Influences on mineralisation rates of organic soils under agriculture

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Abstract

Even though peatlands only cover a minor fraction of the global terrestrial surface, drained organic soils are major contributors to worldwide greenhouse gas (GHG) emissions. Due to alterations of hydrological and biogeochemical processes caused by drainage and land-use these soils are now hotspots of GHG emissions from agricultural soils. Caused by both drainage-induced mineralisation of soil organic matter (SOM) and anthropogenic modifications of the soil profile, like peat-sand mixing, large areas of former peatlands underwent a secondary pedogenetic transformation. A large share of these organic soils have strongly degraded topsoils with low soil organic carbon (SOC) contents at the boundary between mineral and organic soil, with regard to definition. Previous research has shown that increasing anthropogenic disturbance enhances GHG emissions from organic soils, but it remains sparsely studied which indicators influence their vulnerability.

Therefore, the aim of this thesis was to investigate the sensitivity of drained organic soils under agricultural use to mineralisation and to determine hydrological and biogeochemical parameters that influence their GHG emissions. Thereby the focus was on low carbon (C) organic soils and peat-sand mixtures, where applied sand was mixed into the uppermost peat layer. For this purpose, two laboratory experiments were conducted using the valuable selection of samples of the first German Agricultural Soil Inventory. The first part of the thesis was directed at the evaluation of SOM vulnerability of disturbed organic soils using a broad range of samples, including C-rich and low C organic soils as well as C-rich mineral soils. The second and third part of the thesis elucidated the influence of hydrological and biogeochemical soil properties as well as chemical composition of the peat substrate on mineralisation rates by comparing peat-sand mixtures and strongly degraded organic soils of bog and fen peat.

In the first experiment, the potential carbon dioxide (CO_2) production rates of 62 soil samples (76–526 g kg^{-1} SOC) were measured under aerobic conditions. Bog and fen peat samples were grouped according to their degree of disturbance using mapped soil information. The results indicated that SOM vulnerability increased with increasing degree of anthropogenic disturbance and concurrently decreasing SOC content. Additionally, the variability of CO_2 production rates increased with increasing disturbance. Even though a clear influence of a single soil property was not found, mineralisation rates tended to be increased with narrow C:N ratios, high pH-values and high contents of plant-available phosphorus (P).

In the second experiment, topsoil and subsoil columns from ten different organic soils under grassland use were incubated for six months. Previously to launch, all columns were water-saturated. During the incubation, the columns were drained stepwise and concentrations of CO_2, nitrous oxide (N_2O) and methane (CH_4) were measured continuously. The chemical composition of all samples was analysed using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and wet chemical extractions for fibre analysis. CO_2 fluxes and water-filled pore space (WFPS) showed a parabolic dependence, with maximum CO_2 fluxes at 84% WFPS. Thereby magnitudes of topsoil fluxes clearly outreached subsoil fluxes. The highly variable N_2O fluxes reached maximum values at WFPS over 80%. This implies that – under equilibrium conditions – highest GHG emissions in the field would occur at a water table of 20 to 60 cm below the surface. Systematic influences of sand addition or peat type on GHG emissions were not discovered. However, slight differences in CO_2 fluxes were found between the well-preserved subsoils. High densities of plant-available P and potassium (K) correlated with maximum values of CO_2 and N_2O fluxes. The chemical composition of bog and fen peat was similar for the topsoils, while the subsoil samples among themselves were differentiable by their botanical origin. Overall subsoils had higher shares of carbohydrates and aromatic compounds than topsoils. Differences in decomposition between topsoil and subsoil alone, evident from the age of the samples, fell short in explaining these higher amounts in subsoils. No reliable indicators describing the influence of peat quality on decomposition were detected.

All in all, this thesis improved the understanding of SOM decomposition in organic soils under agricultural use by leaning on a broad sample basis and including low C organic soils. The results showed that especially peat-derived soils with low SOC contents had potentially high GHG emissions. The variability of GHG emissions and the SOM vulnerability for decomposition increased with increasing degree of anthropogenic disturbance, suggesting that peat-sand mixtures do not seem like a mitigation option for GHG emissions. The nutrient status of N, P and K, probably heavily influenced by fertilization, seemed to be the most important parameter for peat mineralisation, overshadowing the influence of peat type, chemical composition and sand addition. Furthermore, the findings of this thesis imply that the chemical composition of topsoil peat is a consequence of decomposition instead of a source behind higher mineralisation rates compared with subsoil peat. Thus, a decrease in peat quality might not necessarily slow down future decomposition in drained organic soils.

Zusammenfassung

Obwohl Moore nur einen kleinen Teil der globalen Landoberfläche bedecken, tragen entwässerte organische Böden wesentlich zu den weltweiten Treibhausgasemissionen (THG-Emissionen) bei. Aufgrund von Veränderungen der spezifischen hydrologischen und biogeochemischen Prozesse, die durch Entwässerung und Landnutzung verursacht werden, sind diese Böden heute Hotspots der THG-Emissionen aus landwirtschaftlichen Böden. Sowohl durch die entwässerungsbedingte Mineralisierung der organischen Bodensubstanz als auch durch anthropogene Veränderungen des Bodenprofils, wie z.B. die Vermischung von Torf und Sand, kam es zur sekundären pedogenetischen Transformation in großen Flächen ehemaliger Moore. Ein großer Anteil dieser organischen Böden hat stark degradierte Oberböden mit niedrigen Gehalten an organischem Kohlenstoff (SOC) an der definitorischen Grenze zwischen mineralischem und organischem Boden. Bisherige Forschungen haben gezeigt, dass zunehmende anthropogene Störungen die THG-Emissionen aus organischen Böden erhöhen, jedoch ist noch wenig untersucht welche Indikatoren die Vulnerabilität dieser Böden beeinflussen.

Ziel dieser Arbeit war es daher, die Empfindlichkeit von drainierten, organischen Böden unter landwirtschaftlicher Nutzung gegenüber Mineralisierung zu untersuchen und hydrologische und biogeochemische Parameter zu bestimmen, die deren THG-Emissionen beeinflussen. Dabei lag der Fokus zusätzlich auf organischen Böden mit niedrigem Kohlenstoff (C)-Gehalt und Torf-Sand-Gemischen, bei denen aufgebrachter Sand in die oberste Torfschicht eingemischt wurde. Zu diesem Zweck wurden zwei Laborexperimente unter Verwendung der Proben der ersten deutschen Bodenzustandserhebung Landwirtschaft durchgeführt. Der erste Teil der Arbeit befasste sich mit der Bewertung der Vulnerabilität organischer Bodensubstanz gestörter, organischer Böden unter Verwendung eines breiten Spektrums von Proben einschließlich C-reicher und C-armer organischer Böden sowie C-reicher Mineralböden. Der zweite und dritte Teil der Arbeit befassen sich mit dem Einfluss hydrologischer und biogeochemischer Bodeneigenschaften sowie der chemischen Zusammensetzung des Torfsubstrats auf die Torfmineralisierung. Dafür wurden Torf-Sand-Gemische und stark degradierte, organische Böden aus Hoch- und Niedermoortorf verglichen.

Im ersten Experiment wurden die potentiellen Kohlenstoffdioxid (CO_2)-Produktionsraten von 62 Bodenproben (76-526 g kg^{-1} SOC) unter aeroben Bedingungen gemessen. Die Gruppierung der Hoch- und Niedermoortorfproben erfolgte anhand der Bodeninformationen nach dem Grad der anthropogenen Beeinträchtigung. Die Ergebnisse zeigten, dass die Vulnerabilität der organischen Bodensubstanz, mit zunehmendem Grad der anthropogenen Störung und gleichzeitig abnehmendem SOC-Gehalt, zunahm. Zusätzlich erhöhte sich die Variabilität der CO_2-Produktionsraten mit steigendem Störungsgrad. Obwohl kein eindeutiger Einfluss einer einzelnen Bodeneigenschaft gefunden wurde, waren die Mineralisierungsraten bei engen C:N-Verhältnissen, hohen pH-Werten und hohen Gehalten an pflanzenverfügbarem Phosphor (P) tendenziell erhöht.

