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# Effect of peat quality on microbial greenhouse gas formation in an acidic fen

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Received: 16 July 2009 – Accepted: 23 August 2009 – Published: 3 September 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Peatlands play an important role in the global carbon cycle and represent both an important stock of soil carbon and a substantial natural source of relevant greenhouse gases like CO<sub>2</sub> and CH<sub>4</sub>. While it is known that the microbial availability of organic matter affects degradation and mineralization processes in peatlands, the manner in which peat organic matter affects the formation of CO<sub>2</sub> and CH<sub>4</sub> remains unclear. In this study we developed a fast and simple peat quality index in order to estimate its greenhouse gas potential by linking the thermo-degradability of peat with anaerobic CO<sub>2</sub> and CH<sub>4</sub> formation rates. Peat samples were obtained at several depths (0–40 cm) at four sampling locations from an acidic fen (pH~4.7). CO<sub>2</sub> and CH<sub>4</sub> formation rates were highly spatially variable and depended on depth, sampling location, and the composition of pyrolysable organic matter. Peat samples active in CO<sub>2</sub> and CH<sub>4</sub> formation had a quality index above 1.35, and the fraction of thermally labile pyrolyzable organic matter (comparable to easily available carbon substrates for microbial activity) obtained by thermogravimetry was above 35%. Curie-point pyrolysis-gas chromatography/mass spectrometry mainly identified carbohydrates and lignin as pyrolysis products in these samples, indicating that undecomposed organic matter was found in this fraction. In contrast, lipids and unspecific pyrolysis products, which indicate recalcitrant and highly decomposed organic matter, correlated significantly with lower CO<sub>2</sub> formation and reduced methanogenesis. Our results suggest that undecomposed organic matter is a prerequisite for CH<sub>4</sub> and CO<sub>2</sub> development in acidic fens. Furthermore, the new peat quality index should aid the estimation of greenhouse gas formation potential resulting from peatland restoration and permafrost thawing and help yield more robust models of trace gas fluxes from peatlands for climate change research.

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## 1 Introduction

Peatlands maintain an imbalance between net primary production and decomposition, leading to the accumulation of large carbon (C) stocks due to the slow mineralization of plant biomass (Clymo, 1983; Gorham, 1991; Botch et al., 1995; Turunen et al., 2002).

5 However, peatlands are also known to be sources for greenhouse gases like CO<sub>2</sub> and CH<sub>4</sub> (i.e. Aselmann and Crutzen, 1989; Charman et al., 1999), which are also important indicators of total C mineralization (Bridgham and Richardson, 1992). As atmospheric concentrations of both CO<sub>2</sub> and CH<sub>4</sub> are increasing rapidly, with consequences for future global climate (Bridgham and Richardson, 1992; Houghton, 2005), it is crucially  
10 important to fully understand both sinks and sources in the global carbon cycle.

Measured emission and formation rates of CO<sub>2</sub> and CH<sub>4</sub> demonstrate strong spatial variation between peatland sites (i.e. Moore et al., 1990; Whalen and Reeburgh, 1990) which may result from such site-specific factors as temperature, oxygen availability and ground water level (Yavitt et al., 1987; Moore and Knowles, 1990; Bridgham and Richardson, 1992; Roulet et al., 1992a; Petrescu et al., 2008). Although there has  
15 been some success in relating water level and temperature to CO<sub>2</sub> and CH<sub>4</sub> emissions within particular wetlands (Roulet et al., 1992b; Walter and Heimann, 2000; Strack and Waddington, 2007; Petrescu et al., 2008), these variables are insufficient for predicting emissions across a variety of peatlands (Whiting and Chanton, 1993). Another important factor that influences the chemical composition, degradability of peat, and its  
20 potential for producing CO<sub>2</sub> and CH<sub>4</sub> is the botanical origin of the plant litter (Moore et al., 2007). For example, *Carex* peat contains much less cellulose and hemicellulose compared to *Sphagnum* peats (Bohlin et al., 1989). Because both carbohydrates are likely substrates for hydrolytic fermentation (Zeikus, 1983) these different peat types  
25 will likely also yield differing amounts of precursors for anaerobic CO<sub>2</sub> formation and methanogenesis.

Although temperature, water saturation, redox conditions, vegetation, and degree of peat decomposition are often similar on a local scale, CO<sub>2</sub> and CH<sub>4</sub> formation rates are

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still often spatially variable at this scale and a peatland may include areas with negligible activity (Svensson and Rosswall, 1984; Whalen and Reeburgh, 1990; Reiche et al., 2008). Consequently, the factors listed above are not sufficient to explain CO<sub>2</sub> and CH<sub>4</sub> formation rates reliably on either large or small spatial scales. In order to reliably estimate the greenhouse gas formation potential of peat in general, a parameter based on both the quality and quantity of bioavailable organic matter present in peat, which should in turn control CO<sub>2</sub> and CH<sub>4</sub> formation (Yavitt and Lang, 1990; Bridgham and Richardson, 1992; Valentine et al., 1994; Christensen et al., 2003; Reiche et al., 2008), may be required. However, there is currently no common definition or widely accepted quantitative index of “organic matter quality” that can be used to determine greenhouse gas emission potential (Rubino et al., 2007).

A previous study demonstrated that thermogravimetry (TG) can easily estimate the decomposition potential of organic matter in upland soils (Rubino et al., 2007). In this study we applied the same technique to derive a quality index for peat organic matter. Using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), we identified the biological precursors of pyrolysis products present in peat samples (Kracht and Gleixner, 2000). The peat quality index was then compared to anaerobic CO<sub>2</sub> and CH<sub>4</sub> formation rates to determine the influence of the chemical composition of peat on the extent of both gas forming processes. We hypothesized that peat with a higher proportion of thermally labile organic matter would correspond to higher potential CO<sub>2</sub> and CH<sub>4</sub> formation rates.

