be due to decomposition (e.g., Clymo & Pearce, 1995), but it could also be by self-weight compaction as plant components come under pressure from the fall of fresh litter. Measurement and assessment of self-weight consolidation has been studied in a range of engineering contexts (e.g., mine tailings, Wickland and Wilson (2005); storage of dredged materials, Berilgen et al. (2006); back-filling of voids, Fahey et al. (2010)), but to date this has not been explored in peats.

Studies in peat soils that measure the bulk density profile of peats are common, but studies where the down profile change in bulk density of peat is the actual purpose of the study are rare. Bulk density profiles are commonly reported as part of studies of the age of peats and the conversion of dated peat profiles to long term carbon accumulation rates (LARCA – long-term apparent rate of carbon accumulation, sometimes also LORCA – Clymo et al., 1998). For example, Loisel et al. (2014) examined 232 peat cores from 181 locations across the Northern Hemisphere and included bulk density to measure LARCA, though the focus of that study was the accumulation rate and not the analysis of the change in density with depth. Milner et al. (2020) considered four 50 cm cores from a peat in North Wales and in all cases the bulk density increased with depth in the peat profiles. Tolonen (1977) and Vardy et al. (2000) both considered peat profiles from Arctic peats which do show increases in bulk density over depths of metres but there are local maxima visible in the top 1 m. Frogbrook et al. (2009) examined the uncertainty behind C stock estimates in peat soils by examining multiple soil cores across two 1 km^2 of soil in Wales and Scotland. By examining three horizons in the peat soils of each location down to 65 cm, they found that there was a significant decline in dry bulk density with depth for each location. Similarly, Tomlinson and Davidson (2000) in Ireland, and Parry and Charman (2013) in southwest England, report significant declines in bulk density with depth, but do not discuss the reasons for this relationship. Tallis (1985), in blanket bogs of the English Peak District, found the highest bulk densities in the top 15 cm with a decrease in bulk density below – although the study profiles were associated with proximity to erosion gullies.

Studies have often considered the impact of management on peats and the consequences of damage for peat properties. Therefore, there is a more mixed picture of peat profile development in terms of both bulk density and what models of peat development have implied that bulk density controls. Several studies have shown changes in bulk density of peat with management intervention. In Scotland, Shotbolt et al. (1998) (later confirmed by Chapman, 2001) considered profiles of peat bulk density along transects through forested and unforested peatlands and found decreasing bulk density with depth. In Finland, Minkkinnin and Laine (1998) showed significant subsidence occurred upon the drainage of peat bogs for forestry and this led to a 62% increase in dry bulk density of the peat. Likewise, Leifeld et al. (2011) and Wittnebel et al. (2021) have shown that peat bulk density increased with drainage of peat for agriculture. Further, Liu et al. (2020) reviewed the impact of peat drainage upon in hydrophysical properties of peat, including bulk density, and showed that bulk density increased rapidly in the first few years after management intervention with the rate of change decreasing over time. Although these studies show a mechanism by which peat bulk density could increase, they did not study the change down the peat profile. Howson et al. (2023) compared three land cover types in Scotland (intact bog, afforested blanket bogs and forested to bog transition) and also report declines in dry bulk density for depths to 1 m; again, the change with depth was not the aim of the study and was not discussed. For tropical peatlands, Könonen et al. (2015) considered peat soils under four different land uses and found that for three of the settings that bulk density did decline down profile to 115 cm. Hooijer et al. (2012) investigated subsidence rates in tropical peatlands and found that bulk density in their peat cores decreased from the surface to 50 cm depth and then bulk density was constant below 50 cm depth. Sinclair et al. (2020) considered the impact of drainage in tropical peatlands and observed declines in bulk density with depth although this was not demonstrated statistically.

Clay and Worrall (2015) studied peat profiles from eight locations across the UK to understand the variation in oxidation state of the peat soils relative to mineral soils. While not the focus of their study, Clay and Worrall (2015) observed that at none of the eight locations was there a significant increase in bulk density with depth in the peat profile – again this is the exact opposite of that expected from models of peat development but may accord with observations of profiles in damaged or degraded peatlands. The study of Clay and Worrall (2015) could not consider this observation further. Therefore, the aim of the present study was to assess whether bulk density of peat increases with depth across a wider range of peat soil settings in the context of other down profile changes.

2 | MATERIALS AND METHODS

This study builds on the dataset from Clay and Worrall (2015) to assess the controls on the development of peat soils by:

1. Extending the analysis to additional sites across a range of peat settings and climatic gradients;
2. Including dating so that rates of processes can be compared rather than just comparing depth in the profile;
3. Considering other depth profile changes as alternative explanations of peat formation.

2.1 | Sampling sites and methodology

Peat cores were taken from 13 locations across a climatic gradient through the UK (Figure 1, Table 1). At each sampling location, two peat cores of up to 1 m depth were taken using a 70 mm diameter gouge auger. Peat bulk density profiles may vary across a site and so the duplication across so many sites was included (eg. Laiho et al., 2004). Equally, bulk density may vary with microtopography of a peatland, but over the timescale of the peat accumulations in this study, microtopography of any sampling site will not have remained constant. At all locations, the organic layer was at least 50 cm thick and so could be classified as being taken from a peat soil (Avery, 1973; Lilly et al., 2010). Each core was subdivided into 50 mm sections in the field and placed into sealed plastic sample bags. In addition to collecting two peat cores at each site, representative samples of dominant vegetation types and surface litter were also collected. The exact vegetation composition varied among sites, but typically at each site the following were sampled: mosses (e.g., *Sphagnum* spp.); sedges (e.g., *Eriophorum* spp.); and shrubs (e.g., *Calluna vulgaris*).

All samples were dried at 105°C for 48 h prior to further analysis. Bulk density was then calculated on a dry weight per wet volume basis. Samples were ground prior to analysis using a cryomill.

2.2 | CHNO analysis

Samples were analysed for their carbon, hydrogen and nitrogen (CHN) concentration on a Costech ECS 4010 elemental combustion system with pneumatic autosampler. It was set up for CHN analysis, where Reactor 1 consisted of chromium (III) oxide/Silvered cobaltous-cobaltic oxide catalysts at 950°C and Reactor 2 consisted of reduced high purity copper wires at 650°C. Helium was used as the carrier gas at a flow rate of 95 mL min^{-1}.

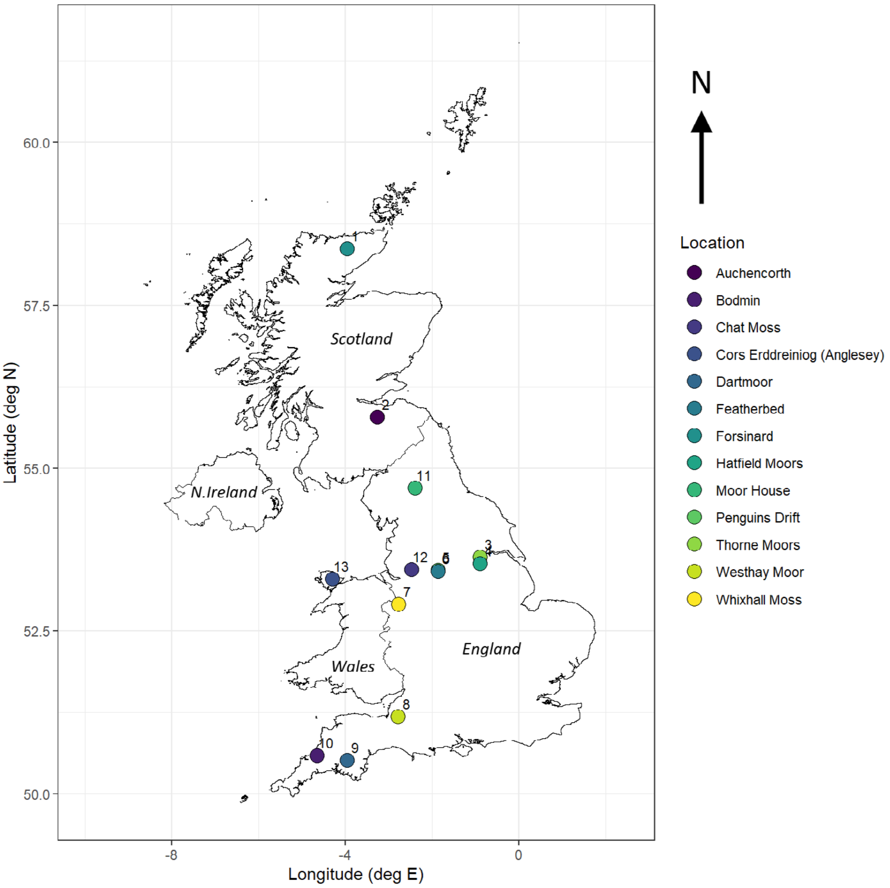

FIGURE 1 Map of the study locations.1. Forsinard, 2. Auchencorth, 3. Thorne Moors, 4. Hatfield Moors, 5. Doctor's Gate, 6. Featherbed, 7. Whixall, 8. Westhey Moor, 9. Dartmoor, 10. Bodmin, 11. Moor House, 12. Chat Moss, and 13. Cors Erddreiniog.