Im zweiten Experiment wurden Oberboden- und Unterbodensäulen aus zehn verschiedenen Mooren unter Grünlandnutzung für sechs Monate inkubiert. Vor dem Start des Experiments wurden alle Säulen wassergesättigt, anschließend wurden die Säulen schrittweise entwässert und kontinuierlich die Konzentrationen von CO_2, Lachgas (N_2O) und Methan (CH_4) gemessen. Die chemische Zusammensetzung des Torfes wurde mittels ^{13}C-Kernresonanzspektroskopie (NMR) und nasschemischen Extraktionen zur Faseranalyse bestimmt. Die CO_2-Flüsse und der wassergefüllte Porenraum (WFPS) zeigten eine parabolische Abhängigkeit, mit maximalen CO_2-Flüssen bei 84% WFPS. Dabei übertrafen die Größenordnungen der Oberbodenflüsse die der Unterbodenflüsse deutlich. Die insgesamt sehr variablen N_2O-Flüsse erreichten Maximalwerte bei einem WFPS von über 80%. Unter Gleichgewichtsbedingungen wären daher im Feld die höchsten THG-Emissionen bei einem Grundwasserspiegel von 20 – 60 cm unter der Geländeoberkante zu erwarten. Systematische Einflüsse auf die THG-Emissionen durch Sandbeimischung oder Torfart wurden nicht entdeckt, jedoch wurden leichte Unterschiede zwischen den CO_2-Flüssen der gut erhaltenen Unterböden gefunden. Hohe Dichten an pflanzenverfügbarem P und Kalium (K) korrelierten mit maximalen Werten der CO_2- und N_2O-Flüsse. Die chemische Zusammensetzung von Hoch- und Niedermoortorf ähnelte sich in den Proben der Oberböden, während sich die Unterbodenproben untereinander deutlich durch ihre botanische Herkunft voneinander unterscheiden ließen. Insgesamt wiesen die Unterböden höhere Anteile an Kohlenhydraten und aromatischen Verbindungen auf. Unterschiede in der Zersetzung zwischen Ober- und Unterboden allein, ersichtlich aus dem Alter der Proben, konnten diese höheren Anteile in Unterböden nicht erklären. Zuverlässigen Indikatoren, die den Einfluss der Torfqualität auf die Zersetzung beschreiben, konnten nicht gefunden werden.

Insgesamt verbessert die vorgelegte Arbeit das Verständnis des Abbaus organischer Bodensubstanz in landwirtschaftlich genutzten organischen Böden, indem sie sich auf eine breite Probenbasis stützt und organische Böden mit niedrigem C-Gehalt einbezieht. Die Ergebnisse zeigten, dass insbesondere torfhaltige Böden mit niedrigem SOC-Gehalt hohe potentielle THG-Emissionen aufwiesen. Die Variabilität der THG-Emissionen und die Anfälligkeit der organischen Bodensubstanz für Zersetzung nahm mit zunehmendem Grad der anthropogenen

Beeinträchtigung zu. Dies deutet darauf hin, dass eine Einmischung von Sand in Torf keine Option zur Minderung von THG-Emissionen zu sein scheint. Der Nährstoffstatus von N, P und K, der wahrscheinlich stark von der Düngung beeinflusst wird, schien der wichtigste Parameter für die Torfmineralisierung zu sein und überprägte den Einfluss von Torfart, chemischer Zusammensetzung und Sandbeimengung. Darüber hinaus deuten die Ergebnisse dieser Arbeit darauf hin, dass der chemische Aufbau des Oberbodentorfes eine Folge der Zersetzung und nicht der Grund für höhere Mineralisierungsraten im Vergleich zum Unterbodentorf ist. Damit muss eine Abnahme der Torfqualität nicht unbedingt die zukünftige Zersetzung in entwässerten organischen Böden verlangsamen.

1 Introduction

1.1 Background

1.1.1 Greenhouse effect and carbon cycle

The greenhouse effect is a natural phenomenon making life on earth possible in the first place. Solar radiation is absorbed by the earth's surface and heats it. Greenhouse gases (GHG; e.g. carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) and water vapour (H_2O)) absorb and re-emit infrared radiation emitted by the earth's surface, thereby heating up the troposphere (Kraus, 2004). The tremendous increases in greenhouse gas emission in the last centuries caused by anthropogenic activities and the conjoint warming attracts more and more notice outside the scientific community. In several international agreements (Framework Convention on Climate Change (UNFCCC), 1992; Kyoto Protocol, 1997; Paris Agreement, 2015) globally leading industrial countries agreed on national reports of anthropogenic GHG sources and sinks. However, to develop mitigation strategies knowledge of the underlying carbon (C) cycle and perturbations in the natural balance of C fluxes is crucial. Soils are playing a key role in the C cycle being the third biggest store of carbon next to the oceanic and geological pool (Lal, 2008). Overall the world's soils are estimated to contain 1400 Pg C in the uppermost meter, which is roughly twice the amount of the atmospheric carbon pool (Batjes, 2016).

1.1.2 Intact peatlands

About one third of the global soil organic carbon (SOC) pool is stored in peatlands (Yu et al., 2010). In intact, growing peatlands gross primary production exceeds the rate of substrate decomposition, making them long-lasting C sinks. The reason for the low decomposition rate lies in the complex interplay of substrate composition of the vegetation, pH value, temperature, nutrients and water saturation among other things (Succow and Joosten, 2001). Worldwide organic soils cover approximately 2.2 to 3% of the terrestrial surface, with the majority located in the cold and temperate regions of the northern hemisphere and the tropics (Leifeld and Menichetti, 2018; Tubiello et al., 2016).

The composition of peat is dependent on hydro-climatic conditions during peat-growth, depth and age. With increasing depth the age of plant residues increases as well as their degree of decomposition on the von Post scale (von Post, 1922), which again impacts the hydraulic properties. A peat body can be divided into two layers: the acrotelm, the upper part, and the catotelm, the lower and main part of the peat. The acrotelm is dominated by a mixture of living and recent dead plant material, which is rich in carbohydrates (O-alkyl C) and phenolic substances (Reddy and DeLaune, 2008), characterized by a fluctuating water table, predominantly oxic conditions and high microbial activity (Succow and Joosten, 2001). The catotelm is permanently water-saturated and therefore anoxic, consisting of dead plant material (Succow and Joosten, 2001). With increasing depth and ongoing anaerobic transformation of peat, the dominant chemical composition changes to more recalcitrant compounds such as alkyl C and aromatic C (Hammond et al., 1985; Hopkins et al., 1997).

Furthermore, peat composition is a reflection of botanical origin. Peatlands can be classified into two types, bog and fen, next to several transition types. Bogs are characterized by oligotrophic conditions, fed by precipitation only and dominated by *Sphagnum spp.* vegetation. Fens can be described as minerotrophic or mesotrophic by receiving water from both groundwater and precipitation. The fen vegetation is a mixture of moss species, graminoids, shrubs and trees (Mitsch et al., 2009). Differences in chemical composition caused by the vegetation composition might influence the peat type's particular decomposability (Aerts et al., 2006; Bengtsson et al., 2018; Duval and Radu, 2018). Specific chemical compounds of peat plants have an inhibitory effect on microbial breakdown, which again differs between fen and bog peat origin. Whereas vascular plants, representing the main constituent in fens, contain lignins and tannins (Zak et al., 2019), *Sphagnum,* as dominant plant in bogs, forms polymeric lignin-like phenolics and polymerised uronic acid as substitutes for lignin (Verhoeven and Liefveld, 1997).

Peatlands provide a significant number of ecosystem services. Next to their immense C storage peatlands can accumulate nutrients and improve water quality. They support the hydrological cycle by holding large amounts of water and therefore – as the case may be – attenuate flood risks or augment groundwater resources (Maltby and Acreman, 2011). Peatlands serve as a cultural and natural heritage and paleo-ecological knowledge archive by preserving anthropogenic artefacts and natural fossils, plants and pollen. Furthermore, peatlands provide important wildlife habitats, recreational areas and host a rich biodiversity (Bonn et al., 2016).

