

Sensitivity of peatland carbon loss to organic matter quality

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[1] Peatland soils store substantial amounts of organic matter (OM). During peat formation, easily decomposable OM is preferentially lost and more recalcitrant moieties accumulate. In a peat profile, OM quality thus scales with depth. Drainage and ongoing climate change poses the risk of rapid OM loss when formerly anoxic peat layers oxidize. During peat decomposition, deeper, more recalcitrant peat is exposed to the oxygen-rich surface, which may influence the decomposition rate. We show that the soil respiration rate of a disturbed temperate peatland is strongly controlled by the peat's quality and especially its polysaccharides content. The polysaccharide content of soil profiles in a wider range of peatland sites with differing degrees of disturbance was inferred by means of solid-state ¹³C NMR and DRIFT spectroscopy. The data confirmed a strong decline in polysaccharide content with depth and a poor OM quality of surface peat in soils drained decades ago. We combined the evidence from respiration and spectroscopic measurements to deduce the sensitivity of peatland carbon loss with respect to OM quality by scaling measured quality to a 142-years record of peatland subsidence and carbon loss at one of the sites. According to the functional relationship between quality and respiration, the measured average annual carbon loss rate of 2.5 t C ha⁻¹ at that site was 20 t C ha⁻¹ at the onset of peatland drainage and dropped to less than 1 t C ha⁻¹ in recent times. **Citation:** Leifeld, J., M. Steffens, and A. Galego-Sala (2012), Sensitivity of peatland carbon loss to organic matter quality, *Geophys. Res. Lett.*, 39, L14704, doi:10.1029/2012GL051856.

1. Introduction

[2] Carbon dioxide (CO₂) emitted from drained, carbon-rich soils such as peatlands is increasingly recognized as an important flux in the global carbon cycle [Parish *et al.*, 2008]. For the year 2008, global emissions from drained peatlands have been estimated at 0.35 Pg C [Joosten, 2010], a substantial flux compared to emissions related to land-use change that currently account for 0.9 Pg C, excluding peatland drainage [Friedlingstein *et al.*, 2010]. Carbon

accumulates in mires – intact, peat-forming ecosystems – mainly due to oxygen-poor conditions hindering decomposition but not ecosystem productivity, thus leading to a small positive imbalance between carbon input and loss [Moore, 2002]. The protective effect of frequent or permanent water saturation on the soil carbon stock is reversed once the water table drops due to drainage. Higher temperatures and changing patterns of rainfall or permafrost melting under global warming as well as drought are also thought to impair peatland carbon storage [Fenner and Freeman, 2011; Strack *et al.*, 2008]. Carbon loss rates in disturbed peatlands mainly depend on climate, the water table level, and the intensity of after-use [Augustin *et al.*, 1996; Byrne *et al.*, 2004; Couwenberg *et al.*, 2010; Dawson *et al.*, 2010]. However, even under similar conditions regarding drainage, climate, or management, loss rates vary substantially across peatlands [e.g., Byrne *et al.*, 2004; Höper *et al.*, 2008]. Water table level was no significant factor for peatland carbon loss at sites of different drainage history [Byrne and Farrell, 2005] or for emissions along gradients of water table levels [Chimner and Cooper, 2003]. Byrne and Farrell [2005] hypothesized that a decline in OM quality with depth may be an important factor controlling CO₂ emissions from peat.

[3] Unlike in mineral soils, in which two protection mechanisms – aggregation and organo-mineral association – are the most important drivers for long residence times of soil organic matter (SOM) [Golchin *et al.*, 1994], these mechanisms are negligible in organic-rich soils due to the lack of minerals. In these soils, a third factor deemed important for OM decomposability is its chemical composition, which controls degradability, among other factors, through the different activation energies associated with the various chemical bonds or OM ‘qualities’ [Conant *et al.*, 2011; von Lütow and Kögel-Knabner, 2009]. Peat formation is accompanied by substantial decomposition of the fresh plant residues, presumably leaving less labile OM behind that finally makes up the peat. In his classical paper on the formation of peatlands, Clymo [1984] estimated that approximately 80–90% of the net primary production entering the temporary oxic upper horizon or acrotelm of a mire soil eventually decomposes before it is buried in the deeper, permanently water-saturated catotelm. Decomposition also proceeds in the latter, but at much lower rates. From this concept it must be inferred that OM composition should change steadily down the soil profile. Particularly oxygen-rich compound classes, such as hydrophilic polysaccharides, should diminish during peat formation, whereas lignin and polyphenols that rely on oxic conditions for their decomposition together with hydrophobic aliphatic microbial products should show relative accumulation. A possible decline in oxygen-containing moieties would be of particular relevance because it has recently been shown that the O-alkyl-C content in OM-rich mountain soils scales linearly with the carbon mean residence time [Budge *et al.*, 2011].