## 2 Materials and methods

### 2.1 Peat sampling

Samples were obtained from an acidic fen (Schlöppnerbrunnen, fen area: 0.8 ha, pH 4.7) located in the northern Fichtelgebirge region in east-central Germany (50°7'54" N, 11°52'51" E, 700 m a.s.l.) as previously described (Reiche et al., 2008). The mean an-

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nual precipitation at this site between 1995–2006 was approximately 953 mm and the mean annual air temperature was 6.1°C. The Schlöppnerbrunnen fen has an average peat accumulation of about 50 cm and soil is Histosol on granite bedrock. Vegetation is dominated by *Carex canescens*, *Carex rostrata*, *Juncus effuses*, *Molinia caerulea*, and *Eriophorum vaginatum*. Ground water moves through the fen from the north to the south (Paul et al., 2006), with higher water saturation in south than in the north due to a slight slope. Thus, the northern part of the fen is naturally affected by water table fluctuations during dry seasons. This fen has been studied in detail with respect to anaerobic microbial processes since 2001. Based on these earlier investigations, peat was sampled at four locations in November 2006, from the middle to the southern part of the fen, following the hydrological gradient. Sampling locations were named C2, D2, sD1, M according to previous investigations (Reiche et al., 2009). The maximum distance between C2 and M was approximately 25 m. Peat obtained at C2 and D2 was dark brown to black in color and the degree of decomposition according to von Post's humification scale (Clymo, 1983) was higher (moderately decomposed, H6-7) than for the brownish peat at sD1 and M (slightly to moderately decomposed H3-5). Peat samples from 0–40 cm depth were obtained using an 8 cm diameter peat corer. Fresh plant litter was removed from the top and cores were separated in 10 cm depth segments (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm, IV: 30–40 cm). Peat samples were then transported to the laboratory in airtight plastic bags at 4°C and processed the same day.

## 2.2 Microcosm incubations and headspace gas determination

To study the formation of CO<sub>2</sub> and CH<sub>4</sub>, 20 g of peat (fresh wt) was placed into a sterile 180 mL incubation flask (Mueller and Krempel, Buelach, Switzerland) in three replicates under a continuous flow of sterile argon. Flasks were closed with rubber stoppers and screw-caps and incubated in the dark with an initial overpressure of ~100 mbar at 15°C. Headspace concentrations of CO<sub>2</sub> and CH<sub>4</sub> were determined every 2 to 3 days over a 31 day incubation period. Headspace gases were measured with Hewlett

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Packard Co. 5980 series II gas chromatographs according to Reiche et al. (2008). First, a sample volume of 100  $\mu$ l was obtained from the headspace of microcosms after shaking them to release gas trapped inside the peat. CO<sub>2</sub> analysis was then carried out by a thermal conductivity detector and CH<sub>4</sub> concentrations were determined with a flame ionization detector.

## 2.3 Analytical techniques

Fresh duplicate peat samples were dried at 105°C for 24 h to determine water content (WC) and then burned at 500°C for 4 h to calculate the ash content as loss on ignition (LOI). Total P, Fe, Al, Mg, Ca, S, H, N and C of dried (60°C for 48 h) and milled (Mixer Mill MM301, Retsch, Germany) peat samples were analyzed with an elemental analyzer (vario EL, Elementar, Germany), by flame atomic absorption spectrometry (Perkin Elmer, 3300, USA), or photometrically (Varian, Cary 1E, USA) after acid digestion (Reiche et al., 2008). Total bacteria in peat depth segments obtained at C2 and D2 were enumerated by the 4,6-diamidino-2-phenylindole (DAPI) method as described in Reiche et al. (2008).

Approximately 5 mg of each dried and milled peat sample (in two replicates) was analyzed by thermogravimetry (Mettler Toledo, TGA/SDTA 851e, Switzerland) (TG) (Pope and Judd, 1977). The mass loss at increasing temperatures (0.17°C s<sup>-1</sup>) was measured under a continuous flow of argon from 60 to 850°C followed by a final combustion under oxygen at 850°C (Rubino et al., 2007). For further calculations, mass loss was then normalized to total pyrolyzable matter (between 40 to 95%, data not shown).

Curie-point pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) (Gleixner et al., 1999) was used to identify major pyrolysis products from selected peat samples (C2 I and III, D2 I, II and IV, M I and IV; two replicates each, ~0.7 mg of each sample) (Schulten and Gleixner, 1999). Peat samples were selected for this analysis with respect to their differences in the peat quality index (described below). Py-GC/MS is a powerful technique to distinguish between plant derived “biodegradable” and more

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“humified” compounds. Pyrolysis products like furanes and substituted phenols that derive from carbohydrates and lignin, respectively, indicate the presence of plant material whereas alkanes and unspecific pyrolysis products like benzol, phenol or naphthalene indicate highly humified organic material (Gleixner et al., 1999; Rubino et al., 2007).

5 Pyrolysis was carried out under helium for 9.9 s at 500°C with a Curie point Pyrolyzer 0316 (Thermo Fisher, USA). Volatile pyrolysis products were separated by gas chromatography (HP 5890, Germany) with a BPX5 capillary column (length, 60 m; inner diameter, 0.32 mm; film thickness, 1 µm; SGE, Germany) and analyzed using an ion trap mass spectrometer (Thermo Fisher, GCQ, USA) (Steinbeiss et al., 2006).

## 10 2.4 Calculations and statistics

Rates for CO<sub>2</sub> and CH<sub>4</sub> formation were determined from the linear increase of headspace and dissolved gas concentrations, calculated from three replicates. Peat samples were then grouped according to their CH<sub>4</sub> and CO<sub>2</sub> forming activities by hierarchical cluster analysis, using the Ward method, based on the Euclidean squared distances (SPPS 15.0, SPPS Inc., Chicago, Illinois, USA). Pearson’s correlation coefficients (*r*) were calculated to test for correlations of anaerobic CO<sub>2</sub> and CH<sub>4</sub> formation with chemical peat parameters (SPPS 15.0, SPPS Inc., Chicago, Illinois, USA).

Evaluation of mass spectra obtained by Py-GC/MS was performed according to Schulten and Gleixner (1999) and Kracht and Gleixner (2000) and was compared to spectral databases like Wiley 6.0 (McLafferty, 2001), the National Institute of Standards and Technology, (NIST, 2002) and the Integrated Spectral Data Base System for Organic Compounds, (AIST, 2001). Means of two replicates from the mass list of pyrolysis spectra, the relative abundances of representative precursor groups (lipids, carbohydrates, lignin, and unspecific pyrolysis products normalized to 1 g pyrolyzable sample), were calculated as the summed peak areas of individual pyrolysis products belonging to the same precursor group (Table 1).

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3 Results

3.1 Chemical properties of peat

The C content of peat samples obtained from C2 and D2 increased from 36% at 0–10 cm depth to more than 50% at 30–40 cm depth, respectively (Table 2). In contrast, amount of C decreased with increasing depth at sD1 and M. Proportion of total N decreased at all sampling areas over depth and yielded concentrations from 2.1 to 0.5%. Corresponding C:N ratios were lowest in the upper peat compared with deeper samples and ranged from 18 to 44 over the 0–40 cm depth profile. H content and loss on ignition ranged from 1.4% to 6.7% and from 31% to 92%, and increased at C2 and D2 with depth, but decreased over depth at the southern sampling locations sD1 and M (Table 2). The water content in peat obtained in the northern areas C2 and D2 ranged from 76 to 87%. At sD1 and M, water content decreased from over 91% in upper depth segments to less than 85% below. The highest amounts of total Fe and Al were obtained in the first depth segment of areas D2, sD1 and M and yielded up to 36.4 and 43.8 mg g (dry wt peat)<sup>-1</sup>. Total concentrations of Mg, Ca, P and S were evenly distributed over depth and sampling location with mean values of ~0.8, 0.3 and 1.3 mg g (dry wt peat)<sup>-1</sup> and 0.3%, respectively (Table 2).