This carrier gas was filtered for hydrocarbons upstream of the instrument. A packed 3 m GC column was used for separation of the gases. A thermal conductivity detector (TCD) was used to calculate the signal of each sample. For oxygen (O) concentration, the Costech ECS was also used but was set up for O analysis. Reactor 1 consisted of a nickelised carbon/silica chips/nickel wool pyrolysis tube at 1060°C whilst Reactor 2 was left empty. Helium was used as the carrier gas at a flow rate of 130 mL min^{-1} but no oxygen was used. A 2 m packed oxygen GC column was used for separation of the gases. Chloropentane vapour was added to the carrier gas to enhance decomposition of the oxygen compounds and to reduce possible memory effects from previous samples (Kirsten, 1977).

Three standard materials were included in the analysis: lignin (Aldrich, CAS 8068-05-1), cellulose (Whatman, CAS 9004-36-4) and protein (Sigma, CAS 100684-25-1). The lignin, cellulose (taken as representative of polysaccharides, including hemicellulose) and protein present the three largest components of plants found in a peatland system (McDermott & Loomis, 1981).

Computer software used was EAS Clarity (DataApex Ltd., Prague, Czech Republic). For both CHN and O setups, a calibration curve of $r^2 > .999$ was created using acetanilide as the standard. Samples of acetanilide were included within each run as unknown samples to act as internal quality control checks. Each sample (peat, litter or vegetation) was measured to approximately 2 mg and was analysed in triplicate, i.e., three times on the CHN setup and a further three times on O set up, and a mean calculated for C, H, N and O.

2.3 | Organic matter descriptors

The carbon oxidation state (C_{ox}) can be determined from the measured C, H, N and O compositional data as follows (Masiello et al., 2008):

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

where: $[X]$ = molar concentration of C, H, N, or O. Equation (1) assumes the majority of organic nitrogen exists as amine groups in amino acids. Furthermore, sulphur is not included in this equation as it is assumed to form <0.25% of biomass (Charlson et al., 2000). Equation (1) assumes that there is no contribution to the C_{ox} from S or P, and it has been shown that the error in the OR of making such an assumption would be only ±0.002 (Hockaday et al., 2009). This equation also assumes that the nitrogen source in carbon fixation is N_2 (Masiello et al., 2008):

TABLE 1 Location information for each of the sites. Temperature and precipitation are given as the annual average for 1991–2000 for the nearest UK Meteorological Office weather station (https://www.metoffice.gov.uk/research/climate/maps-and-data).

Location	Longitude, latitude	Altitude (m asl)	Temperature (°C)	Precipitation (mm)	Peatland type	Source
Forsinard	58.37139, −3.96209	217	9.4	949	Intact	Clay and Worrall (2015)
Auchencorth	55.78726, −3.25768	265	8.2	993	Raised bog	Clay and Worrall (2015)
Thorne Moors	53.63450, −0.89133	5	10.3	582	Cutover raised bog	Clay and Worrall (2015)
Hatfield Moors	53.53626, −0.89693	5	10.3	582	Cutover raised bog	This study
Doctor's Gate (Peak District)	53.43509, −1.86518	507	9.8	868	Blanket bog	Clay and Worrall (2015)
Featherbed (Peak District)	53.42233, −1.86608	530	9.8	868	Blanket bog	This study
Whixhall Moss	52.91513, −2.76969	91	9.8	683	Cutover raised bog	Clay and Worrall (2015)
Westhay Moor	51.19080, −2.78276	−5	15.2	787	Cutover raised bog	Clay and Worrall (2015)
Dartmoor	50.51815, −3.96071	355	10.5	1438	Blanket bog	Clay and Worrall (2015)
Bodmin	50.58779, −4.64982	254	9.9	1432	Blanket bog	Clay and Worrall (2015)
Moor House	54.69390, −2.38948	570	7.7	1303	Blanket bog	This study
Chat Moss	53.44726, −2.46833	20	9.7	868	Cutover raised bog	This study
Cors Erddreiniog (Anglesey)	53.29943, −4.28980	65	10.7	856	Raised bog	This study

The degree of unsaturation (Ω; McMurray, 2004) is defined as:

$$\Omega = [C] - \frac{[H]}{2} + \frac{[N]}{2} + 1 \qquad (2)$$

The degree of unsaturation can be interpreted as the number of equivalent double bonds per C atom, or the average number of π bonds per C atom.

2.4 | Radiocarbon dating

Samples were graphitized in preparation for ^{14}C abundance measurement at the Carbon, Water & Soils Research Lab in Houghton, MI, USA. Peat samples were treated with successive washes of acid (1 N HCl) and base (1 N NaOH) to remove any materials which may have adhered to the surfaces of the organics. Samples were weighed into quartz tubes and sealed under vacuum. Samples were combusted at 900°C for 6 h with cupric oxide (CuO) and silver (Ag) in sealed quartz test tubes to form CO_2 gas. The CO_2 was then reduced to graphite through heating at 570°C in the presence of hydrogen (H_2) gas and an iron (Fe) catalyst (Vogel et al., 1987). Graphite targets were then analysed for radiocarbon abundance by Accelerator Mass Spectrometry at the DirectAMS facility in Bothell, WA, USA (Zoppi et al., 2007), and corrected for mass-dependent fractionation following Stuiver and Polach (1977).

2.5 | Statistical analysis

The design of the study allows for a several statistical comparisons to be made using a Bayesian hierarchical approach (Congdon, 2021). We considered the radiocarbon data with Depth as a covariate, while we considered the organic matter descriptors with Depth as a factor. To understand the benefit of the Bayesian hierarchical approach, a simple linear regression analysis was used for the Depth-age model.

2.5.1 | Depth-age models

The Depth age models were analysed by a Bayesian hierarchical model where cumulative C storage at depth was compared with depth in the profile:

$$\text{Age} = N\left(\alpha(\text{Site}) + \beta(\text{Site})[\text{Depth}], \frac{1}{\sigma^2}\right) \quad (3)$$

$$C_{\text{sum}} = N\left(\alpha(\text{Site}) + \beta(\text{Site})[\text{Age}], \frac{1}{\sigma^2}\right) \quad (4)$$

where: Depth = depth in the peat profile (cm); Age = radiocarbon ^{14}C year BP. Equations (3) and (4) are linear regression models for each site but fitted within a Bayesian framework. Similarly, for each peat profile descriptor of interest:

$$Y = N\left(\alpha(\text{Site}) + \beta(\text{Site})[\text{Depth}], \frac{1}{\sigma^2}\right) \quad (5)$$

$$ln(Y) = N\left(\alpha(\text{Site}) + \beta(\text{Site})ln[\text{Depth}], \frac{1}{\sigma^2}\right) \quad (6)$$

where Y = peat profile descriptor for: dry bulk density (ρ); C/N; C_{ox}; and Ω. As with the Equations (3) and (4), Equations (5) and (6) are linear regression models for each site fitted within a Bayesian framework. The carbon accumulation rate can be calculated from the best-fit age model and given the measurements of the dry bulk density and the carbon content of the sampled layers.

2.5.2 | Assessment of depth factor

Our second approach was to consider depth not as a covariate, as in the depth-age model, but as a factor. By considering depth in the peat profile as a factor, it possible to consider the form of the depth profile at each site without the assumption that it is linear or linear in log space, i.e.,

$$Y = N\left(\alpha(\text{Site}) + \beta(\text{Depth}) + \gamma(\text{Site}) * (\text{Depth}), \frac{1}{\sigma^2}\right) \quad (7)$$

In addition, the data were considered relative to the surface value of the peat characteristic of interest. By judging the data relative to surface values, we propose that it would be possible to judge whether the relative change of a peat characteristic down each profile is the same between sites and it is only the source of material that changes.

2.5.3 | Fitting of Bayesian hierarchical models

Fitting of the Bayesian hierarchical approach was achieved by Markov Chain Monte Carlo (MCMC) simulation to estimate the posterior distribution of the determinand of interest (e.g., Age – Equation (3)) using Jags code called from R using the R2Jags library (example R and JAGS code are included in Appendix S1). The length of the MCMC chain was 10,000 iterations after 2000 burn-in cycles with samples saved every 10 cycles and with 3 chains.