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Referring to decomposition studies from single compounds by *Fierer et al.* [2005], *Kleber* [2010] argued that decomposability increased with the oxidation number or the O/C ratio of the compound. These studies indicate that O-substituted OM may represent an important component also for carbon dynamics in disturbed peatlands. From the few detailed studies on OM chemistry in peat profiles it appears that carbohydrate contents, carboxyl-C, and other oxygenated functionalities do indeed decline with depth, whereas aliphatic-C, aromatic C, and microbial mucilage increases [*Cocozza et al.*, 2003; *Delarue et al.*, 2011; *Klavins et al.*, 2008; *Zaccone et al.*, 2007].

[4] Together these findings suggest that peat 'quality' in terms of decomposability changes steadily within a peat profile and that oxygen-containing functionalities may be of particular relevance for the decomposition of the peat deposit after drainage. However, a quantitative relationship between OM composition and vulnerability to carbon loss in disturbed peatlands is essentially missing. In this study we evaluate (hypothesis A) whether peat quality is a function of soil depth and therefore peatlands drained long ago nowadays expose old peat of poorer quality to the atmosphere and (hypothesis B) whether peat quality is an important driver in shaping C loss rates from drained peatlands.

2. Approach

2.1. Sites

[5] Since 2005 we have been sampling six peatlands of different drainage status and management history in Switzerland (see Table S1 in the auxiliary material).¹ Etang de la Gruère (GRC) represents an undrained, unmanaged, semi-natural bog in the Swiss Jura mountains (sampling depth 0–2 m). Eigenried (EGB) and Seebodenalp (SBA) represent drained former bogs in a semi-natural state (cut once a year), but with large historical and ongoing carbon losses (sampling depths 0–2 m, 0–0.36 m). Hagenmoos (HMC) is a formerly drained bog rehabilitated in 1982 (sampling depth 0–2 m), and sites Parzelle 33 (P33) and Lindenhof (WIB) are the most degraded former peatlands drained 140 years ago and nowadays under intensive agricultural management (annuals, partially vegetable cropping; sampling depths 0–1.4 and 0–0.28 m). Site details for GRC, EGB, and HMC can be found in *Leifeld et al.* [2011a], for P33 and WIB in *Leifeld et al.* [2011b], and for SBA in *Rogiers et al.* [2008]. All soils were sampled volumetrically using peat corers (GRC, EGB, SBA, HMC) or from open profiles using steel cylinders (P33, WIB).

[6] Carbon losses in P33 and WIB were estimated at 350 and 490 t C ha⁻¹, based on long-term subsidence records and carbon inventories, and losses of 243 and 590 t C ha⁻¹ were reported for EGB and SBA, based on carbon inventories and the relative accumulation of ash in the upper part of the soil profile. A detailed description of the applied methods can be found in [*Leifeld et al.*, 2011a, 2011b; *Rogiers et al.*, 2008]. We selected these six sites to obtain a representative picture of the variability of key soil parameters and chose SBA, GRC, and P33 for testing hypothesis (B). Peat degradation at P33 corresponds to a volumetric loss or subsidence of 2 m since 1860, i.e., peat exposed nowadays to

the surface was located at a depth of 2 m before the onset of drainage [*Leifeld et al.*, 2011b]. We use the chemical data from GRC, the most natural site, as a proxy for the peat that has been lost at P33 for the discussion of the role of peat quality for carbon loss rates.