3.2 Microbial formation of CO<sub>2</sub> and CH<sub>4</sub>

Peat soil CO<sub>2</sub> and CH<sub>4</sub> formation varied between sampling location and depth (Table 3). In general, anaerobic CO<sub>2</sub> formation rates decreased strongly with increasing depth at all sampling areas with rates up to 12.7 μmol CO<sub>2</sub> g (dry wt peat)<sup>-1</sup> d<sup>-1</sup> in the upper-most peat segment and below 1.2 μmol CO<sub>2</sub> g (dry wt peat)<sup>-1</sup> d<sup>-1</sup> in deeper segments (Table 3). Microbial CO<sub>2</sub> formation was highest at M, the southernmost sampling area, compared with C2, D2, and sD1 peat samples. We found a positive correlation (*p*<0.01) of anaerobic CO<sub>2</sub> formation rates with total amounts of Fe (*r*=0.95), Al (*r*=0.92) and Ca (*r*=0.77) but not with WC, LOI, and total P, Mg, C, H, N and S

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( $p > 0.05$ ).

Peat obtained from the southern areas sD1 and M showed a potential for  $\text{CH}_4$  formation with an apparent delay of 2 and 7 days, respectively, at all depths and initial methanogenesis could be detected below 20 cm depth at sD1. Methane formation rates ranged between 0.04 and 2.11  $\mu\text{mol CH}_4 \text{ g (dry wt peat)}^{-1} \text{ d}^{-1}$  with a notable increase in the 0–10 cm segment of sD1 and the 10–20 cm segment of M (Table 3). Peat obtained from 0–10 cm depth at C2 and D2 showed a potential formation of  $\text{CH}_4$ , which started after an incubation of approximately 8 and 12 days, respectively. In depths below these, no formation of  $\text{CH}_4$  occurred during the prolonged incubation of 31 days. In general, the formation of  $\text{CH}_4$  was positively correlated with the peat WC ( $r = 0.58$ ,  $p < 0.05$ ).

Peat samples were grouped according to their anaerobic  $\text{CO}_2$  and  $\text{CH}_4$  formation rates into two main clusters using hierarchical cluster analysis in Fig. 1. Rates for  $\text{CO}_2$  and  $\text{CH}_4$  formation below 1.2 and 0.1  $\mu\text{mol g (dry wt peat)}^{-1} \text{ d}^{-1}$ , respectively, indicated less active or inactive peat while rates above suggested active peat. The low rates observed in the inactive, deeper peat segments of C2 and D2 could not be explained by differences in microbial cell numbers. Numbers of DAPI counted cells were approximately  $10^{10}$  cells g [dry wt. peat] $^{-1}$  and were similar at all depths.

Other investigations have demonstrated that the anaerobic  $\text{CO}_2$  and  $\text{CH}_4$  formation rate patterns used to create this peat sample classification do not appear to be subject to seasonal shifts as  $\text{CO}_2$  and  $\text{CH}_4$  formation rates from peat obtained at C2 and D2 from 0 to 40 cm depth during 2006 and 2007 were similar (Reiche et al., 2008, 2009, and data not shown). Additionally, the pattern of aerobic  $\text{CO}_2$  formation rates of these peat samples, measured in oxic microcosms over an incubation period of 24 h (Reiche et al., 2009), also supported this classification. In peat obtained from 0–10 cm depth at C2 and D2, aerobic  $\text{CO}_2$  formation rates were up to 1.4( $\pm 0.5$ ) times higher than anaerobic  $\text{CO}_2$  formation rates. Aerobic rates were lower in depths below 10 cm and approximated anaerobic rates. The high anaerobic  $\text{CO}_2$  and  $\text{CH}_4$  formation rates observed from peat sampled at M from 0 to 30 cm were also observed during 2001 and

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### 3.3 Peat quality

The thermal degradability of organic matter of each peat sample was compared with the mass loss at distinct temperature intervals obtained by the TG technique. Four distinct temperature intervals were determined using variance analyses of mass loss spectra (mean of two replicates). The first temperature interval ranged from 205–360°C (rapid mass loss due to labile particulate organic matter;  $\text{pyOM}_{\text{labile}}$ ), the second from 365–480°C (slower mass loss due to more unspecific and more stable particulate organic matter), the third from 585–630°C (slow mass loss due to more recalcitrant particulate organic matter;  $\text{pyOM}_{\text{recalcitrant}}$ ), and the fourth was the sudden combustion under oxygen at 850°C (highly humified and inert particulate carbon compounds;  $\text{pyOM}_{\text{inert}}$ ). We tested different combinations of these four distinct temperature intervals to calculate a peat quality index with the highest correlation to measured anaerobic microbial  $\text{CO}_2$  and  $\text{CH}_4$  formation rates. The best fit equation for the quality index was expressed as ratio between the sum of mass loss of  $\text{pyOM}_{\text{labile}}$  and  $\text{pyOM}_{\text{recalcitrant}}$  with  $\text{pyOM}_{\text{inert}}$ :

$$\text{QI}_{\text{peat}} = \frac{\text{pyOM}_{\text{labile}} + \text{pyOM}_{\text{recalcitrant}}}{\text{pyOM}_{\text{inert}}}$$

In principle, the higher the quality index the higher the quantity of labile and recalcitrant organic matter should be. For further comparisons, mass loss which was not described by these three selected temperature intervals was expressed as  $\text{pyOM}_{\text{other}}$  (Fig. 2).

The proportion of pyrolyzable  $\text{pyOM}_{\text{labile}}$  (38–44%) was highest in the upper segment (0–10 cm) at all sampling areas. The lowest segments (30–40 cm) yielded 23–35% (Fig. 2). The highest proportion of  $\text{pyOM}_{\text{labile}}$  in the 10–30 cm depth segment was found at area M (41–44%).  $\text{pyOM}_{\text{recalcitrant}}$  reached 2.1–3.2% in the first peat segment of D2, sD1 and M, which was twice as high as in samples obtained from C2 or at depths below 10 cm (Fig. 2). In contrast, the percentage of combustible inert carbon

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compounds (pyOM<sub>inert</sub>) increased with depth from approximately 25% to more than 28%.

