



Comparison of the transformation of organic matter flux through a raised bog and a blanket bog

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Abstract This study has proposed that organic matter transfer and transformation into and through a peatland is dominated by preferential loss of carbohydrates and the retention of lignin-like molecules. Here we used elemental analysis and thermogravimetric analysis to analyse the biomass, litter, peat soil profile, particulate organic matter, and dissolved organic matter fluxes sampled from a continental raised bog in comparison a maritime blanket bog. The macromolecular composition and thermodynamic analysis showed that in the raised bog there had been little or no transformation of the organic matter and the accumulation was rapid with comparatively little

transformation with only 13% loss of cellulose by 1 m depth compared to 92% removal of cellulosic material in the blanket bog. The lack of transformation is reflected in a difference in long term carbon accumulation rates between raised and blanket bog sites. We propose that raised bogs, with their lack of a stream outfall, have high stable water tables that mean the pore water become thermodynamically closed and reactions cease higher in the peat profile than in a blanket bog where sloping sites mean a frequent flushing of pore water and discharge of water leading to fluctuating water tables, flushing of reaction products and pore spaces remaining open.

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Introduction

Within the terrestrial biosphere, the northern peatlands are the most important terrestrial carbon (C) store. Although covering only ~3% of the land area of the Earth (Rydin and Jeglum 2013), peatlands store large quantities of carbon. Estimates vary (see reviews of Yu 2012; Loisel et al. 2017 for further discussion), but it is estimated that 500 ± 100 GtC is stored in northern peatlands (Gorham 1991; Yu et al. 2014; Loisel et al. 2014). The amount of C stored in northern peatlands is equivalent to the total terrestrial

vegetation (Stocker et al. 2013), or the cumulative anthropogenic carbon dioxide (CO_2) emissions from fossil fuels, industry and land use change activities for the period 1870–2015 (Le Quéré et al. 2016). Knowledge about the fate of these large carbon stores—due to climate change or drainage or other human activities is imperative. Some substances are preferably decomposed, and others are more recalcitrant. Facing these pressures and given the very high C density of these soils, it is imperative to know about the chemical composition of the peat, the biological components that make up the C store, their potential and actual transformations, and the pathways of carbon cycling.

The very existence of peatlands depends upon there having been, at least for some point in the past, a net accumulation of organic matter, and therefore, the estimation of C budgets of peatlands has been a common research target. An initial approach to estimate C budgets for peatlands was to measure the long-term accumulation rate (LARCA) by dating of the peat profile (e.g. Turetsky et al. 2004). However, this approach must assume accumulation and cannot account for short periods of net loss, nor can it estimate the species of carbon that are lost, i.e. loss of carbon by CO_2 has quite distinct consequences from loss via methane (CH_4). It is vital to know the species of carbon that are being lost, because carbon from a peatland can be lost to the atmosphere as CO_2 or CH_4 and the latter is a more powerful greenhouse gas (Houghton et al. 1995). Further, C from peatlands can be released into water as dissolved (e.g. dissolved organic carbon [DOC]) or particulate forms (particulate organic carbon [POC]). An alternative approach to the estimation of long-term accumulation rates is to measure the contemporary carbon budget as the sum of the fluxes of all carbon species flowing in and out of a peat ecosystem: complete contemporary peatland C budgets are now common (e.g. Worrall et al. 2003; Billett et al. 2004; Roulet et al. 2007; Nilsson et al. 2008).

The approach based on contemporary fluxes does consider the species and forms of carbon entering or leaving a peat ecosystem and, for example this can consider the difference between individual gaseous forms (CO_2 or CH_4). However, within published contemporary C budgets certain carbon flux pathways and species are still considered in no more detail than as lumped terms such as DOC or POC. The

composition of DOC or POC is not considered. For example, primary productivity is viewed as sequestering CO_2 from the atmosphere but, of course, photosynthesis sequesters CO_2 as glucose which is in turn transformed through metabolic cycles, combined with nutrients, and plant components (e.g. lignin, carbohydrates, proteins, and lipids) synthesized (McDermitt and Loomis 1981). It is this organic matter that is subsequently transformed back to CO_2 through root respiration, falls as litter, or is released as plant exudates into the soil pores. It is the litter, or exudates, that then transform to soil organic matter and this transformation may result in the release of CO_2 , CH_4 , DOC or POC. Contemporary carbon budgets have advanced our understanding of processes and drivers, and quantified gaseous, particulate, and dissolved fluxes. However, budgets have rarely considered the form in which carbon transfers through a peatland and is then stored or released.

The composition of organic macromolecules present in peatland ecosystems (e.g. carbohydrates) has been studied by a number of approaches: colorimetric methods from UV/vis spectroscopy (e.g. Blackford and Chambers 1993); coal petrology techniques including rock-eval (e.g. Carrie et al. 2012); elemental ratios (e.g. C/N—Kuhry and Vitt 1996); stable isotopes (e.g. Jones et al. 2010); Fourier transform infra-red spectroscopy (FTIR, e.g. Artz et al. 2008); and pyrolysis gas chromatography mass spectrometry (Py GC–MS, e.g. Buurman et al. 2006). These approaches have commonly been focused upon characterisation of peat profiles for the purpose of understanding humification (e.g. Zaccone et al. 2008) or palaeo-historic reconstructions (e.g. McClymont et al. 2011). However, none of the above techniques were used in the context of a carbon budget or used to interpret observed carbon budgets. In their comprehensive review of the evolution of the methods to determine the degree of humification in peat, Zaccone et al. (2018) point out that these different humification indices don't describe the same parameters—there is no “silver bullet”.

Worrall et al. (2017) used thermogravimetric analysis (TGA) to analyse the organic matter reservoirs and fluxes of an Atlantic blanket bog in northern England in the context of known C budget. The peat ecosystem was shown to preferentially remove polysaccharides (e.g. cellulose) and preferentially preserve lignin. The composition lost from the peat via all

pathways was between 92 and 95% polysaccharide-C and up to 8% lignin-C. The POC and DOC lost via fluvial flux were both dominantly formed from lignin C—89 and 81% respectively. The view that peatlands remove polysaccharide and preserve lignin C was supported by Moody et al. (2018) who used solid state ^{13}C -NMR spectra to show changes in organic matter into and through the same peatland as studied by Worrall et al. (2017) and by Leifeld et al. (2012), who noted peat respiration to be closely related to the O-alkyl concentration in peat -the O-alkyl-peak at 72 ppm in NMR spectroscopy is characteristic for polysaccharides (Kögel-Knabner 1997). The approach of Worrall et al. (2017) implies that organic matter transformation ceases down the profile and this was confirmed for the same study site by Worrall et al. (2018) who showed that there was no change in a key thermodynamic property (Gibbs free energy of formation— ΔG_f) of the organic matter down profile. The thermodynamic limitation of organic matter transformation was also proposed by Beer and Blodau (2007) who showed that the pore water reactions in a peat profile were thermodynamically closed and by Boye et al. (2017), who note thermodynamic limitation of C cycling in floodplains. However, this model of how peatlands process organic matter has not been tested in any other peatland.