Model fit was tested using several approaches. First, the adequacy of the MCMC process was assessed using the convergence statistic ($\hat{R}$), and values of $\hat{R} < 1.1$ were considered acceptable. If $\hat{R} > 1.1$, then the burn-in process and number of iterations were increased. Second, the 95% credible interval for any Site or Depth, does not include zero; this is henceforth referred to as being significantly different from zero at a probability of 95%. Similarly, the credible interval is henceforth referred to as the confidence interval for ease of understanding for those not so familiar with Bayesian methods. Third, that when a factor (Site or Depth) is included then the total model deviance and deviance information criteria (DIC) decrease. Lastly, the fit of any model was judged using a posterior prediction check, i.e., the output of the model was plotted against the observed values and the fitted line between these two was examined. It would be expected that a good fit model would give a 1:1 line between observed and posterior predicted values and so this was tested by considering both r^2 of the line between observed and predicted values and the difference between the fitted and the ideal gradient, i.e., difference from a gradient of 1.

To demonstrate the benefit of the Bayesian hierarchical approach, the analysis was repeated using linear regression for each site separately.

For the models used in this study, the underlying assumption was that the residuals of the models would be independent in time and so the residuals from the preferred model were tested for their normality (or log normality) and homoscedasticity. Normality, before or after transformation, was tested using the Anderson-Darling test (Anderson & Darling, 1952); the presence of homoscedasticity or heteroscedasticity was tested by plotting the residuals against the fitted values and by use of the Breusch-Pagan test (Breusch & Pagan, 1979); and tested for autocorrelation within the residuals using the Durbin-Watson statistic (Durbin & Watson, 1950). The importance of the Depth in explaining the variation in explaining was assessed using eta-squared (η^2).

3 | RESULTS

In total, 348 peat samples were analysed from 13 locations and 22 cores. Compositional data was collected on 424 samples and the data are summarized in Tables 2 and 3, with all data in Tables S1 & S2.

Soil Use and Management

TABLE 2 Summary of the peat soil compositional data for this study. The values in brackets are the 95th percentile range, i.e., 2.5th to 97.5th percentile range.

Location	*N*	Dry bulk density (g/cm^3)	Composition (weight %) C	H	N	O	C_{ox}	Ω
Forsinard	36	0.06 (0.02–0.08)	51.1 (46.0–65.1)	6.23 (5.92–7.78)	1.68 (1.38–2.11)	32.7 (31.2–37.1)	−0.40 (−0.60 to −0.26)	2.22 (1.72–2.68)
Auchencorth	27	0.14 (0.06–0.54)	40.3 (24.0–52.0)	5.17 (4.91–5.35)	1.54 (0.93–2.20)	24.6 (15.1–38.3)	−0.31 (−0.55 to 0.21)	1.97 (1.57–2.73)
Thorne Moors	34	0.06 (0.03–0.09)	51.9 (39.3–57.1)	4.63 (2.19–6.23)	0.98 (0.70–1.56)	33.6 (20.4–37.0)	−0.20 (−0.5 to 0.56)	2.83 (2.21–3.99)
Hatfield Moors	20	0.11 (0.09–0.14)	48.48 (47.1–50.6)	5.22 (5.1–5.58)	0.70 (0.56–0.84)	33.0 (31.0–34.2)	−0.23 (−0.32 to −0.2)	2.46 (2.35–2.58)
Doctor's Gate (Peak District)	39	0.08 (0.04–0.12)	50.8 (47.2–53.0)	5.55 (3.91–6.61)	0.98 (0.84–1.83)	35.4 (29.5–39.4)	−0.19 (−0.51 to 0.11)	2.37 (1.89–3.45)
Featherbed (Peak District)	11	0.06 (0.09–0.26)	50.2 (48.9–51.2)	5.26 (2.31–5.46)	0.98 (0.88–1.23)	29.6 (28.4–29.8)	−0.32 (−0.39 to 0.38)	2.68 (2.45–4.10)
Whixhall Moss	35	0.06 (0.03–0.09)	50.0 (44.6–52.2)	5.74 (5.45–6.31)	0.98 (0.54–1.46)	37.1 (34.2–41.3)	−0.22 (−0.37 to −0.10)	2.33 (1.65–2.49)
Westhay Moor	26	0.08 (0.02–0.12)	48.4 (42.6–50.1)	5.10 (4.15–5.86)	0.77 (0.28–1.12)	34.8 (0–37.3)	−0.12 (−1.36 to 0.05)	2.41 (2.13–2.93)
Dartmoor	35	0.09 (0.04–0.16)	57.6 (43.7–60.2)	5.91 (5.72–6.37)	1.12 (0.82–2.26)	31.0 (26.6–35.3)	−0.40 (−0.48 to −0.31)	2.87 (1.75–3.11)
Bodmin	21	0.10 (0.04–0.13)	50.9 (40.1–54.8)	5.84 (4.70–6.00)	1.54 (1.05–2.03)	27.7 (21.0–37.5)	−0.45 (−0.57 to −0.23)	2.42 (1.78–2.71)
Moor House	44	0.17 (0.10–0.27)	50.3 (46.8–53.1)	5.95 (5.7–6.26)	1.26 (0.98–1.96)	37.1 (34.6–41.1)	−0.25 (−0.32 to −0.13)	2.28 (1.98–2.50)
Chat Moss	9	0.31 (0.15–0.63)	28.9 (22.1–51.2)	3.96 (2.54–5.92)	0.84 (0.62–0.98)	25.1 (18.0–35.9)	−0.24 (−0.35 to −0.01)	1.64 (1.47–2.42)
Cors Erddreiniog (Anglesey)	11	0.11 (0.09–0.13)	43.0 (38.0–46.4)	5.17 (4.91–5.35)	2.8 (2.41–3.32)	36.3 (31.0–37.2)	0.01 (−0.18 to 0.05)	2.10 (1.79–2.31)
All peat	348	0.09 (0.03–0.28)	50.2 (27.9–58.7)	5.76 (2.80–6.59)	1.12 (0.56–2.56)	33.9 (18.4–39.7)	−0.27 (−0.55 to 0.20)	1.36 (0.66–2.44)

TABLE 3 Summary of the litter, biomass and standards compositional data for this study. The values in brackets are the 95th percentile range, i.e., 2.5th to 97.5th percentile range.

Litter/biomass	%C	%H	%N	%O	C_{ox}	Ω
Litter	47.7 (46.3–50.6)	6.4 (5.7–6.7)	1.6 (1.1–2.7)	39.8 (38.8–41.5)	−0.3 (−0.4 to −0.0)	1.9 (1.6–2.5)
Aboveground biomass	44.6 (34.9–51.9)	6.2 (5.2–6.9)	1.4 (0.7–3.2)	43.2 (36.3–52.5)	−0.1 (−0.5 to 0.3)	1.7 (1.1–2.1)
Standards						
Lignin	61.6	6.0	0.8	29.0	−0.4	3.2
Cellulose	43.1	6.3	0	51.4	0.05	1.5
Plant protein	46.6	6.8	13.5	31.2	0.02	2.0

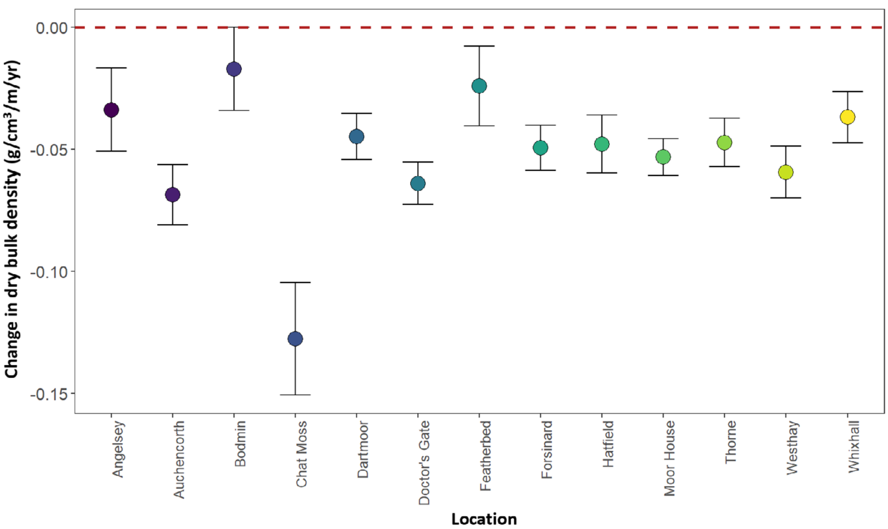

FIGURE 2 The down profile change in dry bulk density at each study location. The values are the mean estimate and the error bars are the 95th confidence interval.