1.1.3 Drained peatlands

Large areas of peatlands have been reclaimed for agriculture, forestry, fossil energy and horticulture (Frolking et al., 2011). Solely for agricultural use 23 to 51 million ha of peatlands have been drained worldwide (Leifeld and Menichetti, 2018; Tubiello et al., 2016), more than half of which are located in the boreal and temperate zones of Europe (Tubiello et al., 2016). In Germany, more than 80% of peatlands have been drained and are used for agricultural purposes or forestry (German Environment Agency (UBA), 2019). Changes in the peatlands' water tables caused by management practices and extensive drainage have tremendous impacts on the hydrologically sensitive nature of peat. Next to considerable deterioration of physical properties like peat subsidence, which manifests itself in soil consolidation, loss of buoyancy, decrease in porosity and shrinkage; biogeochemical peat properties are altered following the increase in aeration and microbial activity, resulting in enhanced SOM mineralisation. It can be assumed that peat formation stopped on all these drained peatlands. Due to thereby increased mineralisation previously organically bound nutrients like nitrogen (N), phosphorus (P) and potassium (K) are enriched in topsoils of drained peatlands (Holden et al., 2004; Laiho et al., 1998). Furthermore, drainage increases the DOC concentration in the soil water and waterborne C losses of peatlands (Evans et al., 2016; Frank et al., 2017).

In opposition to intact peatlands, which release CH_4, but are net sinks of CO_2 (Frolking et al., 2011), drained, cultivated peatlands are major sources of CO_2 and N_2O and are simultaneously either small sinks or sources of CH_4 (Maljanen et al., 2010; Tiemeyer et al., 2016). Drained organic soils account for 0.9 to 1.9 Gt CO_2 eq. a^{-1} (Leifeld and Menichetti, 2018; Smith et al., 2014) of GHG emissions on a global scale. This corresponds to roughly 10 to 20% of the GHG emissions in the sector agriculture, forestry and other land use (AFOLU), which in turn contributes about one quarter to the total anthropogenic GHG emissions (Smith et al., 2014).

1.2 Motivation

1.2.1 Cultivation of organic soils in Germany

Organic soils cover 5% of the total area of Germany (German Environment Agency (UBA), 2019) more than half of it being under agricultural use (Roßkopf et al., 2015). The cultivated peatlands in Germany can be divided into two main categories: drainage and utilization of peatlands by removing the original vegetation, but maintaining the natural soil profile; and drainage and utilization by rearranging the soil profile and/or adding mineral soil on the soil surface. It has been a practice to add a layer of mineral soil on top of the peat to increase yield, improve trafficability and preserve the peat (Göttlich, 1990). Even though this practice specifically instructs for shallow soil cultivation, peat has been ploughed into the mineral soil at many sites creating 'peat-sand mixtures'. The practice of deep ploughing peatlands in Germany (sand-cover and sand-mixing culture) by which underlying mineral soil is ploughed into the peat, resulting in transversal, alternating bars of peat and mineral soil, was deliberately excluded from this thesis.

All anthropogenic conversions from pristine peatlands to arable land result in strong pedogenetic alterations of the soil horizons called secondary pedogenetic processes (Heller and Zeitz, 2012; Zeitz and Velty, 2002). The cultivation initiates the earthification of the topsoil leading to the formation of a crumbly structure. Further proceeding in drainage is inducing the formation of polyhedral or prismatic aggregates with vertical cracks in the subsoil, thereby building a transition zone to underlying intact peat. Finally, the topsoil of intensively drained organic soils has no visible plant residuals and a dusty, fine-grained ('moorshy') structure (Ilnicki and Zeitz, 2003; Succow and Joosten, 2001).

Caused by both, drainage-induced mineralisation and the mixing of peat with mineral soil, the topsoils of peatlands under agricultural use have SOC contents at the transition between mineral (< 150 g SOM kg^{-1}) and peat soils (> 300 g SOM kg^{-1}, Ad-Hoc-Arbeitsgruppe Boden, 2005). In this sense only less than half of the organic soils in Germany can be referred to as peat, the rest has been impaired by either coverage with mineral soil (22%), deep ploughing, low SOC content or shallow peat depth (Jacobs et al., 2018; Wittnebel et al., submitted). The term 'low C organic soils' is used in this thesis for heavily disturbed, drained organic soils with 'moorshy' topsoil horizons and/or sand addition.

1.2.2 Vulnerability of drained organic soils

Most previous studies focused on 'true' peat soils or organic soils that meet the criteria of Histosols according to the World Reference Base for Soil Resources of at least 20% SOC content and a thickness of more than 40 cm (IUSS Working Group WRB, 2015). The IPCC definition however, includes soils with a minimal thickness of 10 cm and 12% SOC as organic soil, already presuming these shallow peat soils and/or low C organic soils behave like 'true' peat soils regarding their GHG emissions (IPCC, 2006). A synthesis of field studies on organic soils used as grassland underpinned this classification by showing similarly high emissions of CO_2 and N_2O of low C and C-rich organic soils (Tiemeyer et al., 2016). Respiration rates and SOC content are closely linked in mineral soils (< 8.7% SOC, Ad-Hoc-Arbeitsgruppe Boden, 2005; Don et al., 2013; Wang et al., 2003). Given this, it is surprising that even low C organic soil with down to 10% SOC (Leiber-Sauheitl et al., 2014) and peat-sand mixtures (Maljanen et al., 2004) emit high amounts of CO_2, although at this point mainly recalcitrant material should be present and readily available SOM for mineralisation should be rare. In contrast, studies on German sand-cover and sand-mixing cultures have found that these practices mitigate CO_2 emissions compared to true peatlands (Bambalov, 1999; Höper, 2015; Zaidelman and Shvarov, 2000).

The aforementioned consequences of anthropogenic interferences result in severe irreversible changes of the soil physical and adjacent hydraulic properties. Macroporosity and total porosity decline while bulk density increases in drained organic soils compared with intact peatlands (Dettmann et al., 2014; Schwärzel et al., 2002; Zeitz and Velty, 2002). Mixing sand into the peat intensifies alterations resulting in modified soil hydraulic parameters (Rovdan et al., 2002; Walczak and Rovdan, 2002) which are important for the system's reaction to changing boundary conditions and soil moisture regulations. The enhancement of SOM surface area leading to increased decomposition and nutrient mobilisation is concomitant with this physical disturbance of the topsoil peat (Ross and Malcolm, 1988). Additionally to the 'natural' enrichment of N, P and K in the topsoils of drained peatlands by increased mobilisation, more nutrients are introduced by fertilization. The soil's nutrient status is directly linked to the microbial activity: decomposition rates increased respiration rates with increased nutrient contents, as previous studies with N,P or K addition showed (Larmola et al., 2013; Pinsonneault et al., 2016a; Sundström et al., 2000). Especially P availability seems to have an accelerating effect on CO_2 and N_2O release (Amador and Jones, 1993; Brake et al., 1999; Liimatainen et al., 2018).

1.2.3 The German Agricultural Soil Inventory

Commissioned by the German Federal Ministry of Food and Agriculture the Thünen Institute of Climate-Smart Agriculture conducted the first German Agricultural Soil Inventory from 2011 to 2018 (Jacobs et al., 2018; Poeplau et al., 2020). It is the first harmonized nationwide inventory of agricultural soils in Germany that intends to describe and improve the understanding of SOC stocks. The data set incorporated 3104 sites in an 8 x 8 km grid where the soil was sampled and mapped according to the German manual of soil mapping (Ad-Hoc-Arbeitsgruppe Boden, 2005). Thereof 146 sites were classified as peat and other organic soils. In addition to the determination of basic soil properties in the laboratory, data from farmer questionnaires was gathered. The inventory laid the framework for this thesis.

1.3 Research gaps

As Tiemeyer et al. (2016) summarized in their synthesis of field studies, there is a high variability in GHG emissions from grassland on drained organic soils, especially for low C organic soils. GHG emissions from organic soils are controlled by numerous interacting variables including hydrology, climate, soil properties and agricultural management. Peat mineralisation rates are significantly influenced by the water table, which indirectly controls the oxygen availability via changes in soil moisture (Kechavarzi et al., 2007). Next to tillage, addition of mineral soil, and fertilization and chalking, water management of drained peatlands is a part of agricultural management. Examining certain drivers for enhanced mineralisation rates is hindered under field conditions, where a systematic evaluation of different variables is hardly possible. However, under controlled laboratory conditions selected boundary conditions can be adjusted and pre-established. The majority of studies investigated 'true' peat soils which are undisturbed or extensively used (e.g. Bridgham and Richardson, 1992; Koch et al., 2007; Reiche et al., 2010; Scanlon and Moore, 2000) leaving the controls of mineralisation in heavily disturbed and intensively used peatlands and low C organic soils undescribed for the most part.