Bog formation may differ in different climatic situations. In the Pennines of Northern England, a maritime, rainy and cool climate favours peat accumulation covering the entire landscape, forming blanket bogs. In this region -and notably, in Moor House (MH) (an Atlantic blanket bog) our understanding of peatland development was coined. As early as 1965, Clymo (1965) examined *Sphagnum papillosum*, *acutifolium* and *cuspidatum* at MH and at lower elevations and noted an annual decay rate of 2.5–5%. A generation later, Latter et al. (1998), noticed that, after 8–10 years, *Calluna* shoots and *Eriophorum vaginatum* leaves in litter bags, but not *Calluna* stems, had reached an asymptote, no longer losing weight. Notably, *Sphagnum* was not a part of the experiment by Latter et al. (1998). In more continental climates, cold winters with long periods of snow cover and high summertime rainfall despite warm conditions and occasional dry spells also allow the formation of peat bogs. Such bogs tend to develop the characteristic lenticular cross-section; thus they are called “raised” bogs. As they cover the entire landscape, irrespective

of relief, blanket bogs have no such “raised” morphology. Recently, a carbon budget (Drollinger et al. 2019b) and information on peat properties (Drollinger et al. 2019a, 2020; Knierzinger et al. 2020) have been published from Pürgschachen Moor (PG), a sub-continental ombrotrophic bog in the Austrian Alps. The presence of bogs in contrasting settings means it is possible to test the results of Worrall et al. (2017) and Moody et al. (2018) and to assess whether a general model of organic matter transformation through peatlands can be constructed.

Therefore, the aim of this paper was to test in a peatland of distinct origin and climatic setting the models of organic matter processing and accumulation previously demonstrated for an Atlantic blanket bog, specifically, the following hypotheses:

- That peatlands favour the accumulation of lignin-like organic matter and preferentially lose polysaccharides.
- The organic matter accumulation is controlled by thermodynamic limitation of decomposition of recently deposited organic matter.

By comparing a previously studied blanket bog with processes in a continental raised bog it is possible to test these hypotheses between peatlands where, a priori, the rates of degradation then accumulation would be expected to differ markedly.

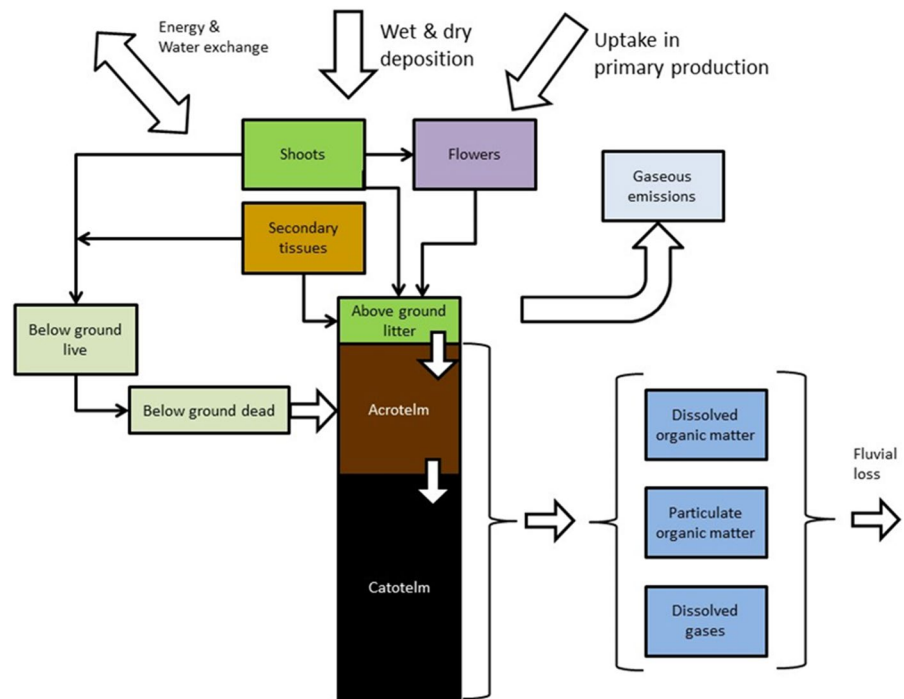
Approach and methodology

The approach taken here was to analyse the composition of the organic matter in a series of carbon pools within the context of a known carbon budget (Fig. 1) and to test hypotheses of organic matter transfer and storage developed at one site (MH) at a second site (PG). The composition of the samples was analysed using thermogravimetry (TGA), bomb calorimetry, and elemental analysis (for C, H, N and O) as a means of calculating oxidation state, thermodynamic properties and macromolecular composition.

Study site

The results from PG were compared to data collected from the site studied by Worrall et al. (2017) and Moody et al. (2018)—MH. MH catchment is

Fig. 1 Schematic diagram of organic matter pools and fluxes considered by this study



an 11.4 km² blanket peat catchment in the headwater of the River Tees (N 54° 41' 18" W 2° 22' 45"). The recent climate of the site has been summarised by Holden and Rose (2011): between 1991 and 2006 the mean annual temperature was 5.8 °C; air frosts were recorded on 99 days in a year; and the mean number of days with snow cover was 41 while the for the same period the mean annual precipitation was 2012 mm. The vegetation is dominated by *Eriophorum sp.* (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum sp.* (moss).

PG is located at N 47° 34' 53" and E 14° 25' 2" in the Enns valley, in a large fault line that separates the Central Alps to the south from the Northern Calcareous Alps in the north (Keil and Neubauer 2009). The long term mean annual temperature in the adjacent town of Admont is 7.3 °C and the annual mean precipitation is 1248 mm (1985–2016, ZAMG 2018), which corresponds well to the average precipitation of 1250 mm recorded in 1990 and 2019 (Drollinger et al. 2019b). The average period of snow cover is 85 days in a year (1971–2017). PG is a raised bog with a present extent of 62 ha with a mean water table of 14 cm below the surface in the center of the bog. The vascular vegetation of the peat bog is comprised by a mosaic of *Pinus mugo* (dwarf pine), *Calluna*

vulgaris (heather), *Andromeda polifolia* and the graminoids *Eriophorum vaginatum* (cotton grass) and *Rhynchospora alba*. The most abundant bryophytes are *Sphagnum capillifolium* (48% coverage) and *Sphagnum magellanicum* (Drollinger et al. 2019b).

Sampling

Given the range of carbon pools and fluxes identified in Fig. 1, the following sampling was carried out. Firstly, the peat profile was sampled. Cores to 1 m depth were taken at three locations in active, deep peat within the PG. The three locations were chosen to be under three dominant plants within the vegetation zonation present at Pürgschachen—heather, dwarf pine and cotton grass. The peat core was sampled every 10 cm between 0 and 100 cm depth. Sampling from MH has been previously published and described (eg. Worrall et al. 2018). At MH, peat cores to 1 m depth in two locations were collected with a gouge auger. Peat core samples were dried at 105 °C overnight and checked for no further mass loss, and their bulk density measured prior to further processing.

Vegetation samples were collected from the site of the peat cores—heather, dwarf pine and cotton grass.