3.1 | Dry bulk density

Fitting the depth profile of the bulk density shows that for 12 out of the 13 locations there was a significant linear change in bulk density (Figure 2 – with all profiles given in Appendix S1). In these 12 cases, the change was a decrease in bulk density with depth; for the other case, there was no significant change at all. The average change in dry bulk density was −0.05 g/cm^3/m depth and for 10 of the locations, the change in dry bulk density with depth was not significant from each other.

When relative change in dry bulk density was assessed, then there was found to be no significant difference between the locations. Therefore, the average relative change in dry bulk density could be calculated across all locations, where the average relative change was a decrease of 67% with a range of 56%–76%. The depth factor explained 13% of the overall variance in the dataset and the general pattern of bulk density change shows a maximum density between 20 and 25 cm and a minimum between 75 and 80 cm (Figure 3). There was no significant relationship between dry bulk density and age.

Therefore, there is no evidence that dry bulk density increases with depth and this is independent of age and independent of peatland type.

3.2 | Radiocarbon ages

All sites showed a significant relationship between depth and age (Table 4), and the calculated C accumulation rates (LARCA) are shown in (Figure 4). For Equation (4) the relationship showed an $r^2 = .98$ with a slope = 0.97 ± 0.04, where the uncertainty is given as the 95% confidence interval, and the predicted vs. observed was not significantly different from 1. The Anderson-Darling test showed that the residuals of the Site+Depth model were not significantly different from normally distributed ($p < .001$). The Breusch-Pagan test showed that residuals of the Site+Depth model were homoscedastic at $p < .001$, and the Durbin-Watson statistic was used for autocorrelation in the residuals. Therefore, the Site+Depth model was sufficient to meet the assumptions of the likelihood function and the Bayesian hierarchical model has removed sufficient temporal structure in the dataset.

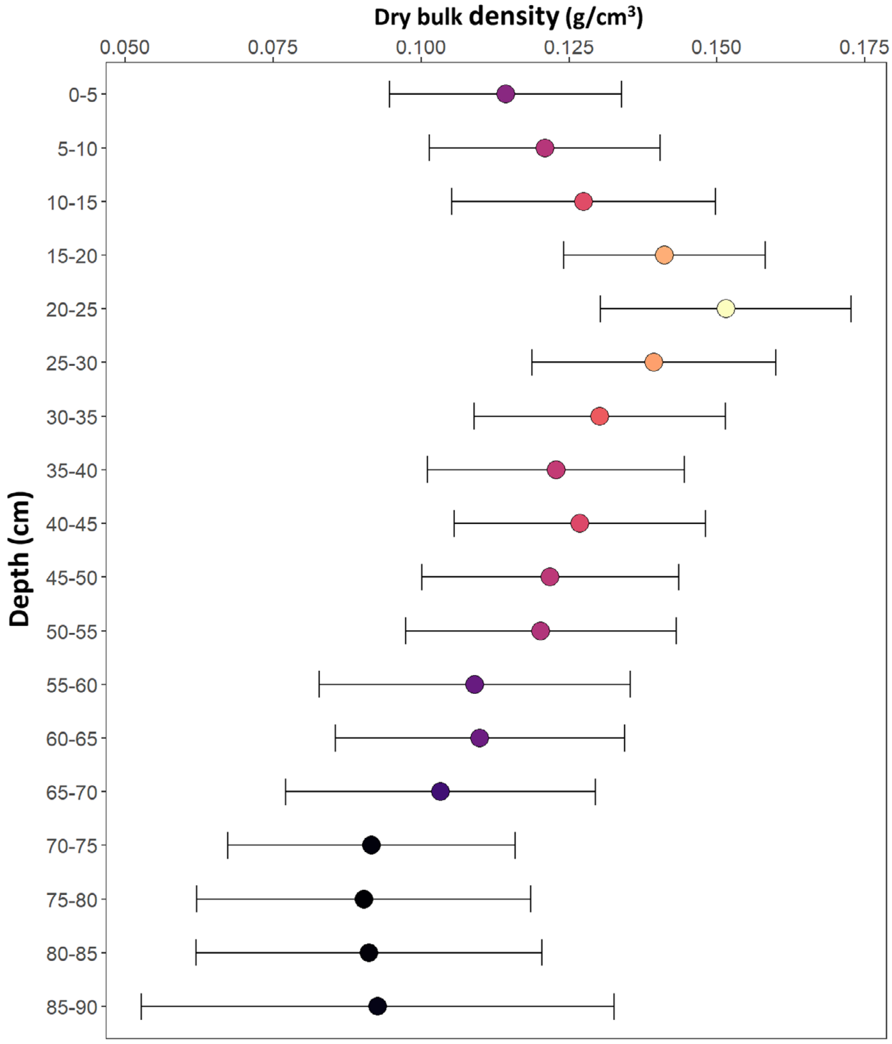

FIGURE 3 The main effects plot of dry bulk density for all locations. The values are the mean estimate and the error bars are the 95th confidence interval.

TABLE 4 Summary of radiocarbon analysis for the study locations. The values in brackets are the 95th percentile range, i.e., 2.5th to 97.5th percentile range.

Location	Date at 1 m depth (years BP)	Depth accumulation rate (cm/kyr)	C accumulation rate ($gC/m^2/yr$)
Auchencorth	2293	64 (9–22)	13.9 (12.0–15.8)
Bodmin	7575	8.0 (7.7–8.3)	4.0 (4.4–3.6)
Forsinard	2110	41 (37–47)	22.5 (21.1–24.0)
Moor House	1895	58 (49–72)	43.0 (41.0–45.1)
Doctor's Gate	1815	51 (43–62)	19.2 (17.4–21.0)
Thorne Moors	2749	48 (41–57)	15.8 (12.6–19.0)
Westhay	4406	24 (22–26)	6.0 (5.1–6.9)
Whixall	861	91 (71–128)	22.9 (19.8–26.1)

The ages at 1 m depth can be somewhat misleading as some of these sites are former cutover peatlands and so we might expect that surface layers are not modern. Modern ages were recorded for the surface peat layer (0–5 cm) at Moor House, Forsinard, Bodmin and Auchencorth. For Doctor's Gate, Whixall and Westhay the surface layer was several 100's of years old while at Thorne Moors the surface peat layer was 1038 years BP. The old surface ages are for the three former cutover peat sites and the modern surface ages are for those we would, a priori, identify as intact. The odd one out is Doctor's Gate (as it is not a cutover peat site) and this may mean that over recent decades (unresolvable by radiocarbon dating) the near-surface peat has been rapidly oxidizing, or it may be indicative of

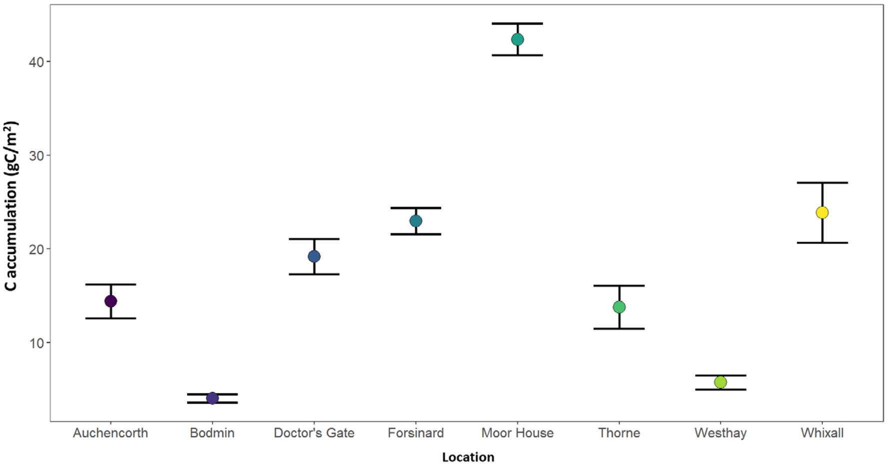

FIGURE 4 The long term carbon accumulation rate (LARCA) at the study locations. The values are the mean estimate and the error bars are the 95th confidence interval.

historic surface erosion perhaps associated with wildfire (e.g., Rothwell et al., 2007) and loss of sphagnum mosses due to legacies of atmospheric pollution.