Calculating the peat quality index with respect to these three categories yielded values from 0.8 to 1.8. The index was highest in peat samples from the upper most peat segment compared with corresponding segments below (Fig. 3). At sD1 and M, a high index >1.35 was also observed up to 30 cm depth. Quality index was lowest for peat samples below 10 cm depth at C2 and D2. In general, peat of the southern, water-logged sampling areas sD1 and M was less degraded and the amounts of pyOM<sub>labile</sub> in depths below 10 cm was high in comparison with samples obtained from the hydrological and redox instable areas C2 and D2. The mean peat quality index was 1.3 times lower in these areas than in peat samples from sD1 and M (Fig. 3).

### 3.4 Major pyrolysis products of peat

The major Py-GC/MS products of all peat samples and precursor classes, according to the molecule from which each Py-GC/MS product was generated, are given in Table 1. The number of peaks detected during the pyrolysis process increased with depth from 46 (0–10 cm) to 64 (20–30 cm) at C2 and from 44 (0–10 cm) to 80 (30–40 cm) at D2. Peaks at sampling area M between 0–10 cm and 30–40 cm depths were as large as 56. The low retention times, between 10.8 and 27.3 min, in the chromatogram of the Py-GC/MS were indicative for toluene, furan, furaldehyde, phenol, and benzene derivatives (Table 1). A “lignin region” between 28.9 and 43.6 min was dominated by methylphenol and methoxyphenol derivatives. Compounds with high retention time, 45.6 to 63.2 min, and higher molecular weight dominated the “lipid region”, i.e. n-alkens and n-alkans, with a chain length of more than C17. The contribution of carbohydrates, as calculated from the peak area of carbohydrate pyrolysis products, decreased with increasing depth from 20% to 7% at C2 and from 17% to 6% at D2 (Fig. 4). Carbohydrates at the most southern sampling area M reached 18% and were constant at all measured depths. The contribution of lipids to the total pyrogram increased in deeper segments of D2 and M, whereas lignin and carbohydrate pyrolysis products decreased

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with depth. Lipid and lignin contribution to the pyrogram of C2 samples reached approximately 24% at depth I (0–10 cm) and 35% at depth III (20–30 cm). Total pyrolyzable matter in relation to dry matter was approximately 48% in peat samples obtained from 20–40 cm depth and 64, 48, 59% in upper peat depths of C2, D2 and M, respectively.

5 The content of lignin was positively correlated with the anaerobic formation rates of CO<sub>2</sub> ( $r=0.86$ ,  $p<0.01$ ) and CH<sub>4</sub> ( $r=0.93$ ,  $p<0.05$ ), whereas the content of lipids were negatively correlated with the anaerobic formation rates of CO<sub>2</sub> ( $r=-0.84$ ,  $p<0.01$ ) and CH<sub>4</sub> ( $r=-0.91$ ,  $p<0.05$ ).

## 4 Discussion

### 10 4.1 Peat composition

The percentage of pyOM<sub>labile</sub> during TG analyses was highest in the 0 to 10 cm segment at C2, D2, and sD1. Similarly, the percentage of pyOM<sub>recalcitrant</sub> was highest in the uppermost segment at D2, sD1, and M (Fig. 2). This high percentage likely indicates an input of fresh and therefore less decomposed plant litter, i.e. from dead roots and leaves of growing vegetation. This vegetation can further increase the pool of easy available carbon substrates, such as carbohydrates and amino acids, through the leakage of exudates from living plant roots (Grayston et al., 1996; Yan et al., 2008). The large number of detectable peaks obtained with Py-GC/MS at C2 and D2 of the lower segments, compared to the upper peat segments, demonstrated a high complexity of organic matter in deep peat segments. Additionally, the increased percentage of unspecific pyrolysis products in depths below 10 cm was indicative of more humified peat.

In all pyrograms, lipids, lignin, and to a lesser extent, carbohydrates, were the major pyrolysis precursors (Fig. 4 and Table 1). Large amounts of long-chain lipids accumulated in deeper peat segments (Fig. 4 and Table 1). Several studies have shown that aliphatic biopolymers are highly resistant to biodegradation and can be well preserved

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in soils (Gleixner et al., 2001; Winkler et al., 2005; Otto and Simpson, 2006). The high proportion of linear alkane/alkene peaks in the Py–GC/MS data in peat segments below 10 cm at D2 and M suggested that aliphatic polymer material is an important part of the lower peat organic matter (Fig. 4 and Table 1). Alkanes/alkenes with chain lengths of more than C16 are common compounds that originate from plant aliphatic polymers such as leaf and root waxes, like cutin- and suberin-derived polymers (Nip et al., 1986; Tegelaar et al., 1995; Gleixner et al., 2001; Kögel-Knabner, 2002). The proportion of carbohydrates in deeper peat segments (II, III, IV) represented more than 30% of the relative carbohydrate proportion in peat segment I. However, we observed almost no difference in the patterns of carbohydrate-related peaks in the different peat segments. Carbohydrates are known to be recycled or newly formed in soils during decomposition (Gleixner et al., 2002) and this may also occur in peat (Kracht and Gleixner, 2000).

## 4.2 Microbial formation of CO<sub>2</sub> and CH<sub>4</sub>

This fen site has been investigated intensively within a national interdisciplinary research group since 2001. According to previous investigations (Küsel et al., 2008; Reiche et al., 2008, 2009), CO<sub>2</sub> and CH<sub>4</sub> formation rates were highly spatially variable and depended neither on peat depth or the hydrological gradient at this site. In all areas, anaerobic CO<sub>2</sub> formation rates were highest in the upper peat segments, suggesting favorable conditions for microorganisms in the segment most influenced by growing vegetation. Positive correlation of CO<sub>2</sub> formation rates with the total amounts of Fe confirmed that high Fe(III)-reducing activity in the upper most peat segment (Küsel et al., 2008) may contribute to anaerobic CO<sub>2</sub> formation. The positive correlation of CO<sub>2</sub> formation rates with Al and Ca in this study can not be attributed to a microbial respiratory process and are better explained by co-precipitation with Fe(III)-oxides during oxygenation or drying events.