For the heather and dwarf pine whole aboveground biomass samples were taken as well as samples of leaves. Furthermore, samples of live *Sphagnum* moss from underneath the heather was also sampled. At MH, six quadrats were randomly located across the peat-covered catchment. The entire above-ground biomass was recovered from three quadrats while in the other three the dominant plant functional groups: shrubs (dominantly *Calluna vulgaris*, henceforward referred to as *Calluna*); grasses and sedges (dominantly *Eriophorum* sp., henceforward referred to as grass/sedge); and mosses (including *Sphagnum* spp., henceforward referred to as mosses). All vegetation samples were dried overnight to 105 °C. The dried samples were then homogenised and powdered as described below.

The PG raised bog has no stream leaving the bog and so dissolved organic matter (DOM) samples were taken from peat porewater and from a lake just inside the boundary of the raised bog. At MH samples of DOM and particulate organic matter (POM) had only previously been sampled from a first-order stream and so for purposes of a fair comparison additional soil water sampling was undertaken. The sampling of peat porewater at MH has been described by Boothroyd et al. (2021). Both at PG and at MH large-volume water samples (approx. 25 L) were collected. On return of these samples to the laboratory, the samples were allowed to settle and the next day the water tapped off from above the sediment layer and evaporated to dryness (between 60 and 80 °C) to collect the total dissolved solids. By using settling as means of separation, no filtration cut-off was being applied; rather this study was defining DOM as being that component which was either colloidal or truly dissolved. The settled sediment layer was recovered, dried at 105 °C overnight and analysed as POM.

Finally, 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 (McDermitt and Loomis 1981).

It is advantageous to study organic matter transformations in peatlands and especially bogs. There, the fluxes and changes in chemical forms can be traced especially easily given the dominance of vertical

fluxes and the fact all organic matter in peat, POM and DOM must originate from plants growing on top of the peat column (Fig. 1). A sub-sample of the biomass, litter, peat, DOM and POM collected was ashed at 550 °C and the residual mass recorded. All subsequent analyses were corrected so that all elemental analyses are quoted on an ash-free basis.

Elemental analysis

Elemental analysis was used to measure the carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) content of the organic matter as means of calculating molecular properties and triplicates of all the collected samples (vegetation, litter, peat soil, and DOM) once dried to 105 °C, were then milled to a sub-mm powder using a Spex 6770 Freezer Mill. For the standard and samples of DOM cryomilling was not necessary. The ground samples were then subject to C, H, N and separately to O analysis on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler. For automation and calibration, the computer software used was EAS Clarity (Data-Apex Ltd, Prague, Czech Republic). For both C, H, N set up and the separate O set up, calibration curves of $r^2 > 0.999$ were 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 was analysed in triplicate i.e. three times on the C, H, N set up and a further three times on O set up, and a mean calculated for C, H, N and O. All samples were corrected for their measured ash content.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was used to measure the macromolecular composition of the organic matter (Lopez-Capel et al. 2005). Thermogravimetric (TGA) traces were measured for all samples as described in Worrall et al. (2017) and recorded on an SGA I TGH 1200. This analyser has the advantage that it is a high mass analyser and between 300 and 400 mg of organic matter and standard samples could be analysed at a time. The samples were run from ambient to 1000 °C at a ramp rate of 10 K/min within a stream of N₂.

The TGA traces were adjusted to be on a common temperature scale and trimmed to the range

150–700 °C so that any influence from inorganic carbon or absorbed water was excluded. Traces were then normalised to the mass loss between 150 and 700 °C so that all traces were then on the same scale, i.e. percentage of organic mass loss per K, given the assumption that it is only organic matter lost between 150 and 700 °C. There have been many indices given for TGA traces of soil organic matter with most focused on defining exothermic peaks, but as Plante et al. (2009) have shown, these definitions vary considerably between studies. More importantly with respect to this study, previous studies have focused on a single type of natural organic matter, i.e. soil organic matter, but this study sampled across the range of natural organic matter in a single environment (i.e. peat, DOM, biomass). Alternatively, Dell'Abate et al. (2002) interpreted their results as percentage mass losses summed into 50 K ranges (150–200 °C, 200–250 °C and so on to 650–700 °C), and in this manner a single trace of 550 data points is summarised into ten variables. In addition, the temperature of maximum mass loss was recorded for each trace.

Drollinger et al. (2019b) have published 2 years of C budget for the site and shown that between 88 and 97% of the carbon fixed GPP is preserved into the peat soil carbon. Knowing the C budget of the study sites means that the TGA traces can be weighted by magnitude of the fluxes. A lost composition could then be defined as the synthetic TGA trace that represents the difference between the TGA trace of the primary productivity and the budget weighted sum of the TGA traces of the resulting carbon reservoirs and fluxes. Note that CO₂ and CH₄ fluxes have no TGA trace but, where applicable, the TGA traces DOM, POM and deep peat. For the C budget of PG, see Drollinger et al. (2019b) and for MH, Worrall et al. (2012).

Bomb calorimetry

The gross heat value of the sampled organic matter was measured on a Parr 6200 bomb calorimeter. A sub-sample of known mass, typically 1 g, had its moisture content raised back to approximately 4% by weight before being combusted in the bomb calorimeter. The 4% moisture does not detract from the calorific value but does aid the combustion process in the bomb as it helps prevent sputtering of the

sample during the ignition process. The bomb calorimeter was calibrated and standardised on each run of samples using benzoic acid. For the samples of DOM for which <0.5 g of sample was available, the sample was doped with a known amount of a benzoic acid standard so that a complete combustion was achieved. For both soil and vegetation samples the calorific value was measured in at least triplicate and adjustment made for the measured ash content of the organic matter sample; in this manner the gross heat value as measured by the bomb calorimeter is equal to the heat of combustion of the substance (ΔH_c^{OM}).

Data analysis

The elemental analysis results were converted to molar percentage and considered as elemental ratios but also as measures of oxidation state (C_{ox} and oxidative ratio [OR], see Masiello et al. 2008) and the degree of unsaturation (Ω —McMurray 2004). The value of C_{ox} can be related to the nominal oxidation of the carbon (NOSC) as developed by LaRowe and Van Cappellen (2011).

$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} \quad (1)$$

where: [X]=molar concentration of C, H, N or O. The degree of unsaturation (Ω) is defined as:

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

The Gibbs free energy of formation (ΔG_f^{OM}) can be readily calculated from the difference between the enthalpy and entropy of formation of the same organic matter:

$$\Delta G_f^{OM} = \Delta H_f^{OM} - T\Delta S_f^{OM} \quad (3)$$

where: ΔG_f^{OM} =the Gibbs free energy of formation of organic matter (kJ/mol); ΔH_f^{OM} =the standard enthalpy of formation of organic matter (kJ/mol); ΔS_f^{OM} =the standard entropy of formation of organic matter (kJ/K/mol); and T=absolute temperature of the reaction (K).

The entropy of formation of the organic matter (ΔS_f^{OM}) was calculated from the elemental analysis based on the method of Vodyanitskii (2000) and as described by Worrall et al. (2018) and further details

are provided in the Supplementary Information. Bomb calorimetry was used to calculate the enthalpy of formation of the organic matter (ΔH_f^{OM}) in each of the pathways.