1.3.1 Influence of soil properties and soil moisture on GHG emissions

The microbial activity and the GHG emissions of drained organic soils are sensitive to changes in soil properties and SOM quality following water level drawdown (Brouns et al., 2016; Laiho, 2006). Previous laboratory studies of organic soils under agricultural use mostly covered a small range of soil properties and focused on a few sites or peat types only to identify the influence of soil properties on decomposition (Ausec et al., 2009; Bader et al., 2017; Kechavarzi et al., 2010). Studies that include fen and bog peat samples as well as heavily disturbed organic soils at the border to mineral soils are sparse. Solely Bader et al. (2018) conducted a study on disturbed organic soil, including samples with SOC contents between 99 to 499 g kg^{-1} SOC. They studied peat mineralisation as a function of management, temperature and SOM composition by incubating samples originating from 21 fen peatland sites in Switzerland. To the best of my knowledge, there are no laboratory studies including fen peat, bog peat and low C organic soils, and covering a wide range of soil properties.

A large set of samples, covering a wide variety of soil properties, multiple sites on a country-scale, and different topography involves challenges regarding logistics and storage. This might result in the circumstance that only dried soil samples are available for further studies. The impact of water content or soil moisture can be examined using sieved and/or dried samples (Hogg et al., 1992; Moore and Dalva, 1997; Moore and Knowles, 1989). However, as previously mentioned, soil physical parameters play a major role in the soil's hydraulics and the control of soil moisture. Coherent influences can only be determined when the soil structure of the sample is still intact. Previous studies that used intact peat soil samples to investigate the influence of soil moisture on GHG emissions concentrated on a marginal number of sites only (Berglund and Berglund, 2011;

Brouns et al., 2016; Kechavarzi et al., 2010; Norberg et al., 2018; van Lent et al., 2018). In some of these experiments gas measurements were done irregularly (Berglund and Berglund, 2011; Norberg et al., 2018; van Lent et al., 2018) instead of a continuous measurement of fluxes. However, again an integration of broadly based sites and samples to systematically evaluate the effects of biogeochemical and hydrological parameters is missing. Even though peat-sand mixtures are quite common in Germany (Jacobs et al., 2018; Schulz and Waldeck, 2015) there is a lack of studies regarding the decomposition of SOM of these soils as well as low C organic soil in general, concerning varying water contents and nutrient concentrations.

1.3.2 Influence of chemical peat composition on GHG emissions

The chemical composition of peat either favours or hinders the microbial turnover of SOM and thereby influences the mineralisation. It has been reported that peat composition has an important influence on decomposition and GHG emissions (Heller et al., 2015; Hoyos-Santillan et al., 2016; Leifeld et al., 2012; Reiche et al., 2010; Tfaily et al., 2014). Due to depth-related differences in chemical composition caused by peat-forming processes, the subsoil is characterized dominantly by recalcitrant chemical compounds that inhibit microbial turnover and reportedly lower mineralisation rates compared with topsoil peat horizons (Bader et al., 2018; Brake et al., 1999; Hardie et al., 2011; Hogg et al., 1992). Triggered by increased agricultural use and enhanced mineralisation of SOM, deeper and older layers of peat were laid open over time, forming the present topsoil peat horizons. These topsoil peat layers might be enriched in recalcitrant compounds: during microbial turnover these compounds are preferably preserved or fresh, available SOM of the uppermost peat layer is already mineralised (Leifeld et al., 2012; Urbanová and Bárta, 2015). Leifeld et al. (2012) and Urbanová and Bárta (2015) proposed the view that these disturbed peatland systems are self-regulated, based on an overall decrease in mineralisation rates over time as chemical composition gradually declines. It has been shown that phenol oxidase plays a key role in peat mineralisation, reducing the protection of e.g. phenolic compounds against decomposition (Freeman et al., 2001). According to the ‘enzymic latch’ theory of Freeman et al. (2001) the enzyme phenol oxidase increased microbial activity sevenfold under aeration compared to anaerobic conditions in peatlands. Even though younger, more labile SOM is favored for decomposition by mircoorganisms, under certain conditions older, more recalictrant SOM can account for CO_2 respiration (Hardie et al., 2011). To properly investigate possible preferential preservation of recalcitrant compounds in topsoil peat, a systematic comparison of topsoil and subosil peat quality at multiple drained sites could be valuable.

1.4 Aims and approach

This thesis aimed to improve the understanding of peat mineralisation in drained organic soils under agricultural use. Therefore, light was shed on the sensitivity of these soils to mineralisation, the interplay of their hydrological and biogeochemical soil properties, the impact of anthropogenic sand addition and peat quality on GHG emissions.

Section 2 describes the first laboratory study of the thesis where 62 rewetted soil samples exceeding a SOC content of 75 g kg^{-1} and covering the whole range of basic soil properties were studied. The CO_2 production rates of the samples were measured in a semi-automatic incubation device (Heinemeyer et al., 1989). Under constant temperature (23 °C) and optimum soil moisture (60% WFPS), basal respiration and substrate-induced respiration were determined:

- to assess the sensitivity of drained, disturbed organic soils under agricultural use to mineralisation under aerobic conditions,
- to shed light on factors and variables that influence the SOM's vulnerability to decomposition.

The ten sampling sites for the second laboratory study have been chosen based on the results of the first study to comprise the detected high variability of mineralisation rates. In this second laboratory study, undisturbed soil columns were used to bring anthropogenic peat-sand mixtures into focus. The samples were installed in a microcosm system (Hantschel et al., 1994) under constant temperature (10 °C) and CO_2, N_2O and CH_4 concentration were measured continuously. Over the course of the experiment, the initially water-saturated soil columns were drained stepwise using suction plates at the bottom. Next to basic soil properties, including nutrient contents, the chemical composition was measured via NMR spectroscopy and wet-chemical fibre analyses. Additionally the ^{14}C radiocarbon age was determined. The analysis of the results was divided into the general topics of agricultural management (section 3) and peat quality (section 4).

The objectives of this study were:

- to elucidate the interrelation of water content and microbial decomposition by ascertaining the optimum soil moisture for the occurrence of maximum GHG fluxes,
- to determine the influence of peat-sand mixtures in the topsoil on GHG fluxes,
- to investigate different peat types by comparing topsoils, subsoils and fen and bog peat, and their corresponding sensitivity to drainage,

- to assess the importance of nutrient status for GHG fluxes,
- to identify differences between the chemical composition of topsoil and subsoil peat and between fen and bog peat origin,
- to examine whether CO_2 fluxes are influenced by the diversity of chemical composition caused by mineralisation and age.

2 Drained organic soils under agriculture — The more degraded the soil the higher the specific basal respiration

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Abstract

Drained peatlands are hotspots of carbon dioxide (CO_2) emissions from agricultural soils. As a consequence of both drainage-induced mineralisation and anthropogenic mixing with mineral soils, large areas of former peatlands under agricultural use underwent a secondary transformation of the peat (e.g. formation of aggregates). These soils show contents of soil organic carbon (SOC) at the boundary between mineral and organic soils. However, the carbon (C) dynamics of such soils have rarely been studied so far. The aim of the present study was to evaluate the vulnerability of soil organic matter (SOM) to decomposition over the whole range of peat-derived soils under agriculture including very carbon rich mineral soils (76–526 g kg^{-1} SOC). A total of 62 soil samples covering a broad range of soil and site characteristics were selected from the sample set of the German Agricultural Soil Inventory. Potential CO_2 production was measured by aerobic incubation. Fen and bog peat samples were grouped into disturbance classes according to their soil properties. Specific basal respiration rates (SBR), i.e. CO_2 fluxes per unit SOC, showed the highest values for the most disturbed samples for both fen peat (13.9 ± 6.0 µg CO_2-C g SOC^{-1} h^{-1}) and bog peat (10.9 ± 4.7 µg CO_2-C g SOC^{-1} h^{-1}). Respiration rates of bog peat increased more strongly with an increasing degree of disturbance than those of fen peat. Perhaps counterintuitively, SOM vulnerability to decomposition thus increased with an increasing degree of disturbance and a decreasing SOC content, indicating positive feedback mechanisms as soon as peat soils are disturbed by drainage. Furthermore, the variability of the SBR increased drastically with increasing degree of disturbance. The turnover of SOM in less disturbed peat samples tended to be higher in samples with higher nitrogen (N) content, higher pH value and lower C:N ratio, while plant-available phosphorus was important for the mineralisation of more severely disturbed peat. However, clear correlations between a single soil property and SBR could not be identified. The high potential of CO_2 emissions from organic soils with a low SOC content implies that mixing

organic soil with mineral soil does not seem to be a promising option for mitigating greenhouse emissions.