Peat below 10 cm depth at C2 and D2 did not form CH<sub>4</sub> during an incubation period of 31 days. In addition, the CO<sub>2</sub> formation rates were very low, although numbers of DAPI counted cells were in the same order of magnitude as in segment I. Peat sampled

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at areas sD1 and M decreased in CH<sub>4</sub> formation rates with increasing depth, similar to other peatlands (Hughes et al., 1999; van den Pol-van Dasselaar and Oenema, 1999; Chow et al., 2006). The activity of methanogenically-active peat segments was in the range as has been reported for boreal peatlands (Bergman et al., 2000; Galand et al., 2005; Metje and Frenzel, 2007; Rooney-Varga et al., 2007). In general, northern wetland CH<sub>4</sub> emissions contribute 10–44 Tg of the greenhouse gas methane (CH<sub>4</sub>) annually (Mikaloff Fletcher et al., 2004; Zhuang et al., 2004; Walter et al., 2006). The long onset of CH<sub>4</sub> formation in the upper peat segments and the low to negligible CH<sub>4</sub> forming activity of deeper peat segments suggested that CH<sub>4</sub> production is not a significant pathway of carbon flow out of this fen. The high spatial heterogeneity of the rates observed even within a small field site like this fen suggests a need for more replicate studies of CO<sub>2</sub> and CH<sub>4</sub> emission rates. Adequate assessment of the contribution of peatlands to the global CO<sub>2</sub> and CH<sub>4</sub> budget will require not only field measurements of gas fluxes over the complete season and a wide range of different peatland sites for CH<sub>4</sub> fluxes Crill et al. (1988), but also at different areas within the same peatland site.

### 4.3 Link of peat quality to microbial activity

The quality of organic matter is a key factor controlling the rate of organic matter mineralization (Yavitt and Lang, 1990; Bridgham and Richardson, 1992; Crozier et al., 1995; Wagner et al., 2005). The poor substrate quality of highly decomposed, humified peat limits both CO<sub>2</sub> and CH<sub>4</sub> production rates, even though the peat can be up to 95% organic matter (Bridgham and Richardson, 1992). Many quality indexes have been proposed in the past, but there is currently no common definition or widely accepted quantitative index of “quality” (Rubino et al., 2007). For example, the ratio of C to N concentration (C:N ratio) or the ratio of lignin to N concentration (lignin: N ratio), have been frequently used as an index of litter quality (Taylor et al., 1989; Enriquez et al., 1993; Valentine et al., 1994; Gholz et al., 2000; Moore et al., 2007). Lignin: N ratios can provide a modest explanation of peat decomposition rates (Moore et al., 2005). In this study, the anaerobic CO<sub>2</sub> formation rates observed correlated negatively with their

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corresponding  $C:N$  ratios ( $r=-0.60$ ,  $p<0.05$ ), but did not with the lignin:  $N$  ratios. In contrast,  $CH_4$  formation rates did not correlate with  $C:N$  or lignin:  $N$  ratios. However, the low  $C:N$  ratios in the upper peat segment (Table 2) suggested a higher peat quality than in depths below. Other correlations indicated that less decomposed plant biomass rich in lignin and poor in lipids at area M and in upper peat of areas C and D is a prerequisite for  $CO_2$  and  $CH_4$  formation in this fen. This finding was confirmed by the von Post's humification scale (Clymo, 1983). However, this was not sufficient to explain the differences of  $CO_2$  and  $CH_4$  formation at all depths.

The TG measurements showed that peat quality can be described as ratio between the sum of labile and recalcitrant carbon compounds and the proportion of highly humified inert C-based compounds. In principle, the lower the quality index, the higher the quantity of inert C-based compounds in the peat should be. Consequently, peat with a high quality index will also show higher concentrations of easily biodegradable organic matter from either  $pyOM_{labile}$  or  $pyOM_{recalcitrant}$ .

The thermal degradability of peat obtained with TG might not agree with microbial availability of peat organic matter. However, assuming that the fraction of  $pyOM_{labile}$  represents easily available substrates for microorganisms (Gleixner et al., 2002), our results showed that peat was active in anaerobic  $CO_2$  and  $CH_4$  formation when this fraction was above 35% and the  $QI_{peat}$  was above 1.35. Correlating TG with Py-GC/MS data suggested that carbohydrates were a relevant part of the  $pyOM_{labile}$  ( $r=0.87$ ,  $p<0.05$ ). A positive correlation ( $r=0.88$ ,  $p<0.01$ ) with  $CO_2$  formation was also found with the fraction of  $pyOM_{recalcitrant}$ . This indicated that thermally recalcitrant carbon compounds can be also efficiently used as a carbon source by microorganisms.

The new peat quality index was successfully used to estimate the formation of the greenhouse gases  $CO_2$  and  $CH_4$  at four areas from this fen. Although it only ranged from 0.8 to 1.8, this small range may be enlarged depending on the proportion of the  $pyOM$  fractions resulting from the diverse botanical origins of peat organic matter found in other peatlands. How stable this current peat quality index is with respect to the potential  $CO_2$  and  $CH_4$  formation is still an open question. Mesocosm experiments

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indicate that a change in the size and/or quality of the labile carbon pool can occur relatively quickly (less than 6 years) (Keller et al., 2004). More research on different types of peatlands, i.e. *Sphagnum*-peat bogs, boreal peatlands, Siberian bogs, and degraded peatland sites is needed to confirm whether this new quality index can be used to estimate the greenhouse gas formation potential of peatlands in general.

## 5 Conclusions

Although parameters like water table depth, moisture content, loss on ignition, and the C:N ratio are easy to determine and can be correlated in several cases with the potential formation rates of CO<sub>2</sub> and CH<sub>4</sub>, they are often not sufficient to explain small spatial heterogeneities in greenhouse gas formation. Our new peat quality index was an easy tool to estimate the greenhouse gas formation potential for both CO<sub>2</sub> and CH<sub>4</sub>. The content of thermally labile and recalcitrant organic compounds appeared to be the most important factor controlling CO<sub>2</sub> and CH<sub>4</sub> formation. Therefore, the direct link presented here between peat quality and microbial CO<sub>2</sub> and CH<sub>4</sub> formation should facilitate predictions with a robust theoretical basis for modeling and calculating element cycles or trace gas fluxes from peatlands for climate change research.

*Acknowledgements.* We thank S. Rühlow and J. Kirschstein for technical assistance and support during Py-GC/MS and TG measurements. The authors thank J. Gelbrecht (IGB Berlin) for providing technical equipment and P. Bouwma for critical reading. This work is part of the research group FOR 562 “Dynamics of soil processes under extreme meteorological boundary conditions” supported by the Deutsche Forschungsgemeinschaft DFG. To the best of their knowledge, the authors of the present manuscript declare that the experiment described above complied with German law.