Gallego-Sala et al. (2016) have reviewed the peat initiation time of blanket bogs (not lowland bogs) across the UK and showed that the current extent of UK blanket bog was in place by 6000 years BP. Included in the analysis of Gallego-Sala et al. (2016) are results for Featherbed Moss (Tallis, 1985, 1991; Tallis & Switsur, 1983). Taking only the radiocarbon data from Gallego-Sala et al. (2016) and only for sites with a depth of more than 50 cm (i.e., that could be classified unambiguously as peat) then the depth ranged from 50 to 990 cm and ranged in age from 973 to 11,310 years BP. The depth accumulation rate varied from 8 to 220 cm/kyr with a median of 25 cm/kyr, which is consistent with the values reported in this study (Table 4).

The long-term C accumulation rates measured for these locations can be compared with measured contemporary net ecosystem carbon balances (C budget). Worrall et al. (2012) published a contemporary C budget for Moor House and over 13 years the C budget ranged from 20 to −90 gC/m^2/yr. (where positive values indicate net carbon loss and negative values net carbon gain by the peat), i.e., the LARCA for this location is within the contemporary range. Billett et al. (2004) measured the C budget for Auchencorth and found it to be a net source of 8 gC/m^2/yr. Worrall et al. (2011) measured the C budget of Doctor's Gate at between 75 to 102 gC/m^2/yr.

When the non-Bayesian approach was used, 7 out of the 8 locations showed a significant change in C accumulation with Age; there was no significant relationship for Auchencorth. This comparison indicated significant differences between LARCA estimates made by the Bayesian and non-Bayesian methods and showed that Bayesian estimates were 9% lower than the frequentist, non-Bayesian method:

$$Acc_{freq} = 1.09 Accum_{Bayes} \quad r^2 = .96 \tag{8}$$

The average standardized 95% confidence interval for the Bayesian method was ±11.6% and for the non-Bayesian approach, the average standardized 95th confidence interval was ±53.6%. Even when results from Auchencorth were excluded the value for Bayesian method was ±18.6%.

3.3 | Degree of unsaturation (Ω)

Fitting the depth profile of Ω shows that for all 13 locations there was a significant linear change in Ω and all were an increase in Ω (Figure 5). The average change in Ω was 0.60 ± 0.09 π-bonds/m depth, where the uncertainty is given as the 95th confidence interval. However, there were significant differences in the rate of change with depth between the locations with the greatest change observed for Dartmoor and the lowest for Hatfield Moors.

The relative change in Ω was found to be positive in all cases and significantly different from zero. The relative change was assessed and there was found to be no significant difference between the locations. Therefore, the average relative change in Ω could be calculated across all locations, where the average relative change in Ω was an 87% increase.

The overall depth factor explained 20% of the overall variance in the dataset. The general pattern of the degree of unsaturation shows a minimum between 0 and 5 cm and a maximum between 85 and 90 cm (Figure 6).

Comparing the age of the samples to their Ω does show a significant relationship (Figure 7):

$$\underset{(0.04)}{\Omega = 1.04} + \underset{(0.00003)}{0.00017 \text{Age}} \quad n = 59, \quad r^2 = .35 \tag{9}$$

where the numbers in brackets below Equation (9) represent the standard error of the terms.

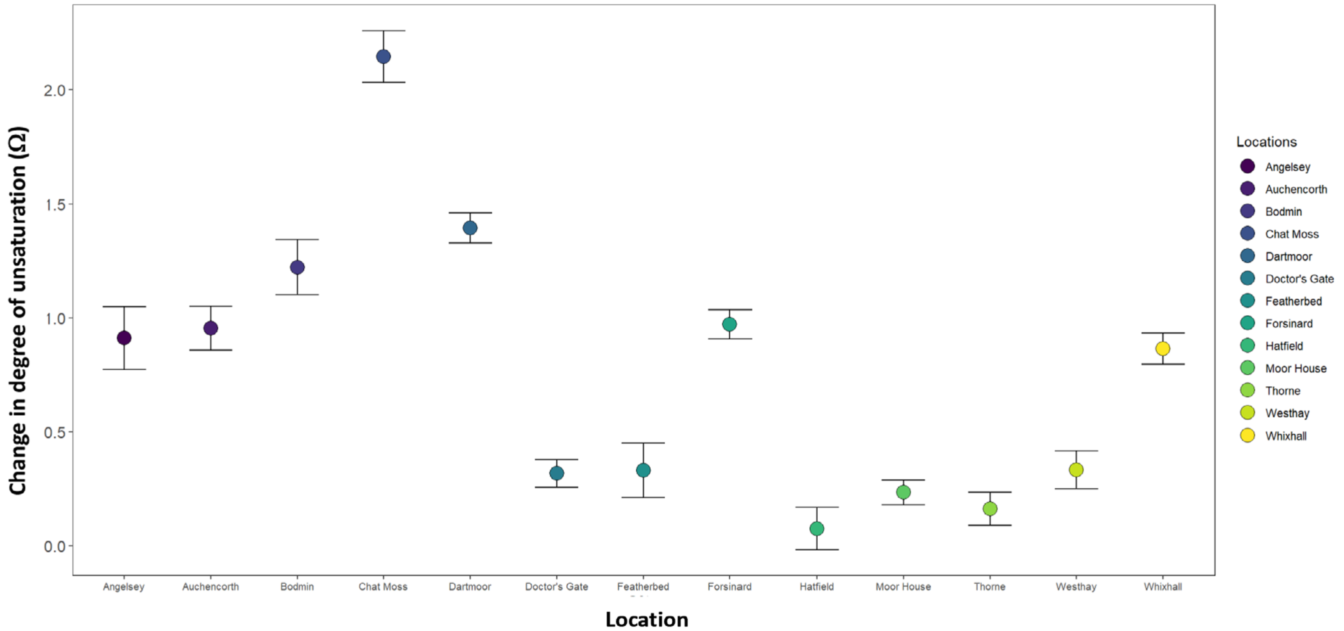

FIGURE 5 The down profile change in degree of unsaturation (Ω) at each study location. The values are the mean estimate and the error bars are the 95th confidence interval; therefore, if the error bars overlap with zero, then the change for that location is not significantly different from zero.

The equation and the data suggest that the peat evolves from a common start point of $\Omega=1.5$. In Figure 7 we have proposed two bounding trends to the data implying that profiles evolve as a mix of either rate. The higher rate, represented by the higher gradient bounding trend, is 1 π-bond/kyr, while the lower bounding trend represents 0.2 π-bond/kyr. In comparison with standard materials, the change with depth shows an evolution toward more lignin-like compositions and away from both protein and cellulose compositions. The biomacromolecular composition of plants is dominated by lignin, carbohydrates (cellulose and hemicellulose), proteins and lipids (McDermott & Loomis, 1981). The mean Ω of aboveground biomass was 1.7 (Table 3) and Figure 7 suggests that all measured compositions are evolving from the composition of average aboveground biomass. Therefore, the evolution of Ω with depth is consistent with the result of Worrall et al. (2017) that showed that peat evolution was marked by the almost complete removal of carbohydrates by 1 m depth in the peat profile.

3.4 | Oxidation state (C_{ox})

Fitting the depth profile of C_{ox} shows that for all 13 locations there was a significant linear change in C_{ox} (Figure 8). For 10 of the locations the significant trend is a decrease, while for three locations (Westhay, Doctor's Gate and Featherbed) there was a significant increase in C_{ox}. The change in C_{ox} was between −0.38 to 0.29/m.

The relative change in C_{ox} was not significant in three cases (Dartmoor, Forsinard and Hatfield) and three cases showed significant negative trends in the relative change (Anglesey, Thorne and Westhay). Depth as a factor was significant but explained only 2% of the variation in the original dataset (Figure 9). There was no significant relationship between C_{ox} and Age.

3.5 | Carbon:Nitrogen ratio

Change in C/N with depth was significant for all but two locations – there was no significant change at Hatfield or Auchencorth (Figure 10). Of the 11 locations that showed a significant change in C/N with depth, one showed a negative change with depth (Whixall), and 10 locations showed a significant positive trend, i.e., showed significant increase in C/N with depth in the peat profile. The relative change in C/N ratio follows the same pattern as the absolute change. The median change in the C/N ratio was an increase of 19.6 or a 62% increase over 1 m depth.

Depth as a factor was significant but explained only 19% of the variation in the original dataset (Figure 11). There was no significant relationship between C_{ox} and Age.