2.2. Methods

[7] Peat elemental composition (C, H, N, O) was measured for all 239 samples from the six sites using an elemental analyzer (Hekatech, Germany). Elements C, H, N were retrieved by dry combustion and oxygen separately by pyrolysis at 1000°C. Samples were free of carbonate and total C and O thus equals organic C and O. The composition of 26 selected samples was studied by solid-state ¹³C NMR spectroscopy. The cross-polarization magic angle spinning (CPMAS) technique with a ¹³C-resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz was applied. A ramped 1 H-pulse starting at 100% to 50% of the initial power was used during a contact time of 1 ms to circumvent spin modulation during the Hartmann-Hahn contact. Pulse delays between 400 and 800 ms were used for all spectra. Preliminary experiments confirmed that the pulse delays were long enough to avoid saturation. Depending on the C contents of the samples, between 1299 and 122397 scans were accumulated and no line broadening was applied. The ¹³C chemical shifts were calibrated relative to tetramethylsilane (0 ppm). The relative contributions of the various C groups were determined by integration of the signal intensity in their respective chemical shift regions according to *Knicker et al.* [2005]. The region from 220 to 160 ppm was assigned to carbonyl (aldehyde and ketone) and carboxyl/amide-C. Olefinic and aromatic C were detected between 160 and 110 ppm. O-alkyl and N-alkyl-C signals were found from 110 to 60 ppm and from 60 to 45 ppm. For the current study, the spectral region from 60 to 95 ppm was used as a quantitative indicator of polysaccharides to avoid possible contributions from C-2 and C-6 of syringyl units from lignin. Resonances of alkyl C were assigned to the region from 45 to –10 ppm.

[8] Samples from all sites and depths were measured with diffuse reflectance infrared spectroscopy (DRIFT) using finely ground samples mixed with KBr, as described in *Leifeld* [2006], in a Perkin Elmer Spectrum One B instrument. DRIFT spectra of organic samples such as peats are mainly characterized by the major organic functionalities with only little interference from minerals. The content of O-alkyl or carbohydrate-C (60–95 ppm) measured by solid-state ¹³C NMR spectroscopy was regressed against the DRIFT spectra using a partial least-squares regression (PLS) to obtain an estimate of the O-alkyl-C content of all samples that were not subjected to ¹³C NMR experiments. The spectral range of 4000 to 600 cm⁻¹ was used for PLS. Spectra were mean-centered and the first derivative was used for full cross-validation of the 26 samples. The PLS model was built with 3 latent variables and explained 97.2% of the variance. With a mean property value of 147.3 mg O-alkyl-C g⁻¹ soil, the mean SEE during calibration was 9.52 and the SEP during validation was 12.3. This performance was deemed sufficient to detect O-alkyl-C patterns in the peat profiles.

[9] As mentioned above, the amount of O-alkyl-C is supposed to be a useful indicator for OM decomposability in organic-rich soils [*Budge et al.*, 2011]. To infer a more direct

¹Auxiliary materials are available in the HTML. doi:10.1029/2012GL051856.

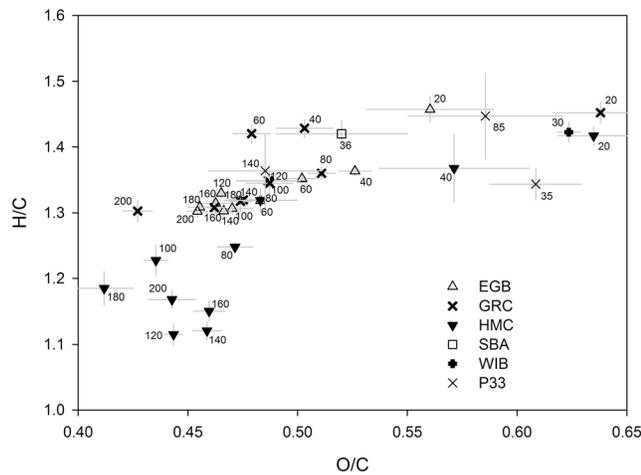


Figure 1. Van Krevelen plot of samples from six peatlands (EGB, GRC, HMC: number shows the lower depth limit of 20 cm increments; numbers for SBA, WIB, P33 indicate the lower depth limit of peat increment [cm]). Error bars are one SE.

measure for its role in the decomposition of peat, 18 of the vegetation-free samples from site SBA, taken with 100 cm⁻³ cylindrical steel cores at depths between 0 and 24 cm, were adjusted to a water potential of 100 hPa (approximated field capacity [Cornelis *et al.*, 2001]). They were then pre-incubated for three days and measured for soil respiration at 25°C for 24 hours in the lab using a respiration chamber as described in Leifeld and Fuhrer [2005]. Respiration rates were normalized to the C content of the samples and then plotted against OM quality parameters to infer useful proxies that were available for all samples. An overview of sampling depths, measured elemental contents, pH values, bulk densities, and samples chosen for NMR and respiration is given in Table S2 of the auxiliary material.