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**Table 1.** Retention time, peak identification, precursor groups, and mass spectrometric characteristics of major pyrolysis products present in selected peat samples (C2, D2, M, according to Fig. 4) obtained over depth (0–40 cm) of an acidic fen.

| Retention time<br>(min) | Identified compound                      | Precursor <sup>a</sup> | Molecular weight<br>(g mol <sup>-1</sup> ) | Base peak<br>(m/z) <sup>b</sup> | Characteristic fragments<br>(m/z) |
|-------------------------|------------------------------------------|------------------------|--------------------------------------------|---------------------------------|-----------------------------------|
| 10.6                    | 2-Methylfuran                            | ch                     | 82                                         | 81                              | 82, 53                            |
| 13.3                    | Benzene                                  | us                     | 78                                         | 78                              | 77, 58, 51                        |
| 17.9                    | Toluene                                  | us                     | 92                                         | 91                              | 92, 65, 50                        |
| 19.5                    | 2[3H]Furanone                            | ch                     | 84                                         | 55                              | 84, 54                            |
| 20.9                    | 2-Furaldehyde                            | ch                     | 96                                         | 95                              | 96, 39, 37                        |
| 22.1                    | Dimethylbenzene                          | us                     | 106                                        | 91                              | 106                               |
| 23.1                    | Ethylbenzen/Styrene                      | us                     | 106                                        | 91                              | 78                                |
| 25.8                    | 5-Methyl-2-furaldehyde                   | ch                     | 110                                        | 109                             | 110, 53, 50                       |
| 26.2                    | Phenol                                   | us                     | 94                                         | 94                              | 66                                |
| 27.4                    | 4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one   | ch                     | 114                                        | 114                             | 58, 85, 57                        |
| 28.9                    | 2-Methylphenol                           | us                     | 108                                        | 108                             | 107                               |
| 29.6                    | 3,4-Methylphenol                         | us                     | 108                                        | 107                             | 108, 77, 79                       |
| 30.2                    | 2-Methoxyphenol                          | lg                     | 124                                        | 124                             | 109, 81                           |
| 32.5                    | p-Ethylphenol                            | lg                     | 122                                        | 107                             | 77, 122                           |
| 33.4                    | 4-Methyl-2-methoxyphenol                 | lg                     | 138                                        | 138                             | 123                               |
| 33.9                    | unknown                                  | n.d.                   | n.d. <sup>c</sup>                          | 57                              | 85, 70                            |
| 34.3                    | 4-Vinylphenol (4-ethenylphenol)          | lg                     | 120                                        | 120                             | 91                                |
| 35.9                    | 4-Ethyl-2-methoxyphenol                  | lg                     | 152                                        | 137                             | 152                               |
| 37.2                    | 4-Vinyl-2-methoxyphenol                  | lg                     | 150                                        | 150                             | 135, 107                          |
| 39.9                    | 4-Formyl-2-methoxyphenol                 | lg                     | 152                                        | 151                             | 152                               |
| 40.8                    | trans-4-(2-propenyl)-2-methoxyphenol     | lg                     | 164                                        | 164                             | 116                               |
| 42.1                    | 4-Acetyl-2-methoxyphenol                 | lg                     | 166                                        | 151                             | 166                               |
| 42.7                    | Levogluconane                            | ch                     | 162                                        | 60                              | 73                                |
| 43.6                    | 4-Vinyl-2,6-dimethoxyphenol              | lg                     | 180                                        | 180                             | 165, 137                          |
| 45.6                    | n-C17 alkene                             | li                     | n.d.                                       | 55                              | 69, 83                            |
| 46.3                    | n-alkene                                 | li                     | n.d.                                       | 111                             | 70, 55, 69                        |
| 47.0                    | Trans-4-(2-propenyl)-2,6-dimethoxyphenol | lg                     | 194                                        | 194                             | 131                               |
| 47.8                    | n-C18 alkene                             | li                     | n.d.                                       | 55                              | 69, 83                            |
| 47.9                    | n-C18 alkane                             | li                     | n.d.                                       | 57                              | 71, 85                            |
| 47.9                    | 4-Acetyl-2,6-dimethoxyphenol             | lg                     | 196                                        | 181                             | 196                               |
| 49.9                    | n-C19 alkene                             | li                     | n.d.                                       | 55                              | 69, 83                            |
| 49.9                    | n-C19 alkane                             | li                     | n.d.                                       | 57                              | 71, 85                            |
| 51.8                    | n-C20 alkene                             | li                     | n.d.                                       | 55                              | 69, 83                            |
| 51.9                    | n-C20 alkane                             | li                     | n.d.                                       | 57                              | 71, 85                            |
| 53.8                    | n-C21 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |
| 55.6                    | n-C22 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |
| 57.3                    | n-C23 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |
| 59.0                    | n-C24 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |
| 61.0                    | n-C25 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |
| 63.1                    | n-C26 alkane/alkene                      | li                     | n.d.                                       | 55                              | 57, 69, 71                        |

<sup>a</sup> ch=carbohydrates; lg=lignins; li=lipids; us=unspecific

<sup>b</sup> mass-to-charge ratio

<sup>c</sup> could not be determined

**BGD**

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**Table 2.** Chemical characteristics of peat obtained from an acidic fen (pH 4.7) along a hydrological gradient (from the middle to the south C2→D2→sD1→M) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm, and IV: 30–40 cm) in November 2006.