2.1 Introduction

Organic soils cover only 2.2 to 3% of the global terrestrial surface (Leifeld and Menichetti, 2018; Tubiello et al., 2016), but store more than one third of global soil organic carbon (SOC) (Scharlemann et al., 2014; Yu et al., 2010). These huge SOC stocks have been built up over millennia, as intact peatlands under waterlogged conditions are persistent carbon (C) sinks due to higher gross primary production compared to respiration (Clymo et al., 1998). One third of all organic soils are found in Europe (Tubiello et al., 2016), corresponding to 3% of the European landmass (Montanarella et al., 2006). In Germany organic soils cover 4.4% of the land area (Roßkopf et al., 2015). Large areas of peatland have been drained for agriculture, forestry and peat mining for energy and horticulture. To date, 25.5 million ha of drained peatlands worldwide are used for agriculture alone, of which around 60% are located in the boreal or temperate zone (Tubiello et al., 2016). The majority of the drained peatlands in Central and Western Europe are used for agricultural purposes, primarily as grassland (Joosten and Tanneberger, 2017). Drainage and agricultural management strongly change the peatlands' hydrological and biogeochemical processes, e.g. by causing strong mineralisation of the soil organic matter (SOM) (Holden et al., 2004). Thus, drainage turns peatlands into hotspots of greenhouse gas (GHG) emissions from soils, which release large quantities of carbon dioxide (CO_2), but also nitrous oxide (N_2O) (Maljanen et al., 2010; Tiemeyer et al., 2016).

Drainage considerably alters physical and chemical peat properties. Following drainage, the intrinsic buoyancy of peatlands due to water saturation is immediately lost and the peat is compacted. Mineralisation and pedogenetic transformation of SOM induce the formation of crumbly and, later on, polyhedral and prismatic aggregates, shrinkage cracks and finally results in a dusty, fine-grained (“moorshy”) topsoil horizon (Ilnicki and Zeitz, 2003). Consequently, the majority of topsoils of drained agricultural peatlands are strongly decomposed without any recognizable plant remains. Altogether, these processes lead to an increase in bulk density and a decrease in total porosity (Rovdan et al., 2002). Compaction, shrinkage and mineralisation jointly cause subsidence of the soil surface and thus increase risk of flooding and damage to buildings and infrastructure (Gambolati et al., 2005; Holden et al., 2004).

Furthermore, drainage favours carbon over nitrogen (N) mineralisation and microbial N immobilisation during decomposition (Wells and Williams, 1996). Thus, the N content increases, and both the C content and C:N-ratio decrease with increasing degrees of SOM decomposition, especially in the topsoil (Wells and Williams, 1996). As aerobic decomposers preferably use lighter isotopes, the remaining peat is enriched both in ^{13}C (Ågren et al., 1996) and ^{15}N (Krüger et al., 2015). The phosphorus (P) content also usually increases after drainage due to ongoing mineralisation of the SOM and concurrent release of previously organically bound P. Under aerobic conditions, P can be immobilized e.g. by Fe(III)-compounds (Sundström et al., 2000; Wells and Williams, 1996; Zak et al., 2010). Furthermore, fertilizer application contributes to the nutrient enrichment of organic soils under agriculture.

Besides drainage, the conversion from pristine peatlands to agricultural land can comprise the active addition of mineral soil to the top peat layer in order to improve trafficability. This can be achieved by mixing with mineral soil layers underlying the peat or by surface application of mineral soil with or without subsequent ploughing (Göttlich, 1990; Okruszko, 1996). As a consequence of both drainage- induced mineralisation and anthropogenic mixing with mineral soil material, especially topsoils of large areas of former peatlands under agricultural use show SOC contents between those of mineral and organic soils (Schulz and Waldeck, 2015). In Germany, nearly 50% of the peat-derived organic soils cannot be classified as “fen peat” or “bog peat” in the strict sense of the German soil classification (Ad-Hoc-Arbeitsgruppe Boden, 2005) anymore due to deep ploughing, coverage by mineral soil material, low SOC content or shallow depth (Jacobs et al., 2018).

As previous investigations have mainly focused either on mineral soils (< 150 g SOM kg^{-1} according to the German definition, Ad-Hoc-Arbeitsgruppe Boden, 2005) or “true” peat soils (> 300 g SOM kg^{-1}), there are very few studies on soil properties or SOM dynamics of “low C organic soils” (between 150 and 300 g SOM kg^{-1}). However, measurements of CO_2 emissions in the field have shown that peat-derived soils even with a topsoil SOC content as low as 100 g kg^{-1} still emit large and similar amounts of CO_2 as “true” peat soils (Leiber-Sauheitl et al., 2014; Tiemeyer et al., 2016). This is rather surprising as the remaining organic matter should not be readily available for mineralisation, given that the SOC content at this stage of decomposition is fairly low and CO_2 emissions and SOC content are closely related in mineral soils (Don et al., 2013; Wang et al., 2003). The reasons behind the relatively high CO_2 emissions of the whole continuum of organic soils, including those bordering mineral ones, are not yet clear. Changes in peat properties following water level drawdown and overall SOM quality were found to influence the microbial activity and therefore the CO_2 emissions of drained peatlands (Brouns et al., 2016; Laiho, 2006). Contrarily, a recent study on the SOM decomposability of 21 drained and intensively managed fen soils found only weak correlations between CO_2 emissions and soil properties (Bader et al., 2018). However, the nutrient status of soils is important for microbial activity: microbial P availability have been shown to favor soil respiration (Amador and Jones, 1993; Brake et al., 1999; Säurich et al., 2019a) and numerous studies have found an increase in CO_2 emissions after the nutrient content was increased by P, K and N addition (Larmola et al., 2013; Pinsonneault et al., 2016a; Sundström et al., 2000).

Under field conditions, it is difficult to disentangle interacting effects of climate, hydrology, agricultural management, and soil properties. Thus, there is a lack of any systematic evaluation of the vulnerability to decomposition of a wide range of organic soils, including heavily disturbed ones. Most previous laboratory studies that examined agriculturally used organic soils under controlled conditions mostly incubated samples of a few sites with a rather narrow range of soil properties (Ausec et al., 2009; Bader et al., 2017; Kechavarzi et al., 2010). Bader et al. (2018) incubated a broad variety of disturbed fen peat samples (99 – 499 g kg^{-1} SOC) and Säurich et al. (2019a) compared respiration rates from intact soil columns of 10 sites with and without sand addition. However, to our best knowledge, there are no laboratory studies including both fen and bog peat and covering a wide range of soil properties.

With our laboratory study under aerobic conditions, we aimed to improve our understanding of the sensitivity of disturbed organic soils to mineralisation. Further, we wanted to elucidate factors governing the vulnerability of the soils' SOM to decomposition. In this context, disturbance was defined as the effect of transformation processes induced by drainage and/or by the mixing of peat with mineral soil. In the present study, 62 samples originating from drained agricultural sites from across Germany were examined, ranging from carbon-rich mineral soil (76 g SOC kg^{-1}) to “true” peat (up to 526 g SOC kg^{-1}). Given that the samples cover country-scale variability and originated from a large inventory (Jacobs et al., 2018) they were available in dried form. As commonly done (Grover and Baldock, 2012), dried samples were adjusted to standardised water content, pre-incubated and aerobically incubated to determine basal and substrate-induced respiration (Anderson and Domsch, 1978; Heinemeyer et al., 1989).