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. DOM samples received no chemical pre-treatment. Samples were then 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).

Statistical analysis

The down profile change in key metrics (C_{ox} , Ω and ΔG_f) were assessed using a two-way analysis of variance (ANOVA) where the two factors considered were depth in the profile with 20 levels, one for each of the depths sampled, and henceforward referred to as Depth. The second factor was the difference between the cores with three levels, one for each of the cores taken, and henceforward referred to as Core. The study design was sufficient to consider the interaction between the two factors. All factors and their interactions were assessed for significance at a 95% probability of being greater than zero ($p < 0.05$ of the difference being zero).

Principal component analysis (PCA) was used to analyse the TGA traces. When summarised into 50 K ranges the dataset can be treated as a multivariate dataset. PCA was also used to assess the differences between organic matter pools and fluxes on the basis of thermal decomposition. Included in this analysis

were traces for standards. In the analysis, the components with an eigenvalue > 1 were considered for further examination, as these components are those which represent more of the dataset variance than any of the original variables (Chatfield and Collins 1980). The PCA was performed including the data from both PG and MH. PCA was performed including information on the lost compositions for both PG and MH.

Results

The results of TGA and elemental analysis for both PG and MH are given in Supplementary Material.

The elemental analysis and derived parameters are outlined in Table 1. The values of C_{ox} did not vary between cores or with depth (Fig. 2, Table 2). At MH, streamwater DOM was noted for its relatively high C_{ox} and indeed even in comparison to this data from Pürschachen the highest C_{ox} value is for stream water DOM, and the second highest value of C_{ox} was for DOM from the Moor Lake. In comparison, the DOM from peat porewater from MH is more reduced than most of the peat or biomass at Pürschachen while the DOM from the peat porewater was still just oxidised (i.e. $\text{C}_{\text{ox}} > 0$).

At PG, the degree of unsaturation (Ω) increased significantly ($p < 0.05$) with depth (Fig. 3, Table 2). Clay and Worrall (2015) also found that Ω significantly increased with depth in all the cores from all the nine peatlands studied, among them MH. However, the comparison between PG and MH shows that over the same depth there is a far greater increase in Ω at MH than at PG implying that more reaction has occurred at MH than over the same depth at PG.

Gibbs free energy (ΔG_f)

There was a significant change ($p < 0.05$) with depth for ΔG_f for 1 out of the 3 cores taken from the study site but there was no general change of ΔG_f with depth across the study site (Fig. 4). At MH, there was a significant change in ΔG_f with depth in the peat profile (Worrall et al. 2018). The significant change observed in this one core and at MH was an increase in ΔG_f . Increases in ΔG_f have to be accompanied by production, and loss from the ecosystem, of low ΔG_f products. These low ΔG_f products could be CO_2 ($\Delta G_f = -32 \text{ kJ/gC}$) and DOC ($\Delta G_f = -16.3$ to

Table 1 The average composition of the carbon pools considered by the study

Carbon pool/type	Elemental analysis (mol/100 g)				Median stoichiometry	C _{ox}	Ω	ΔG _f
	C	H	N	O				kJ/g C
Pürgschachen Moor								
DOM Moor Lake	4.0	5.2	0.2	2.8	C ₂₂ H ₂₉ NO ₁₆	+0.23	2.50	−16.3
DOM peat porewater	3.8	6.1	0.2	2.8	C ₁₇ H ₂₇ NO ₁₃	+0.04	1.84	−19.7
Peat (surface—Calluna)	3.8	5.9	0.05	3.0	C ₇₃ H ₁₁₂ NO ₅₇	+0.06	1.88	−4.6
Peat (deep—Calluna)	3.9	5.7	0.05	2.9	C ₇₂ H ₁₀₄ NO ₅₃	+0.06	2.09	−5.1
Peat (surface—Pinus Mugo)	4.2	6.0	0.10	2.6	C ₄₂ H ₆₀ NO ₂₆	−0.09	1.92	−10.7
Peat (deep—Pinus Mugo)	4.0	5.9	0.06	2.9	C ₇₀ H ₁₀₄ NO ₅₀	−0.01	2.05	−5.5
Peat (surface—Eriophorum)	3.9	5.2	0.04	2.9	C ₉₅ H ₁₃₈ NO ₆₆	−0.04	1.87	−4.1
Peat (deep—Eriophorum)	4.2	6.2	0.05	2.7	C ₈₁ H ₁₂₀ NO ₅₃	−0.15	2.08	−5.4
Calluna biomass	4.4	5.2	0.05	2.5	C ₉₆ H ₁₅₀ NO ₅₄	−0.40	2.00	−8.2
Pinus Mugo biomass	4.3	6.7	0.03	2.6	C ₁₄₃ H ₂₂₃ NO ₈₅	−0.34	1.97	−5.6
Eriophorum biomass	4.0	6.3	0.06	2.8	C ₆₆ H ₁₀₄ NO ₄₆	−0.12	1.88	−3.7
Sphagnum biomass	3.8	6.2	0.07	2.9	C ₅₅ H ₈₉ NO ₄₂	−0.02	1.76	−4.2
Moor House								
DOM first-order stream	3.8	4.6	0.12	2.9	C ₃₁ H ₃₈ NO ₂₄	0.40		−9.04
DOM shallow peat porewater	4.2	5.2	0.14	2.1	C ₂₉ H ₄₁ NO ₁₅	−0.31		
DOM deep peat porewater	4.1	5.8	0.13	2.0	C ₃₀ H ₃₉ NO ₁₅	−0.22		
Standards								
Lignin	5.1	6.0	0.06	1.8	C ₈₇ H ₁₀₂ NO ₃₁	−0.43	3.15	−0.36
Cellulose	3.6	6.3	0.00	3.2	C ₆ H ₁₀ O ₅	0.05	1.47	−5.13
Protein	3.9	6.8	0.96	2	C ₈ H ₇ NO ₂	0.02	2.00	−2.89

Median stoichiometry is expressed relative to nitrogen content except for cellulose which expressed relative to carbon. *Surface* = 0–10 cm depth in the peat profile; and *deep* = 40–50 cm depth in the peat profile

−19.7 kJ/gC). However, the production of CH₄ (ΔG_f = −6.2 kJ/gC) would not always be possible because at some depths ΔG_f of the peat soil OM was lower than that of ΔG_f of CH₄. LaRowe and Van Cappellen (2011) have provided a thermodynamic description of the degradation of OM, and in particular argue that the rate of OM degradation can be related to a thermodynamic driving force which is related to the size of the Gibbs free energy of the decomposition reaction ΔG_f which is in effect the difference between the ΔG_f of the reactants and products. Therefore, the fastest rates of decomposition will be to CO₂ followed to DOC with the slowest, if possible at all, for CH₄. In comparison to the ΔG_f profile at MH, the ΔG_f profile at PG, at 2 out of 3 cores showed no trend of altered ΔG_f, implying slower rates of reaction. At MH, there is no change in ΔG_f after depths of approximately 50 cm implying that OM reaction has stopped by this depth, whereas any change at Pürschachen might be relatively small but is ongoing. The interpretation of

the Gibbs free energy data is that the OM decomposition at Pürschachen is comparatively slower and less advanced than observed for MH and produces CH₄ at a lower rate.