4 | DISCUSSION

The hypothesis of this study was that dry bulk density did not increase with depth as would be expected from

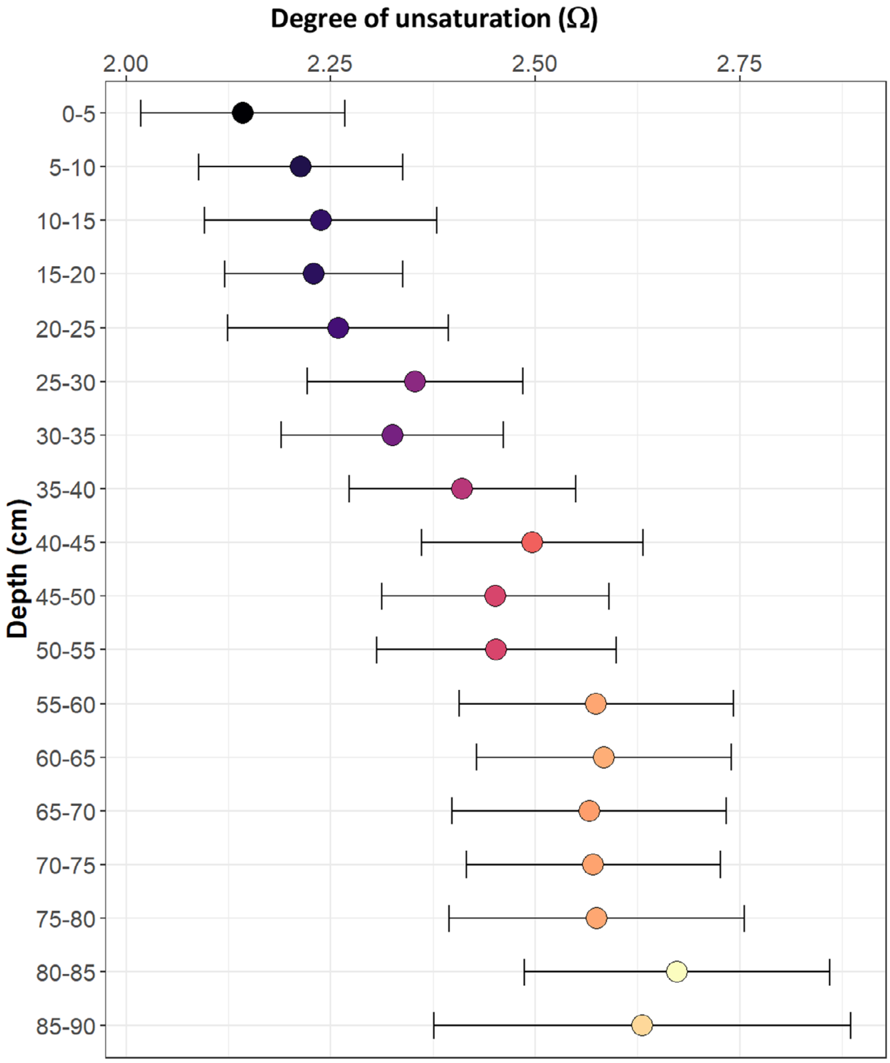

FIGURE 6 The main effects plot of the degree of unsaturation (Ω) for all locations. The values are the mean estimate and the error bars are the 95th confidence interval.

common theories of peat formation (eg. Clymo, 1984). Our hypothesis was not that dry bulk density would decrease at depth rather that there would not be a significant increase. We found no evidence of a statistically significant general pattern that the bulk density increases with depth in peat despite considering 13 distinct locations and 22 cores across a range of climatic and peat settings although all within the UK. In fact, at all locations the dry bulk density was observed to decrease with depth and the common pattern was a maximum at shallow depth (20–25 cm) and minimum at 70–75 cm. There was a consistent change in Ω and no consistent change in C_{ox}.

How can we explain the observed density profiles? Despite a range of studies from across the globe that have shown that dry bulk density declines down profile (Clay & Worrall, 2015; Frogbrook et al., 2009; Hooijer et al., 2012; Howson et al., 2023; Könönen et al., 2015; Parry & Charman, 2013; Shotbolt et al., 1998; Sinclair et al., 2020; Tallis, 1985) none of them offered an explanation for decreasing dry bulk density they had observed in their studies: but in none was change in bulk density with depth the aim of their respective studies. Parry and Charman (2013) did show a relationship between bulk density and depth in the peat profile:

$$BD = 0.162 - 0.000214d \quad \left(r^2 = .70\right) \tag{10}$$

where BD = dry bulk density (g/cm^3); and d = depth (cm). Equation (10) would suggest an average change of 0.02 g/cm^3 over 1 m of depth which is a 13% change relative to surface values, i.e., a smaller magnitude change than observed in this study which was 67%. The published observations cited and the results of this study do not match the model of Clymo (1992), by what mechanism then can peat bulk density decrease with depth?

In soils it is possible to have compaction concentrated into a layer leading to a mid-profile maximum in the bulk density, and this generally occurs due to vehicles loading on the surface or due to compositional changes such as a clay layer occurring over a sand layer. For the soils in this study, cutover peats will have been worked over by vehicles, and most blanket bog soils in this country are grazed

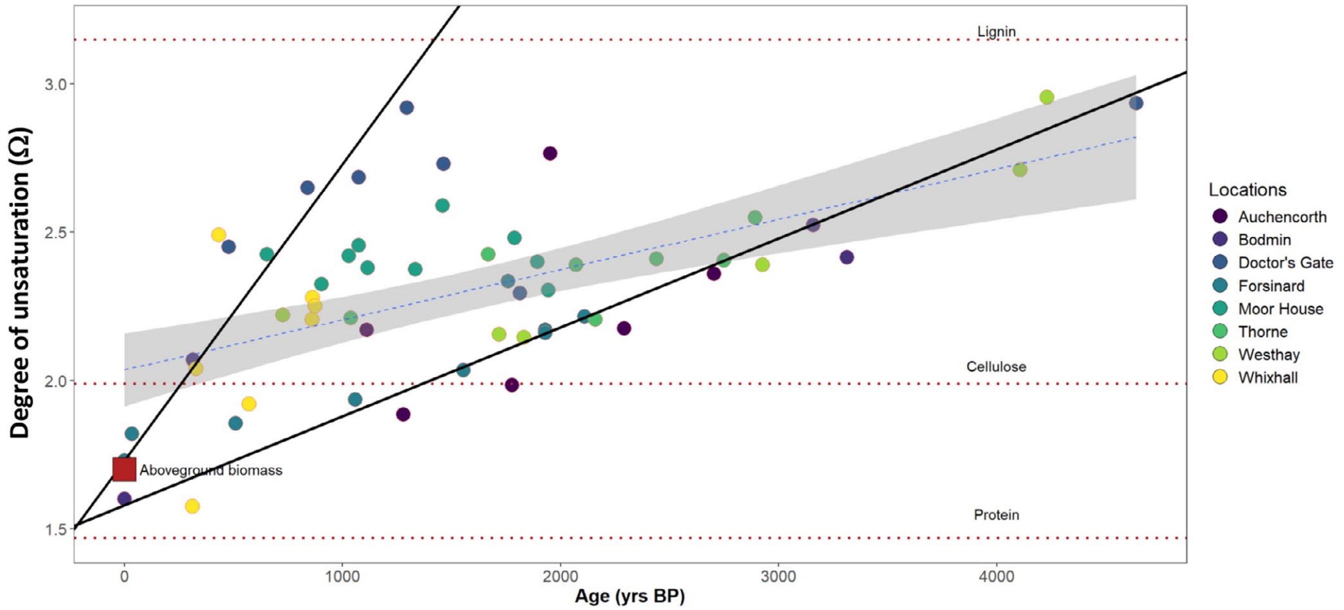

FIGURE 7 The comparison of degree of unsaturation (Ω) and radiocarbon age with the composition of lignin, plant protein and cellulose (…., red dotted lines); the proposed bonding trends (_, thick black lines); the composition of aboveground biomass (■); and the best-fit straight line (---, blue dashed line). The shaded area is standard error on the best-fit straight line.