| sample                | WC <sup>a</sup> | LOI <sup>b</sup> | P <sub>total</sub>                  | Fe <sub>total</sub> | Al <sub>total</sub> | Mg <sub>total</sub> | Ca <sub>total</sub> | S <sub>total</sub> | H <sub>total</sub> | N <sub>total</sub> | C <sub>total</sub> | C/N  |
|-----------------------|-----------------|------------------|-------------------------------------|---------------------|---------------------|---------------------|---------------------|--------------------|--------------------|--------------------|--------------------|------|
| depth                 | (%)             |                  | (mg g [dry wt peat] <sup>-1</sup> ) |                     |                     |                     |                     | (%)                |                    |                    | ratio              |      |
| C2 (I) <sup>c</sup>   | 80.3            | 69.6             | 1.8                                 | 9.5                 | 7.2                 | 0.9                 | 0.2                 | 0.3                | 4.5                | 2.0                | 36.2               | 18.1 |
| C2 (II) <sup>c</sup>  | 81.7            | 83.3             | 1.5                                 | 5.9                 | 4.1                 | 0.3                 | 0.1                 | 0.3                | 5.4                | 2.1                | 47.3               | 22.5 |
| C2 (III) <sup>c</sup> | 81.6            | 88.2             | 0.8                                 | 6.2                 | 3.3                 | 0.3                 | 0.3                 | 0.2                | 5.5                | 1.5                | 51.5               | 34.3 |
| C2 (IV) <sup>c</sup>  | 85.7            | 85.9             | 1.0                                 | 3.2                 | 2.3                 | 0.5                 | 0.2                 | 0.2                | 6.0                | 1.2                | 50.4               | 42.0 |
| D2 (I) <sup>c</sup>   | 87.0            | 74.6             | 1.5                                 | 36.4                | 43.8                | 0.7                 | 0.6                 | 0.3                | 4.5                | 1.7                | 36.4               | 21.4 |
| D2 (II) <sup>c</sup>  | 76.4            | 62.3             | 1.2                                 | 10.4                | 6.7                 | 0.8                 | 0.2                 | 0.2                | 4.4                | 1.3                | 37.6               | 28.9 |
| D2 (III) <sup>c</sup> | 79.8            | 91.6             | 0.8                                 | 5.6                 | 4.3                 | 0.2                 | 0.3                 | 0.3                | 6.7                | 1.3                | 55.3               | 42.5 |
| D2 (IV) <sup>c</sup>  | 84.4            | 85.4             | 1.0                                 | 4.7                 | 3.4                 | 0.5                 | 0.2                 | 0.3                | 6.0                | 1.3                | 51.0               | 39.2 |
| sD1 (I)               | 90.9            | 77.7             | 1.4                                 | 28.7                | 20.2                | 0.6                 | 0.3                 | 0.4                | 4.5                | 1.7                | 39.0               | 22.9 |
| sD1 (II)              | 90.3            | 74.8             | 1.5                                 | 5.7                 | 2.8                 | 1.0                 | 0.3                 | 0.5                | 4.7                | 1.4                | 37.7               | 26.9 |
| sD1 (III)             | 78.6            | 52.1             | 1.3                                 | 6.9                 | 2.1                 | 1.6                 | 0.2                 | 0.3                | 3.4                | 1.0                | 29.4               | 29.4 |
| sD1 (IV)              | 61.8            | 31.3             | 1.3                                 | 6.9                 | 1.8                 | 2.3                 | 0.1                 | 0.1                | 1.4                | 0.5                | 21.9               | 43.8 |
| M (I)                 | 91.2            | 86.3             | 1.3                                 | 19.9                | 15.9                | 0.4                 | 0.4                 | 0.3                | 5.3                | 1.8                | 43.1               | 23.9 |
| M (II)                | 93.3            | 85.0             | 1.5                                 | 8.8                 | 7.8                 | 0.6                 | 0.3                 | 0.4                | 5.3                | 1.5                | 41.6               | 27.7 |
| M (III)               | 92.9            | 82.5             | 1.4                                 | 4.5                 | 3.2                 | 0.6                 | 0.3                 | 0.6                | 5.1                | 1.4                | 41.5               | 29.6 |
| M (IV)                | 85.9            | 68.8             | 1.5                                 | 7.1                 | 3.8                 | 1.1                 | 0.3                 | 0.5                | 4.6                | 1.3                | 37.6               | 28.9 |

<sup>a</sup> water content

<sup>b</sup> loss on ignition

<sup>c</sup> some data were obtained from Reiche et al. (2009)

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**Table 3.** Anaerobic formation rates of CO<sub>2</sub> and CH<sub>4</sub>, and the onset of methanogenesis in peat obtained from an acidic fen (pH 4.7) along a hydrological gradient (from the middle to the south C2→D2→sD1→M) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm and IV: 30–40 cm) in November 2006 (*n*=3).

| Sample                | CO <sub>2</sub> formation rate<br>( $\mu\text{mol g [dry wt peat]}^{-1} \text{d}^{-1}$ ) | CH <sub>4</sub> formation rate<br>( $\mu\text{mol g [dry wt peat]}^{-1} \text{d}^{-1}$ ) | Onset of CH <sub>4</sub> formation<br>(day) |
|-----------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|---------------------------------------------|
| C2 (I) <sup>a</sup>   | 4.3                                                                                      | 0.14                                                                                     | ~ 8                                         |
| C2 (II) <sup>a</sup>  | 1.0                                                                                      | 0.00                                                                                     | n.a. <sup>b</sup>                           |
| C2 (III) <sup>a</sup> | 0.8                                                                                      | 0.00                                                                                     | n.a.                                        |
| C2 (IV) <sup>a</sup>  | 0.8                                                                                      | 0.00                                                                                     | n.a.                                        |
| D2 (I) <sup>a</sup>   | 12.7                                                                                     | 0.32                                                                                     | ~ 12                                        |
| D2 (II) <sup>a</sup>  | 1.2                                                                                      | 0.00                                                                                     | n.a.                                        |
| D2 (III) <sup>a</sup> | 0.9                                                                                      | 0.00                                                                                     | n.a.                                        |
| D2 (IV) <sup>a</sup>  | 0.6                                                                                      | 0.00                                                                                     | n.a.                                        |
| sD1 (I)               | 9.7                                                                                      | 1.25                                                                                     | ~ 5                                         |
| sD1 (II)              | 1.7                                                                                      | 0.32                                                                                     | ~ 2                                         |
| sD1 (III)             | 0.7                                                                                      | 0.08                                                                                     | 1                                           |
| sD1 (IV)              | 0.1                                                                                      | 0.04                                                                                     | 1                                           |
| M (I)                 | 8.9                                                                                      | 0.38                                                                                     | ~ 7                                         |
| M (II)                | 4.9                                                                                      | 2.11                                                                                     | ~ 2                                         |
| M (III)               | 2.3                                                                                      | 0.80                                                                                     | ~ 2                                         |
| M (IV)                | 0.8                                                                                      | 0.07                                                                                     | ~ 2                                         |

<sup>a</sup> some data were obtained from Reiche et al. (2009)

<sup>b</sup> no methanogenic activity within 31 days of incubation

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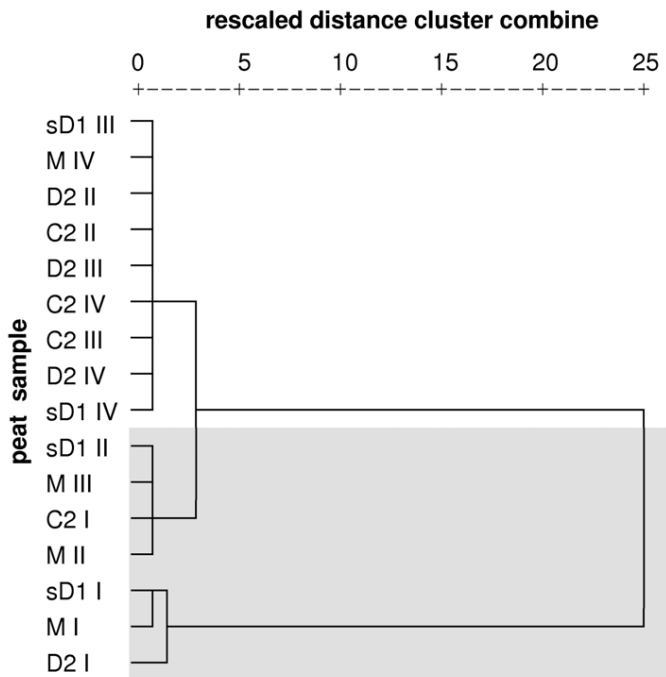
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**Fig. 1.** Grouping of peat samples according to their CO<sub>2</sub> and CH<sub>4</sub> formation rates using hierarchical cluster analysis. The dendrograms were carried out using the Ward method, based on Euclidean squared distances. Samples were obtained at different areas along a hydrological gradient from an acidic fen (from the middle to the south C2→D2→sD1→M) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm, IV: 30–40 cm). Peat samples yielding CH<sub>4</sub> and CO<sub>2</sub> formation rates above 0.1 and 1.2 μmol g (dry wt peat)<sup>-1</sup> d<sup>-1</sup>, respectively, are highlighted (grey box).