3. Results and Discussion

[10] Elemental data indicate changes of peat composition with depth in all peat profiles (Figure 1). This includes a narrowing of O/C and H/C molar ratios and (not shown) an increase in organic carbon concentration with depth [see Leifeld *et al.*, 2011a, 2011b; Rogiers *et al.*, 2008] (Table S2 of the auxiliary material) from values around 45% in semi-natural or less degraded sites (GRC, EGB, HMC) or 20 to 35% in more degraded sites (SBA, WIB, P33; all in the upper 20 cm) to concentrations of around 55% in the deep catotelm (all sites). Solid-state ¹³C NMR spectra underline the change in peat composition with depth and thus the degree of peat formation. For example, aryl-C significantly increased with depth ($r = 0.66$, $P < 0.001$; Pearson's) across all 26 samples, whereas the contribution of O-alkyl-C declined ($r = 0.46$, $P < 0.05$). These trends were significant despite the high variability in OM composition across the sites. Site EGB (Figure 2) exemplifies the increase in both aryl and alkyl-C and the corresponding decline of the dominant O-alkyl-C peak at 72 ppm, which is characteristic for polysaccharides [Kögel-Knabner, 1997].

[11] Laboratory incubations of samples from site SBA indicated O-alkyl-C to be an important factor for oxidative

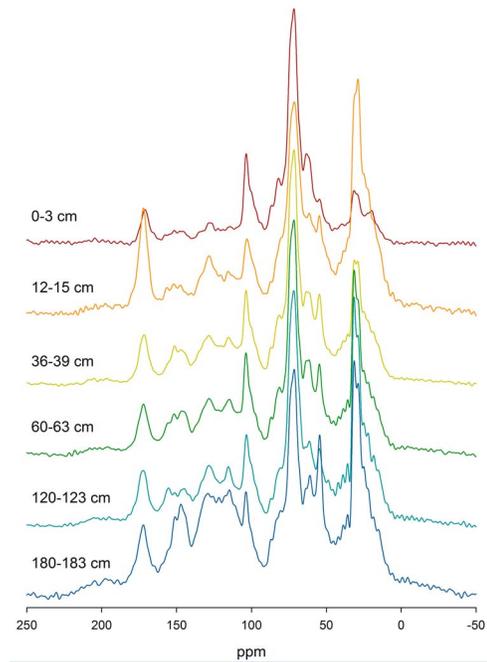


Figure 2. Depth profile of ¹³C NMR spectra of site EGB. Numbers indicate segment depth (cm). The uppermost sample mainly consists of sphagnum. With depth, aryl-C (110–160 ppm) and alkyl-C (–10–45 ppm) increase, whereas O-alkyl-C (ca. 60–110 ppm) decreases. To estimate O-alkyl-C by DRIFT spectroscopy, the most prominent peak covering the range from 60–95 ppm was integrated.

decomposition (Figure 3). O-alkyl-C was the best single proxy for respiration rates among all measured variables (soil depth, C/N, O/C, H/C ratios, soil pH, contents of other carbon moieties, see Figure S2 of the auxiliary material). Soil depth was also significantly related to respiration rates, but explained alone only 68% of the variability compared to 94% by O-alkyl-C. Soil respiration from incubated peatland soil cores typically declines with depth and this has been attributed to the quality or recalcitrance of the material [Scanlon and Moore, 2000; Hardie *et al.*, 2011]. It is obvious, however, that depth is no unique qualifier or surrogate

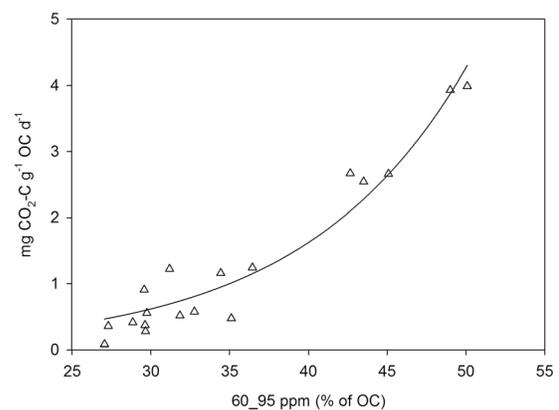


Figure 3. Soil respiration of peatland site SBA as a function of O-alkyl-C. Regression equation: $Y = 0.034 \cdot \exp(0.0966 \cdot x)$, $R^2 = 0.94$.