Thermogravimetric analysis (TGA)

The first three components of the PCA had eigenvalues greater than 1 and explained 73% of the original variance (Table 3). The loadings on principal component 1 show that it is dominated by the positive loadings at high temperatures and the lowest temperature while there are negative loadings in the range 300–400 °C. The loadings on principal component 2 are dominated by contrast across the temperature range 300–450 °C perhaps reflecting multi-peak traces observed in TGA.

In the comparison of PC1 and PC2 (Fig. 5) the standards circumscribe the data with the lowest values of PC1 being for cellulose; the highest value of

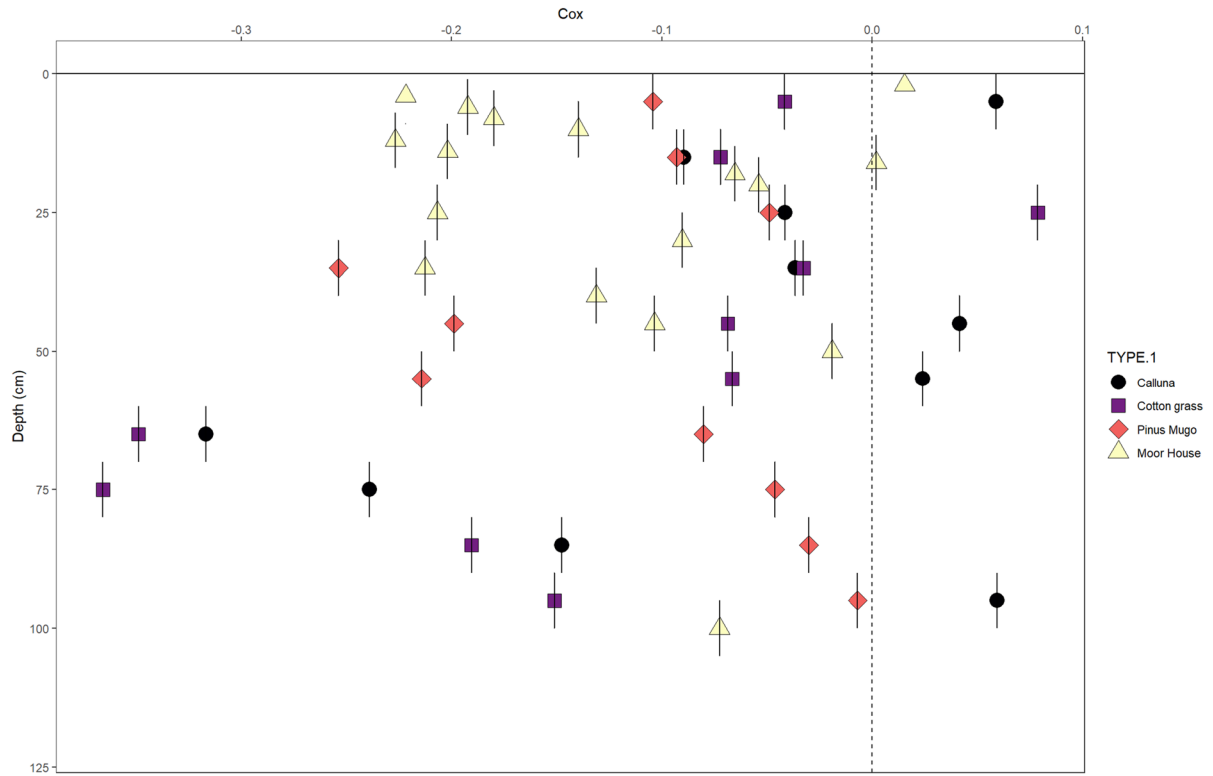


Fig. 2 The peat profiles at Pürschachen Moor cores vegetated by heather (*Calluna*), Cotton grass (*Cotton grass*) and dwarf pine (*Pinus Mugo*) and a Moor House core vegetated by

heather (Moor House) for C_{ox} in 0–100 cm depth. The Y error bar is given as the depth increment of the sampling

Table 2 Results of linear models of C_{ox} , Ω and ΔG_f with depth and between the cores taken from Pürschachen Moor

Parameter	Core	Depth	Core $\times$ Depth	R^2
C_{ox}	ns	ns	ns	–
Ω	0.15	0.23	0.15	0.53
ΔG_f	ns	ns	0.23	0.25

Ns not significant at a probability of at least 5%

PC1 is for the lignin standard and the highest value on PC2 is for peat soil but close to the lignin standard. The protein standard plots between cellulose and lignin standards within the area where the average biomass plots—on this plot the average biomass was 41% lignin and 59% cellulose. The protein standard plots so close to the line between the lignin and cellulose standards that the protein composition is indistinguishable. The humic acid standard plots close to the DOM from PG—the humic acid standard is a fluvial

humic acid. The peat and biomass samples from PG plot across the space defined by lignin and cellulose standards. Given the C budget published for this site (Drollinger et al. 2019a, b) then the lost composition plots very close to the average biomass—the lost composition has 52% cellulose and 48% lignin—that is a 13% loss of cellulose relative to lignin by 1 m depth in the peat. There was no significant relationship ($p > 0.05$) between the principal components and the depth implying no systematic variation in macromolecular composition with depth at PG.

Radiocarbon ages

For the DOM at MH the shallow peat porewater had a date of 1515–1740 ^{14}C yrs BP; the deep peat porewater had a date of 2060–2205 ^{14}C yrs BP; and the streamwater DOM from MH was recent (< 50 yrs BP).

The best-fit depth accumulation for MH is:

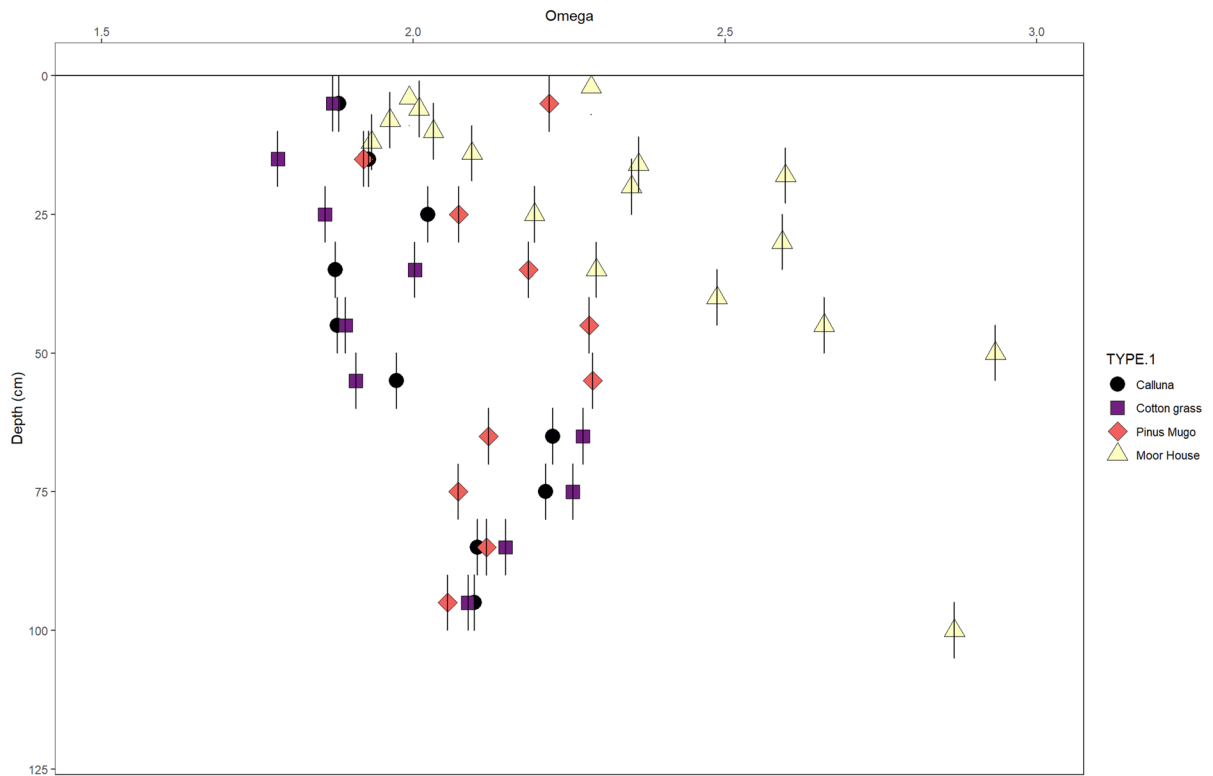


Fig. 3 The peat profiles for Ω in 0–100 cm depth profiles at Pürgschachen Moor cores vegetated by heather (Calluna), Cotton grass (Cotton grass) and dwarf pine (Pinus Mugo) and a

Moor House core vegetated by heather (Moor House). The Y error bar is given as the depth increment of the sampling

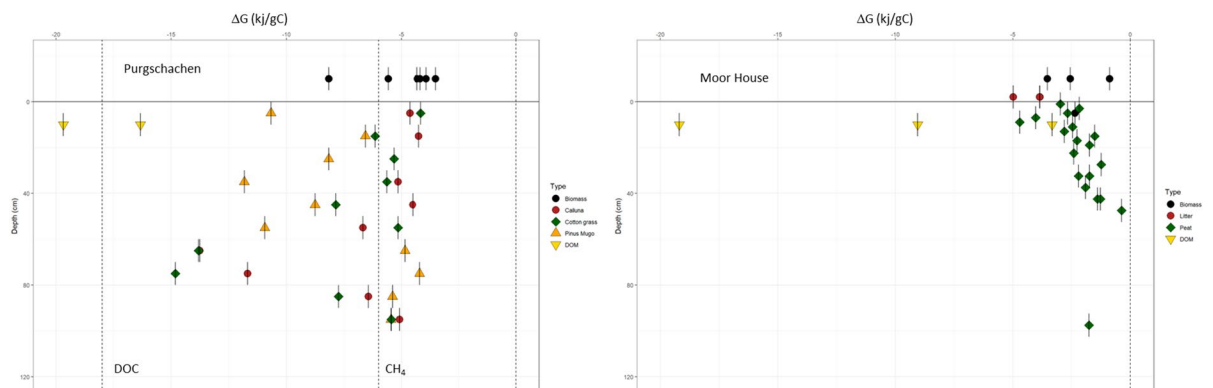


Fig. 4 Biomass, DOM and peat profile data for ΔG_f between 0 and 100 cm depth at Pürgschachen Moor cores vegetated by heather (Calluna), Cotton grass (Cotton grass) and dwarf pine (Pinus Mugo). For comparison the equivalent ΔG values and profile are given for Moor House. The Y error bar is

given as the depth increment of the sampling. The values for the sampled material are compared to the ΔG_f for possible terminal electron acceptors—for DOM (−18.0 kJ/gC) and for CH_4 (−6.0 kJ/gC)—the value of ΔG_f for CO_2 is not shown and would plot at −32 kJ/gC

Table 3 The loadings of the variables on those principal components with eigenvalue > 1

Variable	PC1	PC2	PC3
200	0.44	−0.07	0.12
250	0.17	0.37	−0.34
300	−0.25	0.30	−0.45
350	−0.24	−0.43	−0.28
400	−0.24	−0.24	0.47
450	0.02	0.41	0.39
500	0.31	0.30	0.31
550	0.38	0.13	−0.19
600	0.41	−0.12	−0.26
650	0.30	−0.39	−0.07
700	0.32	−0.29	0.10
Cumulative variance explained (%)	33	54	73

$$\text{Depth} = 0.047\text{Age}_{(0.002)} \quad n = 12, r^2 = 0.98 \quad (4)$$

The best fit C accumulation (C_{sum} —gC/cm²) is:

$$C_{\text{sum}} = 40\text{Age}_{(1.4)} \quad n = 12, r^2 = 0.98 \quad (5)$$

where: Age in ¹⁴C year BP.

Therefore, the LARCA for MH is 40 ± 2.7 gC/cm²/yr, and numbers in brackets represent the standard error in the coefficients. The contemporary C budget for MH was between 20 and 91 gC/cm²/yr with a median value of −56 gC/cm²/yr (Worrall et al. 2012). Given the nominal depth of sampling of the peat pore water DOC at MH of 25 and 75 cm, then the expected ages of the DOC in equilibrium with the surrounding peat would be 722 yr BP and 1550 yr BP respectively. The ages of the pore water DOC are older than their putative depths and may simply mean that their assumed samples depth were incorrect. However, the ages are clearly distinct from the recent age measured