2.2 Material and methods

2.2.1 Sample selection

The samples used in this study originate from the first German Agricultural Soil Inventory (Jacobs et al., 2018) which aimed at an improved understanding of SOC stocks in agricultural soils. During the inventory, 3104 agricultural soils in Germany were sampled following standardised protocols in an 8×8 km grid. For soil sampling and mapping a soil pit was opened at each site down to 1 m. The soil profile was classified according to the German manual of soil mapping (Ad-Hoc-Arbeitsgruppe Boden, 2005) including the degree of decomposition after von Post (von Post, 1922). Soil samples were taken at five depth increments per soil pit (0–10, 10–30, 30–50, 50–70, 70–100 cm). If a depth increment comprised more than one soil horizon, samples were taken from each horizon within this increment. Vice versa, depth increments were divided when they crossed horizon boundaries by > 3 cm. From each increment and/or horizon, volumetric samples were taken in steel rings for the determination of the bulk density, and grab samples for the determination of soil chemical properties. All samples were analysed for SOC and bulk density (ρ), as well as for basic explanatory soil properties (Table 2-1, see section 2.2.2).

Table 2-1: Soil properties of the selected soil samples as medians and standard errors. Standard parameters measured in the German Agricultural Soil Inventory: SOC: soil organic carbon content, N_t: total nitrogen content, C:N-ratio: carbon to nitrogen ratio, ρ: bulk density, pH-value ($CaCl_2$), texture (*only determined for samples with SOC < 174 g kg^{-1}). Additional parameters of this study: P_{CAL}: calcium acetate lactate (CAL) extractable phosphorus content and $\delta^{15}N$.

Parameter	Median	Min.	Max.
SOC (g kg^{-1})	309.0 ± 18.9	75.7	525.9
N_t (g kg^{-1})	13.1 ± 0.9	3.4	27.5
C:N-ratio	17.2 ± 1.8	9.9	72.6
ρ (g cm^{-3})	0.24 ± 0.03	0.07	0.99
pH	5.0 ± 0.2	3.1	7.4
Sand content (%)*	44.7 ± 6.2	8.3	87.9
Silt content (%)*	25.0 ± 2.5	6.4	41.8
Clay content (%)*	24.0 ± 4.0	4.8	49.9
P_{CAL} (mg kg^{-1})	17.9 ± 9.0	1.3	365.6
$\delta^{15}N$ (‰)	2.35 ± 0.28	-2.55	9.30

For this study, 62 samples from C-rich horizons from 47 sites were selected. The basic criteria were a SOC content > 75 g kg^{-1} and a sampling depth > 10 cm. The latter criterion was chosen to reduce the influence of potential fresh plant or root biomass residues in the samples, although roots have been separated by hand. The final sample selection was based on Ward's hierarchical cluster analysis using k-means as partitioning method for 10 clusters. Resulting samples optimally covered the total parameter range (Table 2-1), as well as land use, major peat substrates (bog/fen) and geographical position. We did not, however, include C-rich samples from organic sediments (e.g. gyttja), marsh or other soils without peatland origin (e.g. plaggen soils) here. Sampling sites were used as cropland (18%) and grassland (82%), which corresponds to the dominant agricultural land use of organic soils in Germany. The selected samples were collected between March 2011 and

November 2014 and originated from various depth increments (see data.xlsx file in the supplement for detailed information).

2.2.2 Soil properties and degree of disturbance

Samples for soil chemical analysis were dried at 60 °C until constant mass and sieved to < 2 mm. Contents of total C (C_t) and N (N_t) as well as the total inorganic carbon content for samples with carbonate ($pH_{CaCl2} > 6.2$) were measured by dry combustion (RC 612, LECO Corporation, St. Joseph, USA). The SOC content was calculated as difference between C_t and total inorganic carbon.

Stable isotope analysis ($\delta^{15}N$) was performed on grinded samples using a mass spectrometer coupled with an elemental analyzer (Isoprime 100 and Vario Isotope, Elementar, Hanau, Germany) via a continuous flow system. The isotope ratio is expressed in per mill relative to atmospheric nitrogen standard.

Contents of plant-available phosphorus were determined by calcium acetate lactate (CAL) extraction (P_{CAL}) (Schüller, 1969). P_{CAL} contents were measured using the molybdenum blue method. The ammonium molybdate solution and the phosphate ions form a blue compound which is then measured with a spectrophotometer (Murphy and Riley, 1962). The pH values were measured using 5 mL soil and 25 mL of a 0.01 mol/L $CaCl_2$ and a glass electrode.

The fractions of the texture classes sand, silt and clay of samples with SOC < 174 g kg^{-1} were quantified by a semi-automated sieve- pipette machine (Sedimat 4–12, UGT, Müncheberg, Germany) after aggregate destruction and the removal of salt and SOM using H_2O_2 (DIN ISO 11277, 1998). Bulk density was determined by drying the volumetric samples at 105 °C until constant mass and subsequent weighing.

Here, we use a classification of anthropogenic disturbance based on the mapped soil horizons (Ad-Hoc-Arbeitsgruppe Boden, 2005; see also Ilnicki and Zeitz (2003)) and further soil properties (details in Table S1). Fen (F) and bog (B) peat samples were divided into five and three disturbance classes, respectively, according to the severity of secondary pedogenetic transformation (Table 2-2): no disturbance (D0F/D0B), slight disturbance (D1F/D1B), moderate disturbance (D2F/D2B), strong disturbance (D3F) and heavy disturbance (D4F). “Slightly disturbed” horizons experience drainage and are influenced by a fluctuating water table. Thus, they are temporarily subjected to aerobic conditions but there has not yet been a secondary transformation of the peat structure. As the transformation sequence of a drained peatland starts with the formation of an earthified topsoil horizon, these horizons are defined as “moderately disturbed”. Under intensified drainage, the subsoil peat starts to develop secondary pedogenetic features, characterised by blocky to prismatic aggregates and/or the formation of shrinkage cracks, therefore they are defined as “strongly disturbed” horizons. In the present sample set, this level of disturbance only occurred in fen peat. “Heavily disturbed” samples all originate from the topsoil and cannot be classified as peat anymore due to mineralisation and addition of mineral soil material. Given that this classification was developed after the sample selection, the distribution among the groups is not uniform.

Table 2-2: Classification of the anthropogenic disturbance and corresponding mean and standard deviation of soil properties: SOC: soil organic carbon content, C:N-ratio: carbon to nitrogen ratio, $\delta^{15}N$, N_t: total nitrogen content, P_{CAL}: calcium acetate lactate (CAL) extractable phosphorus content, pH-value ($CaCl_2$), ρ: bulk density

Degree of disturbance	Description	Peat-land type	Label	n	SOC (g kg^{-1})	C:N	$\delta^{15}N$ (‰)	N_t (g kg^{-1})	P_{CAL} (mg kg^{-1})	pH	ρ (g cm^{-3})
No disturbance	Permanently water-saturated	Fen	D0F	8	426 ± 90	23 ± 8	0.3 ± 1.3	19.8 ± 6.7	8.4 ± 6.0	5.5 ± 1.0	0.13 ± 0.02
		Bog	D0B	4	510 ± 25	52 ± 16	1.5 ± 1.9	10.9 ± 4.7	10.0 ± 11.5	3.2 ± 0.1	0.10 ± 0.02
Slight disturbance	Alternating aerobic-anaerobic conditions	Fen	D1F	10	410 ± 58	24 ± 11	2.2 ± 2.9	19.4 ± 6.1	14.5 ± 14.7	5.3 ± 1.2	0.2 ± 0.04
		Bog	D1B	4	462 ± 34	50 ± 16	1.2 ± 1.7	9.9 ± 3.1	34.6 ± 33.9	3.5 ± 0.2	0.11 ± 0.03
Moderate disturbance	Earthification or moorsh	Fen	D2F	6	283 ± 91	15 ± 2	2.6 ± 1.5	19.6 ± 5.6	28.2 ± 21.3	5.1 ± 0.6	0.44 ± 0.15
		Bog	D2B	6	281 ± 145	26 ± 5	2.4 ± 1.2	11.1 ± 5.9	100.2 ± 52.3	3.9 ± 0.4	0.4 ± 0.3
Strong disturbance subsoil	Polyhedral aggregates or cracks	Fen	D3F	6	307 ± 46	14 ± 2	2.1 ± 1.1	22.0 ± 3.7	35.7 ± 40.8	5.3 ± 1.3	0.26 ± 0.06
Heavy disturbance topsoil	Mineral soil addition, low SOC content	Fen	D4F	18	127 ± 41	15 ± 4	4.3 ± 1.8	9.2 ± 3.2	88.6 ± 108.1	5.9 ± 1.2	0.68 ± 0.20