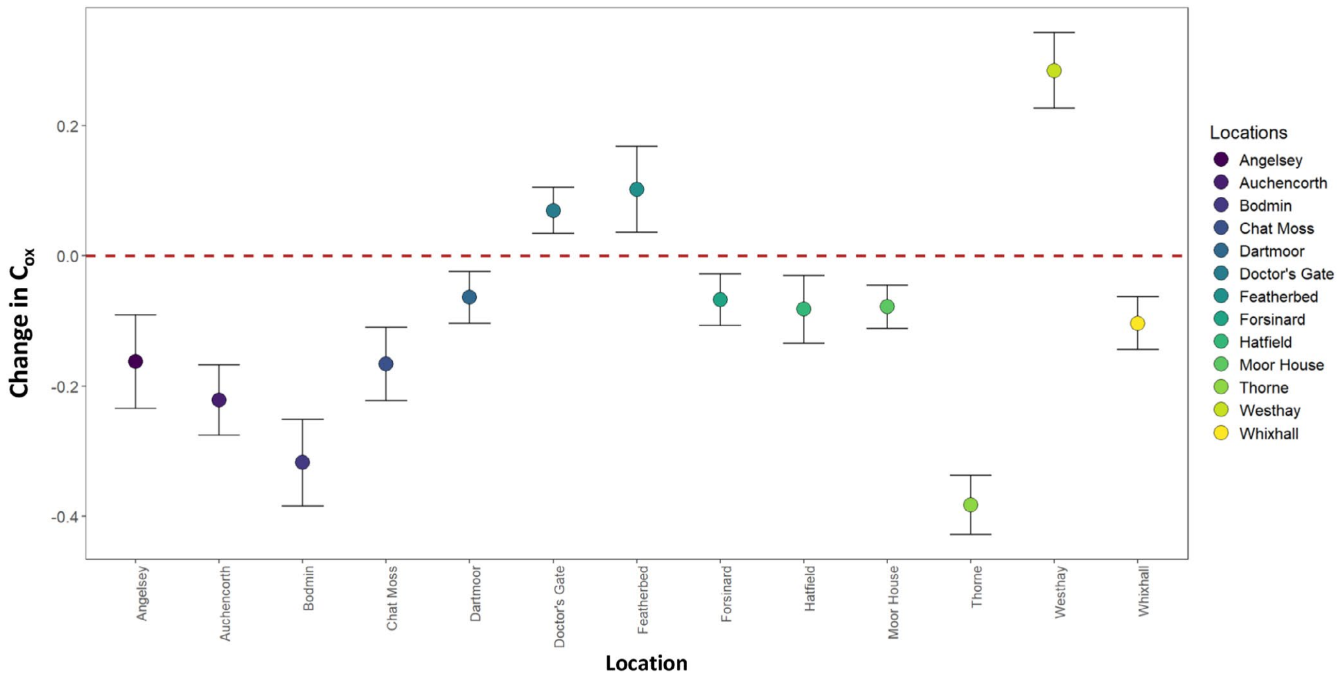

FIGURE 8 The down profile change in C_{ox} at each study location. The values are the mean estimate and the error bars are the 95th confidence interval; therefore, if the error bars overlap with zero then the change for that location s not significantly different from zero.

and so therefore will have been trampled by animals (Clay & Worrall, 2013).

Könonen et al. (2015) in their study of tropical peatlands, ascribed their observed decreases in bulk density in the peat soil with depth to the presence of wood debris in the surface layers. None of the peatlands in this study are currently wooded and, there was no visual evidence that these peatlands were forested within the last several hundred years. While upland blankets in the UK such as at Moor House are above tree lines, the lowland bogs included in this study (e.g., Hatfield Moors) are not. A range of studies have reported bulk density increase upon drainage of soils (e.g., Liu et al., 2020) and so if damage to peatland was limited to surface layers rather than propagating through to depths of 1 m then this would cause the bulk density profile to be reversed.

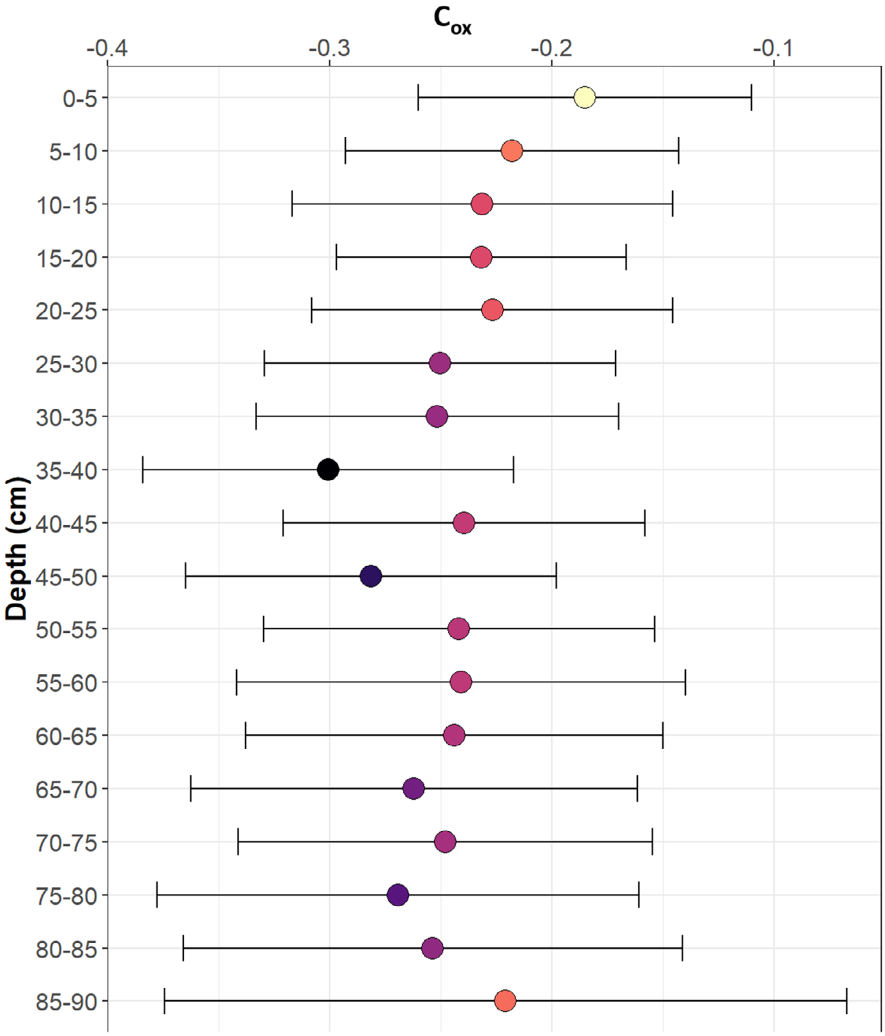

FIGURE 9 The main effects plot of the C_{ox} with depth for all locations. The values are the mean estimate and the error bars are the 95th confidence interval.

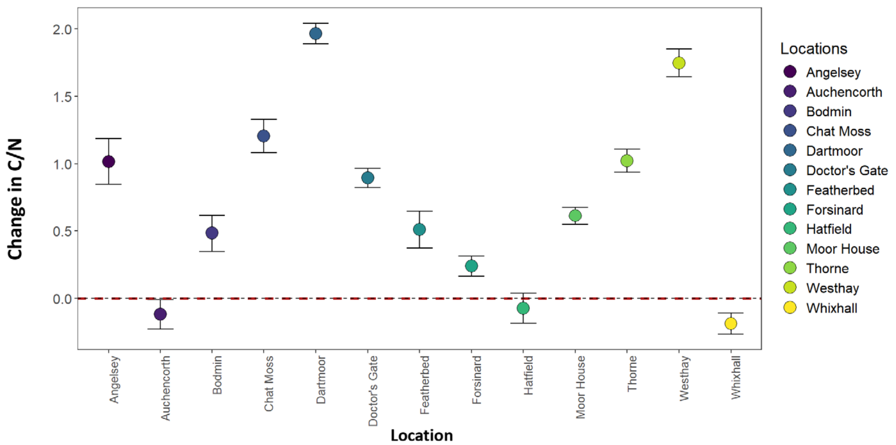

FIGURE 10 The down profile change in C/N at each study location. The values are the mean estimate and the error bars are the 95th confidence interval.

The effect observed could be due to a methodological limitation. When taking peat cores with gouge augers, the most likely sections to be damaged or incompletely extracted in the process are the very top and very bottom sections. However, the result of this study would not change if the top and bottom sections were excluded from the analysis.