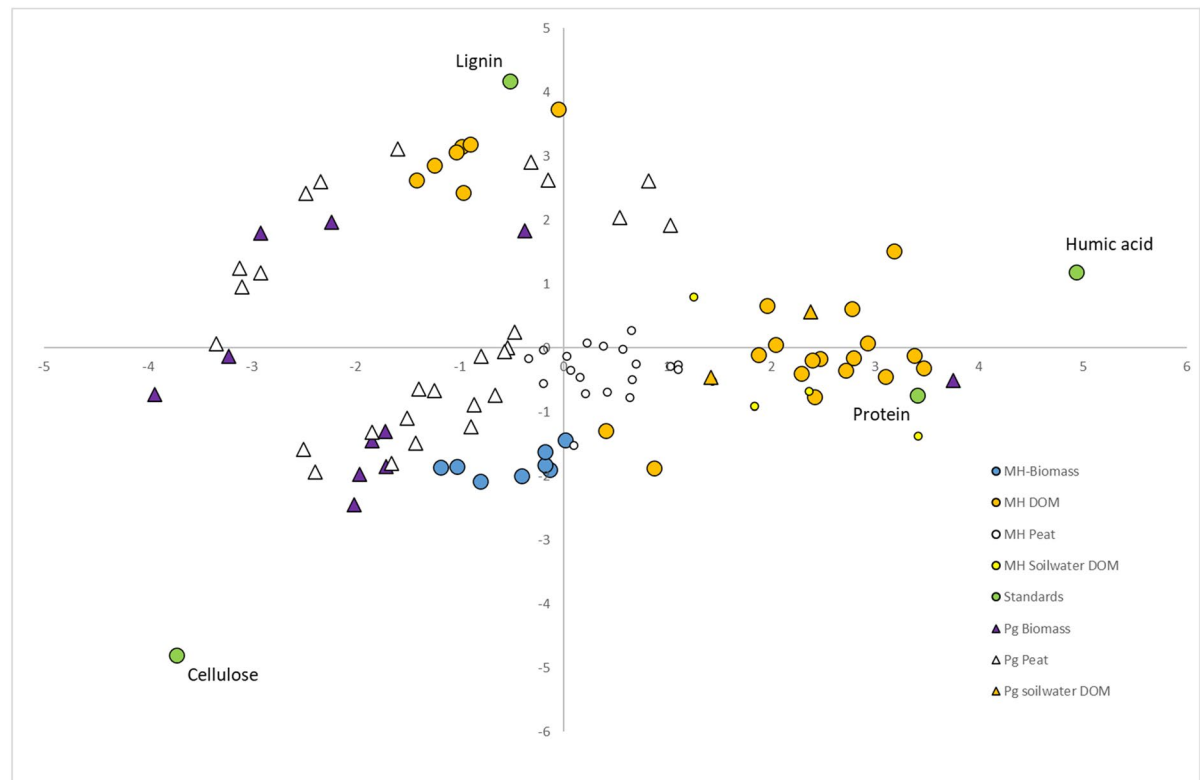


Fig. 5 The comparison of PC1 and PC2 for the TGA data for biomass, DOM, peat and soil water samples both Pürschachen Moor and Moor House as well as for cellulose, lignin and protein standards

for the DOC in the first-order streams of the MH catchments.

For PG, the DOM from shallow peat porewater was measured to be modern (<50 yrs BP) and the DOM from the mid-bog lake was 75 yr BP. The date of the peat at 1 m depth was 1130 yr BP and the depth accumulation rate was almost twice that found at MH:

$$Depth = 0.096Age_{(0.009)} \quad n = 6, r^2 = 0.85 \quad (6)$$

The best fit C accumulation (C_{sum} —gC/cm²) is:

$$C_{sum} = 129Age_{(18)} \quad n = 5, r^2 = 0.99 \quad (7)$$

Therefore, the LARCA for PG was 129 ± 36 gC/cm²/yr, and numbers in brackets represent the standard error in the coefficients and the uncertainty in the LARCA is given as the 95th percentile confidence limit. Note that this LARCA is larger than the 2 years of contemporary C budget recorded by Drollinger et al. (2019b).

In summary, our results point out a strong contrast in the flux and preservation of organic matter in PG compared to MH. The OR records no reduction of the peat with depth at PG, but this is not the case at MH. All other examined parameters indicate a stronger preservation of peat down to 1 m at PG compared to MH: the increase in Ω with depth at MH is more pronounced, there is no general trend of an increasing ΔG_f at PG with depth, TGA reveals no systematic variation of the macromolecular composition with depth at PG and the ¹⁴C data records a faster accumulation of organic matter at PG compared to MH.

Discussion

It might be expected that a peat column that records successively rising degradation with depth can be expected to have a C_{ox} , or OR, changing with depth, i.e. as organic carbon if the organic matter is progressively reduced with the release of oxidised products such as DOM and CO₂. However, such a change in C_{ox} is observed at neither PG nor MH. A lack of a progressive change in C_{ox} with depth does not necessarily mean a lack of degradation, just not a change in the redox status of the organic C in an ecosystem often noted for its reducing conditions. Clay and Worrall (2015) studied nine peatlands across the

UK (including MH) and also found no significant change in C_{ox} with depth. At the time, Clay and Worrall (2015) were not able to conclusively explain this lack of change of C_{ox} with depth, but they called for the characterization of individual components of the carbon pools to better explain the underlying controls on OR in the terrestrial environment. Some of these means are elaborated in the following paragraphs.

Conversely, a significant change in the degree of unsaturation (Ω) was observed for both PG and MH. An increase in the degree of unsaturation is associated with a decrease in molecular weight and low molecular weight substances are the final products of humification (Schnitzer and Khan 1972). The elevated Ω of the peat column at MH as compared to PG indicates stronger chemical alteration at MH relative to PG. Clay and Worrall (2015), in their study of nine peatlands across the UK found that the only consistent down profile change in chemistry between the nine locations was a significant change in Ω .

This study proposed mechanisms of organic matter accumulation. First, that accumulation favours lignin-like organic matter with preferential loss of cellulosic compounds. This study did find that peat at PG was marginally enriched in lignin-like organic matter relative to polysaccharides and cellulose-like organic matter. However, the enrichment was 13% by 1 m depth at PG while at MH it was 92% loss of cellulosic C relative to lignin C. This mechanism corroborates earlier work: Leifeld et al. (2012), reports the preferential decay of polysaccharides coupled to the accumulation of newly formed more recalcitrant substances in deep horizons of the examined peat columns. In the Königsmoor (Germany), Biester et al. (2014) noticed the degradation of peat to be accompanied by the preferential decomposition of phenols and polysaccharides and a relative enrichment of aliphatics during drier periods. Pipes and Yavitt (2022) and Santelmann (1992) also observed the superficial decomposition of plant material to coincide with decomposing cellulose in the topsoil, but not in deeper peat. Examining PG and neighbouring, more degraded peat bogs, Drollinger et al. (2020) found the loss of carbohydrates to be a key process of decomposition in degraded sites so the enrichment of lignin-like organic matter relative to polysaccharides and cellulose-like organic matter even at the better-preserved PG shows that even well-preserved peat experiences

some alteration leading to relative enrichment in lignin over cellulosic material. On the other hand, Schellekens et al. (2015) note a preferential degradation of phenolics (sphagnum acid) over polysaccharides (Sphagnum), suggesting that polysaccharides as Sphagnum provide a degree of recalcitrance to Sphagnum cell walls, as reported by Hájek et al. (2011).

The higher LARCA measured for PG when compared to MH appears consistent with the peat accumulation rates ranging between 0.65 and 1.09 mm/yr that Drollinger et al. (2020) detected until 4900 years BP. These rates were higher (> 1 mm/yr) at > 3000 years BP than in younger parts of the core (< 1 mm/yr). Knierzinger et al. (2020) examined anthropogenic and climatic influences on a deep (500 cm) peat core at PG. Knierzinger et al. (2020) noted a remarkably constant peat composition until at least 4900 years BP and detected some climate dependence on humification at 380 cm depth, corresponding to the late Atlantic climate optimum, which probably initiated a relatively dry phase at 3950 years BP. However, this trend was an exception in the 500 cm core which is remarkable for its low fluctuation of humification. Thus, the data by Drollinger et al. (2020) and Knierzinger et al. (2020) provide evidence of a continuous long-term trend of high C accumulation rates at PG. These consistent indicators for a high rate of preservation of assimilated carbon already at a low peat depth at PG are in sharp contrast to the greater changes indicators of peat preservation and alteration at MH. In contrast to MH, there is no fluvial export of peat at PG. This long-term record of C accumulation provides evidence for a high continuity of wetness in the mire and a positive climatic water balance over the past ca. 5000 years at PM, despite Holocene warm periods (Mann et al. 2009; Swindles et al. 2019).