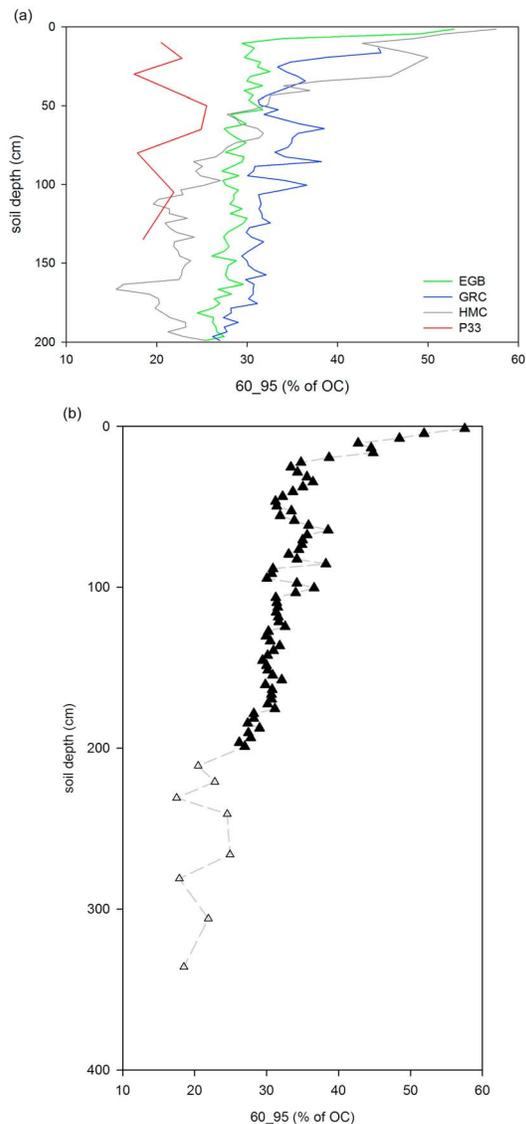


Figure 4. O-alkyl-C content of peat profiles. P33 has been drained since AD 1860 and agriculturally managed; GRC is a pristine bog; EGB has been drained since AD 1919, but is semi-natural (annual cut); and HMC has been drained since the 19th century, but has been rehabilitated since 1982 and peat re-growth is observed. The upper 20 cm at GRC, HMC, and EGB represent fresh or only partially degraded litter above the catotelm (4a). 4b: Constructed artificial O-alkyl-C profile (referring to 60–95 ppm ^{13}C NMR spectral region) plotting data from P33 below the current GRC profile at 2 m depth under consideration of a 2 m peat loss at P33 since 1860.

for decomposability when peatlands of different drainage status and hence different volumes of already oxidized surface peat are compared. Peat quality also depends on mire vegetation, which itself changes with climate during peat accumulation. Because of these arguments and the thermodynamic rationale behind the relationship, we used the contribution of O-alkyl-C to SOC as a reliable indicator for OM decomposability at the various sites and soil layers.

[12] DRIFT-PLS allowed assignment of O-alkyl contents with much higher depth resolution than NMR analysis alone.

For those sites where deep profiles could be sampled (EGB, GRC, HMC, P33), the O-alkyl-C content declined with depth (Figure 4a). There are also differences between sites. Considering that GRC is a ‘pristine’ bog, EGB is a moderately managed and drained former bog, P33 is a heavily drained and agriculturally managed peatland, and HMC is a formerly drained but now rehabilitated peatland, differences may be related to the land-use history of the site. From previous studies [Leifeld *et al.*, 2011a, 2011b] we know that P33 and EGB lost 350 and 243 t C ha $^{-1}$ due to drainage, which corresponds to roughly two m of subsidence in the case of P33. This means that the former peatland nowadays exposes peat that was buried at a depth of two m before drainage, as also indicated by the surface peat having a high ^{14}C age of close to 4000 years [Leifeld *et al.*, 2011b]. Hence, in addition to variations in litter/peat quality as a function of site vegetation, which we cannot track back, different degrees of peat degradation explain the differences in composition across the sites. The small amount of O-alkyl-C in conjunction with a high aromaticity in the topsoil of P33 indicates that any contribution from recent plant litter to the total soil carbon stock must be small.