2.2.3 Incubation experiments: Basal respiration and substrate-induced respiration

The soil samples were incubated aerobically under optimum moisture conditions and constant temperature (23 °C) to determine basal soil respiration (BR) and substrate-induced respiration (SIR). The latter was in turn used to calculate microbial biomass (Anderson and Domsch, 1978). An optimum standardised water content of 60% water-filled pore space was determined by pre-tests. To calculate the necessary amount of water, the apparent porosity φ of the dried and sieved sample was calculated as follows:

$$\Phi = 1 - \frac{\rho_{loose}}{\rho_s}, \tag{2.1}$$

where ρ_{loose} [g cm^{-3}] is the bulk density of the loose sample and ρ_s [g cm^{-3}] is the particle density. The particle density ρ_s was estimated according to Eq. 2.2 for organic soils given by Bohne (2005):

$$\rho_S = 0.086 * AC + 1.44, \tag{2.2}$$

where *AC* [%] is the ash content of the sample. The water was then applied to the soil samples under continuous stirring to ensure uniform rewetting. Afterwards, the moistened samples were pre-incubated in darkness under aerobic conditions for 7 days at 6 °C and then for a further 7 days at 23 °C (Jones et al., 2019). On day 14, the soil samples were adjusted in their water content if necessary and transferred to a semi-automatic incubation device using its flow-through mode (Heinemeyer et al., 1989). Three replicates (20 g dry wt.) of each sample were put loosely in acrylic glass tubes (4 cm diameter) and enclosed at both ends with polystyrene foam stoppers. Humidified ambient air flowed through 24 independent lines containing the soil samples at flow rates between 160 and 180 ml min^{-1}. Three of the lines were ran as blanks. An infrared CO_2 gas analyzer (ADC-255-MK3, Analytical Development Co. Ltd., Hoddesdon, UK) was used to measure CO_2 concentrations. Each tube was measured hourly over an incubation time of at least 40 h or until a relatively constant BR was reached (up to 90 h).

Afterwards soil samples were amended with a mixture of 100 mg glucose and 100 mg talcum using an electronic stir for 30 s to determine the active microbial biomass by the SIR method. The mixture was then incubated and measured again for 6 h to obtain the maximal initial respiratory response of the microbial biomass (Anderson et al., 1995).

2.2.4 Data analysis

Data and statistical analysis was performed using the R software environment (version R-3.5.0, R Core Team, 2018).

2.2.4.1 Determination of basal and specific basal soil respiration

The basal respiration (BR) is expressed as µg CO_2-C g soil^{-1} h^{-1} and the specific basal respiration (SBR) is normalized by the sample's SOC content into µg CO_2-C g SOC^{-1} h^{-1}. An exponential model was fitted simultaneously to all three incubation replicates to determine the equilibrium values of the SBR (Figure S1):

$$\mathrm{CO_2\text{-}C\ (t)} = \mathrm{a} - (\mathrm{a} - \mathrm{SBR})\,(1 - \mathrm{e}^{-\mathrm{k}*\mathrm{t}}), \tag{2.3}$$

where CO_2-C (t) [µg CO_2-C g SOC^{-1} h^{-1}] is the specific CO_2 production per hour, *a* [µg CO_2-C g SOC^{-1} h^{-1}] is the initial respiration and *k* [h^{-1}] is the change rate of SBR. SBR is the asymptotic value of Eq. 2.3.

To achieve an objective quantification of the basal and the specific basal respiration and its uncertainty, the R package "dream" was used (Guillaume and Andrews, 2012), which is based on the iterative Markov Chain Monte Carlo (MCMC) approach. This method is basically a Markov chain that generates a random walk through the high-probability-density region in the parameter space, separating behavioral from non-behavioral solutions following the probability distribution (Vrugt et al., 2009b). The differential evolution adaptive metropolis (DREAM) algorithm is an efficient MCMC sampler that runs multiple Markov chains simultaneously for global exploration of the parameter space. In doing so, DREAM uses a differential algorithm for population evolution and a metropolis selection rule to decide whether a population of candidate points is accepted or not. After the burn-in period, the convergence of individual chains is checked using the Gelman and Rubin (1992) convergence criterion, which examines the variance between and within chains (Vrugt et al., 2009a).

Once the convergence criterion of Gelman and Rubin was < 1.01, another 500,000 simulations were run to determine the posterior probability density functions of the model parameters, which were used to calculate the median and the 2.5 and 97.5% quantiles of the SBR.

For the evaluation of the SIR, the value of the maximum initial respiratory response was identified manually and then transcribed via a conversion factor to microbial biomass (SIR-C_{mic}) [µg g^{-1} soil] as follows (Kaiser et al., 1992):

$$\text{SIR-C}_{\text{mic}} = \mu\text{l CO}_2\ \text{g}^{-1}\ \text{soil h}^{-1} * 30. \tag{2.4}$$

As in the case of BR, we normalized SIR-C_{mic} by the samples' SOC content. This is referred to as "specific SIR-C_{mic}" in the following. To quantify the efficiency of microbial respiration per unit biomass, the metabolic or respiratory quotient q(CO_2) [mg CO_2-C h^{-1} g^{-1} biomass SIR-C_{mic}] was calculated by dividing the BR by the SIR-C_{mic} (Anderson and Domsch, 1985):

$$\text{q(CO}_2) = \frac{BR}{\text{SIR-C}_{\text{mic}}/1000}. \tag{2.5}$$

The metabolic quotient q(CO_2) indicates the efficiency of soil microorganisms in acquiring organic carbon (Dilly and Munch, 1998) and depends, among other factors, on nitrogen availability and pH (e.g. Spohn, 2015).

2.2.4.2 Statistical analysis

Spearman's rank correlation coefficient r_s was evaluated for the specific basal respiration and all measured explanatory variables using the R package "Hmisc" (Harrell, 2016). The p-values were adjusted using the method after Bonferroni. Correlation coefficients of $0.3 \geq r_s \geq 0.7$ will be referred to as "moderate correlation" and $r_s > 0.7$ as "strong correlation" in the following.

Differences in BR, SBR, SIR-C_{mic} and $q(CO_2)$ between the disturbance classes and in SBR between sample with the same degree of decomposition (H) were determined by using a generalized least squares (gls) model with the varIdent variance structure from the R package “nlme” (Pinheiro et al., 2015). This variance structure allows for handling the unbalanced data of the present study by taking into account the specific variances of the different classification factors. P-values were computed with the Tukey’s honest significant differences test ($\alpha = 0.05$) and adjusted with the Bonferroni correction using the R package “multcomp” (Hothorn et al., 2008).

The results for every disturbance class given below are means with standard deviations, unless otherwise stated.

2.3 Results

2.3.1 Vulnerability of SOM to decomposition as determined by respiration rates

Basal respiration (BR) of all samples was highly variable, ranging from 0.5 to 7.0 µg CO_2-C g soil^{-1} h^{-1}. Overall, bog and fen samples had similar BR rates of 2.5 ± 1.7 µg CO_2-C g soil^{-1} h^{-1} and 2.4 ± 1.2 µg CO_2-C g soil^{-1} h^{-1} respectively. Furthermore, there were no consistent patterns of BR and disturbance rates (Fig. 2-1a, Table S2). In the case of fen peat, the BR rates of heavily disturbed samples were significantly lower compared to strongly and slightly disturbed samples, but not compared to moderately and undisturbed ones.