There are no indicators of strong alteration of the peat in the rhizosphere in PG: Müller et al. (2022) found no indicators of priming effects after spiking PG mesocosms with artificial, ^{13}C labelled root exudates (following Basiliko et al. 2012) and report a pronounced immobility of the labelled substance, which to a large part remained in the depth of spiking (15 cm depth). Müller et al. (2022) found 31.4% of the added ^{13}C to leave the mesocosm as $^{13}\text{CO}_2$ and 2.6% as $^{13}\text{CH}_4$, so a substantial portion of very

recently assimilated C is respired very quickly, but a larger portion remains in the solid state or as POC or DOC.

It is not surprising that, in a strongly acidic environment where the lack of gradient and stream outflow from the bog leads to consistently high, stagnant groundwater tables with limited flushing of the porewater, a large proportion of the assimilated C remains stored and experiences little alteration. Here, we relate this situation to a “soup bowl” (Fig. 6), e.g. a system where there is no seepage to groundwater due to the clayey till at the bottom of the peatland, no fluvial export due to flat terrain and no surface runoff due to the lenticular shape of the raised bog where all potential surface runoff would end up in the lagg and evapotranspiration as the sole relevant pathway of water leaving the system. In such a system, the only pathway of carbon loss is gaseous. The porewater is not flushed and in these relatively high standing water tables the porewaters become closed and reactions stop as they attain equilibrium (Beer and Blodau 2007).

Similar situations are probably not rare. Williams and Yavitt (2003) examined three peatlands in

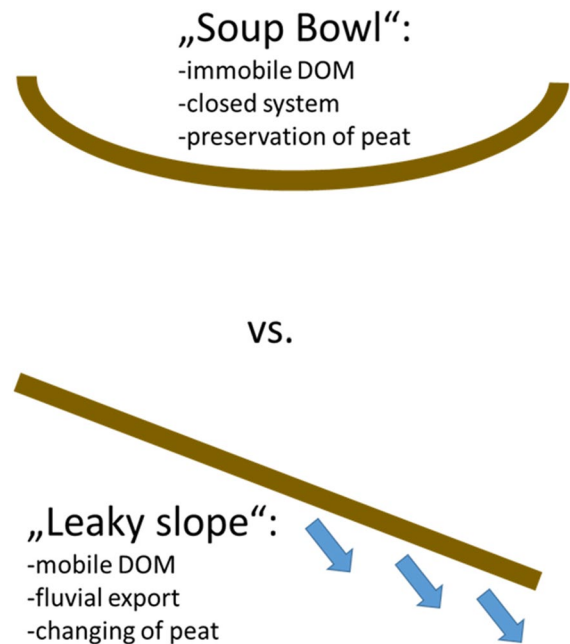


Fig. 6 Visualisation of the “acidic soup bowl” and the “leaky slope” situation at the continental raised bog and the Atlantic blanket bog

the Appalachians, situated in a continental climate: Spring Pond in the Adirondacks, NY, USA; Buckles, MD, USA; and Big Run Bog, WV, USA (which is –despite its name–, a poor fen). Williams and Yavitt (2003) found that the greatest degree of variability in different chemical indices of the peat (lignin concentration, pyrophosphate degree of decomposition, cinnamic acid to vanillyl phenolic ratio, and lignin diagenetic indicators) occurred in the surface layers of the profiles down to 290 cm depth and that the degree of decomposition did not increase linearly with depth in a peat profile. The authors explain this on the one hand with site specific lignin and phenolics chemistry and decomposition and on the other hand with relatively undecomposed nature of deep peat as a result of past environmental conditions.

More recently, Pipes and Yavitt (2022) reported an extremely slow decay rate in peat with almost all chemical changes in the peat column occurring between 0 and 20 cm depth. The authors examined the C:N ratio, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, lignocellulose index, and the lignin nitrogen index. They explain this phenomenon with the amount of pectin compounds and their location within and between cells in Sphagnum tissue and do not attempt any further explanation. The peatlands (two small bogs in a depression and one fen) examined by Pipes and Yavitt (2022) are all located in upstate New York, close to Ithaca, also in a continental climate, and are underlain by glacial till in small depressions (bogs) or fed by a local spring (fen).

It is interesting that these conditions were also encountered in fens. It is important to note that Big Run Bog has a surface pH of 3.9, consists of Sphagnum-sedge peat, covers a mere 15 ha and occupies the lowest portion of a 276 ha forested watershed, with a first-order stream running through the center of the peatland (Williams and Yavitt 2003). The fen examined by Pipes and Yavitt (2022), Labrador Hollow, is a riverine fen, with 75% Sphagnum cover. It resembles PM more strongly than MH as in this geomorphic setting, there is also no vertical flushing of the peat column.

In contrast, at MH, and for blanket bogs, we describe the situation as “leaky slope” (Fig. 6), where fluvial export is an important pathway for water and C leaving the system. As a consequence of frequent rainfall, the peat column is regularly flushed with water and the peat is altered and leached. The peat pores higher in the profile remain open and are

often flushed, thus driving reactions, while at PG the pores are closed relatively higher in the profile leading to stable, chemical equilibrium conditions that stabilise more the of the input more rapidly. Such a lack of flushing in the raised bog means it has a higher accumulation of less altered organic matter and the absence of chemical thermodynamic gradients (changes in ΔG_f) that would indicate ongoing reactions.

Our study supports the general concept that decomposition of plant material takes place, to a large part, in the acrotelm (Clymo 1984). It does however show that the shape of the curve describing the change of the decomposition rate with depth, is controlled by the hydrologic setting and the resulting mobility of DOM.

Conclusions

The study of the organic matter transition into and through a raised, continental peat bog in contrast to a blanket peat bog confirmed both hypotheses. Even PG, with its high degree of preservation of organic matter loses polysaccharides and accumulates lignin-like substances starting a very shallow depths (ca 10 cm below the surface). Our examinations also confirmed the second hypothesis that organic matter accumulation is controlled by thermodynamic limitation of decomposition of recently deposited organic matter. We were able to show that comparatively, in the raised bog the peat profile more rapidly becomes thermodynamically closed. This means that the composition of the organic matter retains more of the character of the plant species growing on the bog. For the blanket bog 92% of the cellulose and 50% of the lignin input from plants was removed by 1 m depth, but for the raised bog 13% of the cellulose was removed by 1 m depth. The lack of DOC flux and the high stagnant water tables mean that the pore space in the raised bogs rapidly closes, and thermodynamic equilibrium is achieved leading to a lack of transformation of plant organic matter. The rapid closure of the pore space and high preservation of the plant matter resulted in a long-term carbon accumulation rate of the raised bog almost 3 times that of the blanket bog. The raised bog acts as acidic soup bowl, in contrast to the blanket bog which acts as a leaky slope.

Author contributions SG and FW contributed to the study conception and design. Material preparation, data collection and analysis were performed by SG, FW, IMB and KH. The first draft of the manuscript was written by SG and FW and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets generated during and/or analysed during the current study are given in the supplement of this publication.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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