[13] A hypothetical former pristine profile of O-alkyl C at P33 can be reconstructed assuming that the lost top part of the profile can be approximated to that of the top 2 m of the GRC profile (Figure 4b): i.e., we regard GRC as the most pristine peatland as a representative of the material that has already been lost at P33 in terms of composition. Based on C inventories and long-term subsidence records, we previously measured a total C loss of 350 t C ha $^{-1}$ for P33, corresponding to the above-mentioned loss of two m peat [Leifeld *et al.*, 2011b]. This number integrates over 142 years of drainage. The relationship between O-alkyl-C and decomposition (Figure 3) and high resolution information on O-alkyl-C along the peat profile can be used to calculate the susceptibility to peat decomposition along the peat profile as follows:

$$k_F = \sum_{i=1}^n (k_{L,i}) \cdot \frac{m_i \cdot f_1}{f_2}$$

with k_F = field decomposition rate, k_L = laboratory decomposition rate per unit O-alkyl-C following the regression equation in Figure 3, m = O-alkyl-C content of soil carbon per soil increment, f_1 = factor to normalize the sum of products of $k_L \cdot m$ to the total amount of C lost at P33 by using the MS Excel solver function [4.83], and f_2 = factor to convert number of years (142) to number of measured soil increments (67) [2.12] to get emissions per year rather than per soil increment.

[14] The results show a substantial decline in annual C loss rate over time (average: 2.5 t C ha $^{-1}$), if the rate at that particular site would have been a function of peat quality alone (Figure 5). The rate varies by about a factor of twenty, and current rates would be at around 1.0 t C ha $^{-1}$ a $^{-1}$ as compared to initial loss rates of approximately 20 t C ha $^{-1}$ a $^{-1}$. The typically observed nonlinear subsidence and peat loss in drained peatlands has been attributed to three processes: primary consolidation of low-density peat layers at the beginning of drainage as a result of loss of supporting pore water pressure followed by shrinkage resulting from evaporation loss, and carbon loss by decomposition [Kasimir-

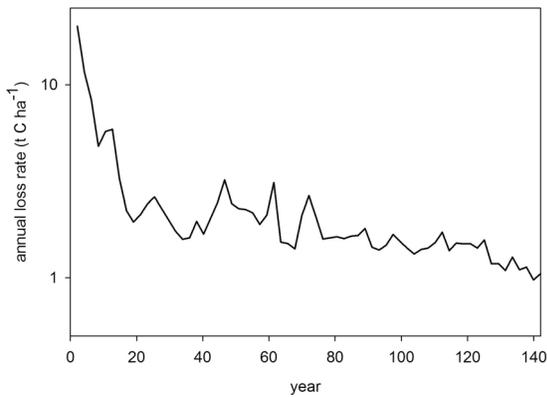


Figure 5. Estimated shift in annual loss rate as a function of O-alkyl-C content in the peat profile of GRC, based on an cumulative CO₂-C-emission of 350 C ha⁻¹ over 142 years of drainage.

Klemetsson et al., 1997]. Our current analysis indicates that the latter process alone would induce a similar subsidence pattern. The result also illustrates that, if CO₂ emission is measured over a degraded peatland over short periods only, the result strongly depends on the amount of C already lost due to global warming-induced changes in peat hydrology or, in the case of drainage, the time since the onset of hydrological measures and its effect on the quality of the remaining substrate. For future studies, two approaches are deemed suitable for validating the change in emission over time as depicted in Figure 5: Decadal CO₂ flux measurements at single field sites or simultaneous flux measurements at multiple field sites typified by different drainage histories.

4. Conclusions

[15] The composition of OM in peatlands strongly varies with depth as a result of the peat-forming process. During peat build-up, easily degradable compounds in upper, young layers are preferentially decomposed; remaining and newly formed recalcitrant compounds accumulate in deeper layers. Drainage or climate-related changes in hydrological conditions trigger the loss of younger topsoil carbon from peatlands. This loss results in the exposure of older and recalcitrant OM, eventually controlling decomposition rates. Our results indicate that, in addition to other environmental drivers reported in the literature, carbon loss from disturbed peatlands depends on peat composition, which is well represented by the amount of O-alkyl-C. Thus depth-related substrate quality may be an important factor in explaining the missing relationship between water table level and heterotrophic respiration in some peatland studies. Quality-dependent carbon loss rates from impaired peatlands may help to target management schemes aiming at carbon stock preservation to sites which are particularly vulnerable to further carbon depletion.

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