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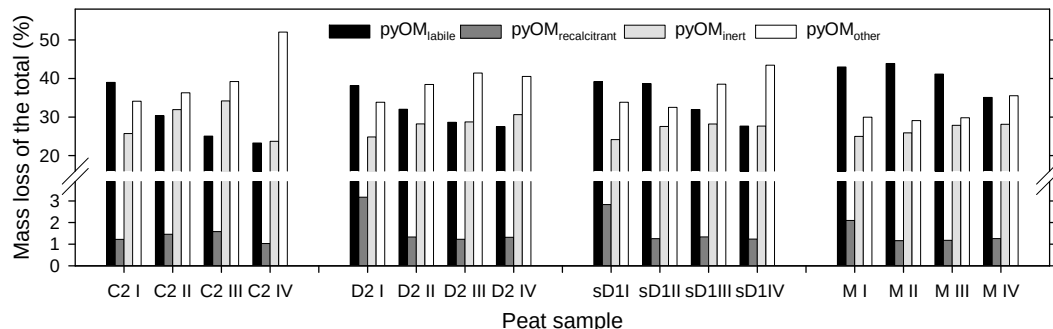
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**Fig. 2.** Percentage of mass loss during thermogravimetry analyses ( $n=2$ ) over three temperature intervals corresponding to labile carbon ( $\text{pyOM}_{\text{labile}}$ : 205–360°C), recalcitrant carbon ( $\text{pyOM}_{\text{recalcitrant}}$ : 365–480°C) and inert carbon ( $\text{pyOM}_{\text{inert}}$ : 850°C+oxygen) with respect to total pyrolyzable organic matter. Mass loss which is not explained by these three temperature intervals is expressed by  $\text{pyOM}_{\text{other}}$ . Peat was obtained from 4 different sampling sites in an acidic fen along a hydrological gradient (from the middle to the south C2→D2→sD1→M) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm and IV: 30–40 cm).

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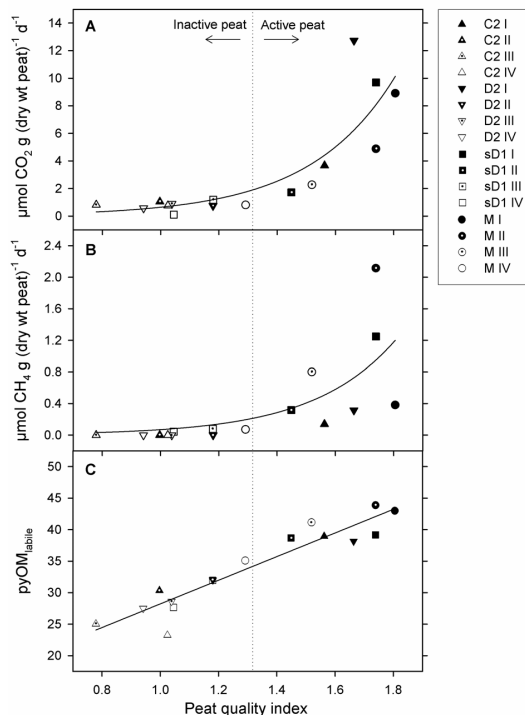
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**Fig. 3.** Correlation of peat quality index as ratio between the sum of thermal labile and recalcitrant C-based compounds and inert carbon compounds,  $(\text{pyOM}_{\text{labile}} + \text{pyOM}_{\text{recalcitrant}}) / \text{pyOM}_{\text{inert}}$ , obtained with thermogravimetry analyses with formation rates of CO<sub>2</sub> (A) and CH<sub>4</sub> (B), and proportion of thermal labile particulate organic matter (pyOM<sub>labile</sub>) (C). Peat was sampled at 4 sampling sites along a hydrological gradient of an acidic fen (from the middle to the south C2→D2→sD1→M) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm and IV: 30–40 cm). The best fit equation for CO<sub>2</sub> formation, CH<sub>4</sub> formation and pyOM<sub>labile</sub> with peat quality is expressed by:  $y = 0.025e^{3.19x}$  ( $r^2 = 0.71$ ,  $p < 0.01$ ),  $y = 0.002e^{3.54x}$  ( $r^2 = 0.49$ ,  $p < 0.01$ ) and  $y = 18.75x + 9.5$  ( $r^2 = 0.89$ ,  $p < 0.01$ ), respectively.

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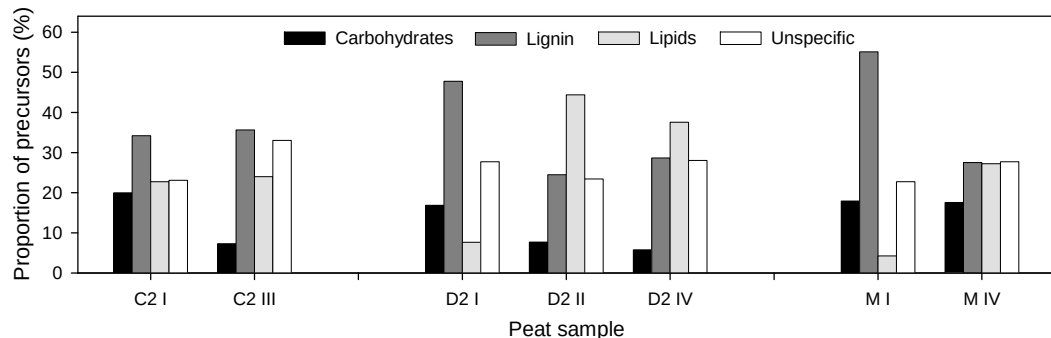
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**Fig. 4.** Relative proportion (% of total pyrolyzable compounds) of identified compounds grouped by precursor classes of chemical compounds (carbohydrates, lignin, lipids and unspecific C-based compounds) from different peat samples obtained from an acidic fen (C2: middle part, D2: more southern part, M: most southern part) over 4 depths (I: 0–10 cm, II: 10–20 cm, III: 20–30 cm and IV: 30–40 cm). Compounds were identified using Curie-point pyrolysis-gas chromatography/mass spectrometry ( $n=2$ ).

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