Is the result due to something peculiar about UK peatlands? The profiles in bulk density were taken from a range of sites both in blanket and raised bog settings and the same pattern was observed for both. The locations were deliberately taken across the climate gradient in the UK from south to north and east to west. The radiocarbon evidence suggests that a number of locations

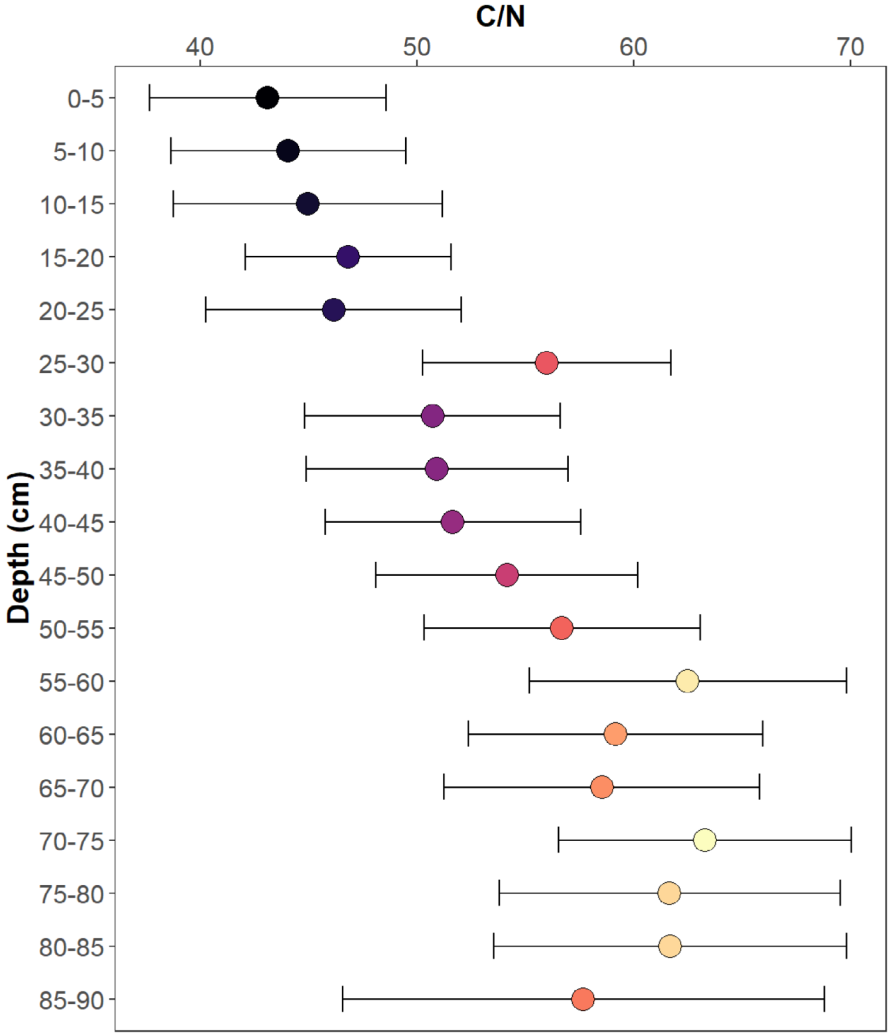

FIGURE 11 The main effects plot of the C/N with depth for all locations. The values are the mean estimate and the error bars are the 95th confidence interval.

were active sinks and some were not, i.e., a mixture of sink/source status was included. However, the majority of the raised bog sites were formerly cutover raised bog (e.g., Thorne Moors) and not intact. The previous studies that have shown increases in bulk density may have concentrated on intact raised bogs (e.g. Sinclair et al., 2020), and so therefore the pattern seen in this study may result from the greater level of anthropogenic disturbance found in such a densely populated country as the UK where peatlands, if they have not been directly used (as in forestry, agriculture or for peat extraction), have been heavily impacted by proximity to human activity and habitation through visitor pressure and atmospheric deposition. A common pattern in the bulk density profiles of UK peatlands may simply be due to the fact that all UK peatlands are damaged and that we should expect none to follow the ideal models such as that of Clymo (1992).

So how can we explain the general density profile observed? We propose that the bulk density profile is the result of competing processes. Fresh material is subject to decomposition and self-weight compaction in the surface layers, and this does result in increasing density with depth in the surface layers: in the case of this study that would be the top 25 cm (Figure 3). However, decomposition over time is more likely for some components of organic matter than others and that different components of the organic matter are more-or-less susceptible to compaction. As differential decomposition occurs, then density changes down profile reflect the progression of decomposition and preferential removal of organic matter components of differential compressibility. Several studies have shown that peat shows preferential decay of polysaccharides (Biester et al., 2014; Leifeld et al., 2012; Pipes & Yavitt, 2022; Santelmann, 1992; Worrall et al., 2017). Worrall et al. (2017) have shown that with preferential removal of carbohydrates then lignin-like components preferentially persist. Figure 7 supports the interpretation of the preferential survival of lignin-like components with depth in the peat profile. If plant carbohydrates are more compressible than lignin components, then loss of carbohydrates could result in increased porosity.

However, the density profiles observed in this study are independent of the radiocarbon age and similar density profiles (Figure 3) were observed despite some of the peats being former cutover raised bogs with surface layers being 100's of years old. Therefore, the peat density profile appears not to be related to processes happening over time but to respect the current conditions of the peatland. Therefore, the alternative explanation of the peat density profile is that it relates to current conditions common to all peatlands, for example, water table fluctuations. If there is an optimal moisture content for decomposition of organic matter, then maximum decomposition will occur at the position relative to the long-term water table. Furthermore, fluctuating water table will bring in water with fresh supply of terminal electron acceptors and flush the porewaters taking away reaction products. Beer and Blodau (2007) identified that closure of pore waters, not only with respect to oxygen, is the cause of organic matter preservation in peats. The zone of maximum water table fluctuation would be the zone of maximum decomposition and so the zone with the greatest potential for porosity loss. Whereas in areas of stable, stagnant porewater, decomposition virtually ceases and bulk density change could only occur by self-weight compaction in the absence of decomposition. The presence of drainage has been shown to cause subsidence and density increase in the surface layers of peat and thus causing decrease in density of bulk density down the peat profile (Hooijer et al., 2012): many UK peats have experienced periods of drainage.

Alternatively, or additionally, Reynolds et al. (1992) proposed that gas bubbles in peat pore spaces could alter the hydraulic conductivity of peat soils. Baird and Waldron (2003) were able to show that gas bubbles do limit the horizontal hydraulic conductivity in peat soils, and Kellner et al. (2005) found that up to 15% of the porosity below the water table in a peat was gas-filled. The presence of gas bubbles in the peat acts to maintain porosity but still acts to limit hydraulic conductivity – so the presence of gas bubbles at depth in the peat acts to decouple porosity from hydraulic conductivity. In the theory of peat formation, it is hydraulic conductivity that is critical and the link to porosity has been assumed. Anshari et al. (2022) followed subsidence for sites in drained tropical peatlands over 4 years and although they do not explicitly consider change in bulk density with depth they do note that even with ongoing subsidence in these drained peats the bulk density profile appears to move with subsidence, and therefore, is reflecting the current context of the peat. The observations of Anshari et al. (2022) parallel those found in this study, i.e., that density profiles mimic current conditions. As noted above, if damage to peatlands in the recent past has impacts dominantly in the near surface layers, then profiles of declining bulk density with depth could result.

Changes in bulk density have been associated with the diplotelmic structure of peat profiles (Clymo, 1978, 1992) – the acrotelm (thin, upper layer) and the catotelm (thick, underlying layer). However, in most studies the layer structure is defined by the position of the long-term water table and not the bulk density (Ingram, 1978; Ivanov, 1948, 1981). The acrotelm being defined as the region of fluctuating water table and is often described as oxic or at least seasonally oxic (Clymo, 1978); however, oxygen may not be the dominant oxidizing agent and alternative electron acceptors are known to be used and consumed in the acrotelm (Boothroyd et al., 2021; Worrall et al., 2012). The catotelm being the region of the profile that is permanently saturated. Therefore, the diplotelmic model of peat formation does not require an increase in bulk density with depth.

5 | CONCLUSIONS

This study tested models of peat formation that require bulk density to increase with depth. Examining the peat profile of 22 cores across 13 locations across the UK, we tested changing density with depth in the peat profile in comparison to radiocarbon age and organic matter composition. The study found that:

1. All locations showed significant decreases in dry bulk density with depth in the peat profile, no matter whether the profiles were assessed in absolute or relative terms and regardless of the type of peat ecosystem and its known history of use.
2. The degree of unsaturation (Ω) showed significant down profile increase in all locations. The change of Ω with depth and time is consistent with evolution of organic matter away from bulk plant biomass to more lignin-like compositions.
3. The oxidation state of the organic carbon (C_{ox}) showed no consistent pattern of change with depth.

We provide four alternatives, although not necessarily competing, concepts of how peat profiles may evolve and how this is reflected in: (i) differential rates of organic matter components; (ii) the water table history and fluctuation; (iii) the presence of gas bubbles at depth; and (iv) consequences of contemporary damage being concentrated in to surface peat layers and not propagating to depth. Ultimately, the presence of a common peat density profile that does not match standard models across such a diversity of locations may reflect the widespread damage of UK peatlands.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the Appendix S1 of this article.

ORCID

Fred Worrall https://orcid.org/0000-0002-4139-1330

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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