Normalizing BR to SOC content resulted in highly variable specific basal respiration (SBR) rates between and within classes, which ranged from 1.5 to 23.8 µg CO_2-C g SOC^{-1} h^{-1}. Overall, fen samples had higher SBR rates (10.4 ± 5.6 µg CO_2-C g SOC^{-1} h^{-1}) than bog samples (7.0 ± 4.8 µg CO_2-C g SOC^{-1} h^{-1}; Fig. 2-1b). However, SBR of moderately disturbed D2B samples, i.e. the strongest disturbance assigned to bog peat samples, was comparable to strongly and heavily disturbed fen samples (D3F, D4F; Table S2). In contrast to BR, there were strong patterns as SBR rates clearly increased with increasing soil disturbance for both fen and bog peat. Significant differences could be found between undisturbed bog samples (D0B) and the disturbed fen sample classes D3F and D4F ($p < 0.001$) and D1F and D2F ($p < 0.01$, all further p values are given in Table S3 and Table S4). The heavily disturbed fen samples (D4F) reached the highest SBR rates that were significantly higher than the undisturbed and slightly disturbed samples of both fen and bog peat. The highest variability of SBR also occurred for the most disturbed fen and bog peat samples, respectively (Fig. 2-1b, Table S2).

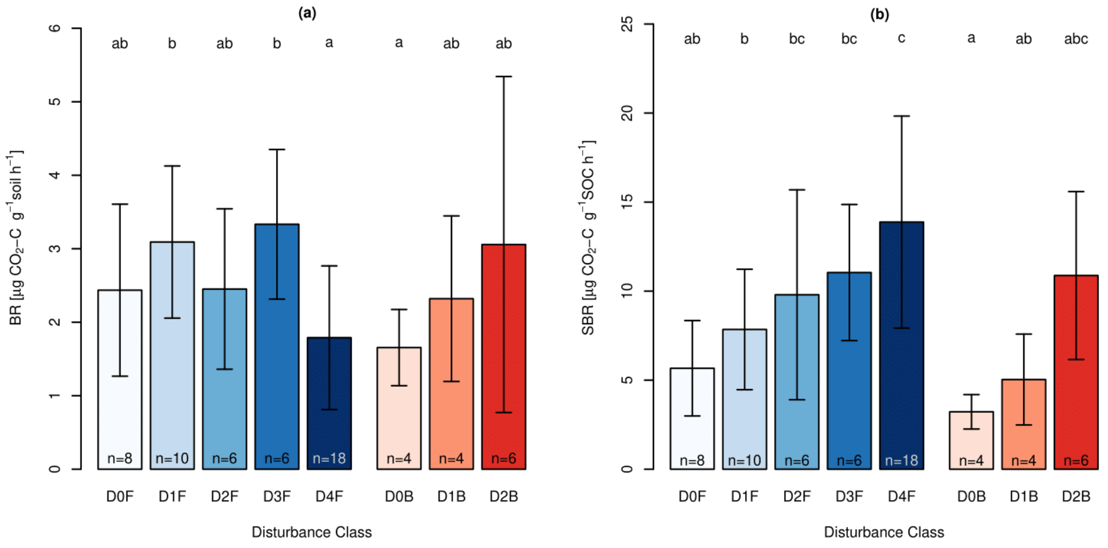

Figure 2-1: a) Mean of basal respiration (BR) rates and b) specific basal respiration (SBR) rates for all disturbance classes: F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance. Bars show the standard deviation. Different letters represent significant differences (Tukey's test, $p < 0.05$).

2.3.2 Influence of organic matter quality and soil characteristics

The BR rates for the whole dataset could hardly be explained by any of the measured soil characteristics (Fig. S2, Table S3) as there was only a moderate positive, but significant correlation with N_t, but not with SOC. Soil properties also correlated with each other, for example there were strong negative correlations between SOC and ρ as well as between C:N-ratio and pH value (Fig. S2, Table S3). In the following, we will limit results on SBR rates as these are assumed to be better indicators for the SOM vulnerability to decomposition than BR rates.

In the case of SBR rates of the whole dataset (Fig. 2-2, Table S3) moderate positive correlations with $\delta^{15}N$ values, phosphorus content and bulk density were observed. Significant negative relationships were found between SBR and SOC content and the C:N-ratio.

Fig. 2-3 shows soil characteristics and SBR rates of individual samples grouped by disturbance classes. Consistent with the increase of SBR rates with disturbance classes (Fig. 2-1b) the SBR rates were significantly higher ($p < 0.001$) at higher degrees of decomposition (von Post values, Fig. 3-3a). Slightly and moderately decomposed samples, i.e. those with von Post values of H3 and H5, had significantly lower SBR rates (5.8 ± 3.6 and 6.7 ± 3.2 µg CO_2-C g SOC^{-1} h^{-1} respectively) than strongly decomposed samples mapped as H10 (13.0 ± 3.7 µg CO_2-C g SOC^{-1} h^{-1}) or low C organic soils deriving from peat (NA; 13.5 ± 6.3 µg CO_2-C g SOC^{-1} h^{-1}).

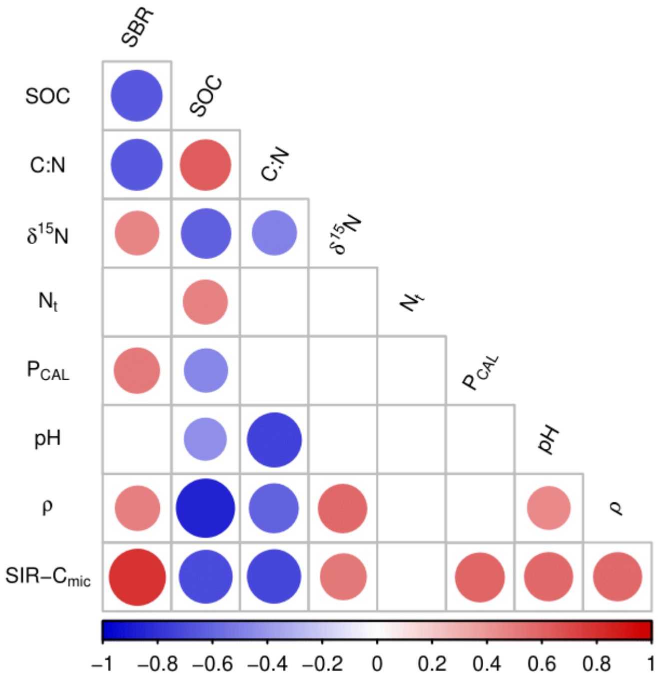

Figure 2-2: Significant ($p < 0.05$) correlation coefficients after Spearman for specific basal respiration rates (SBR) with soil properties (SOC: soil organic carbon content, C:N-ratio: carbon to nitrogen ratio, $\delta^{15}N$, N_t: total nitrogen content, P_{CAL}: calcium acetate lactate (CAL) extractable phosphorus content, pH-value and ρ: bulk density) and specific microbial biomass (SIR-C_{mic}).

Furthermore, both variability and magnitude of SBR rates increased with decreasing SOC content (Fig. 2-3b), i.e. SBR rates were highest and most variable for soil samples with a low SOC content (mainly heavily disturbed fen peat samples; see Table 2-2). This negative relationship between SOC and SBR remained also apparent when correlating soil characteristics separately for each disturbance class (Fig. 2-4, Table S4). Fig. 2-3b also exemplarily shows the 2.5 and 97.5% quantiles of the DREAM-fit, i.e. the uncertainty of the calculated SBR rates. While there were several samples mainly of the D4F class for which SBR rates could only be determined with large uncertainties, most quantile ranges were small and thus partially invisible in Fig. 2-3b. Even disregarding the samples with large uncertainties would not change the overall picture of high and highly variable SBR rates at low SOC content.

With decreasing C:N-ratios, SBR rates increased in an exponential manner (Fig. 2-3c). However, when splitting the sample set at C:N=25 into two groups, there was no longer any correlation for neither group. Again, the highest and most variable rates of 11.1 ± 5.4 µg CO_2-C g SOC^{-1} h^{-1} were measured for mostly highly disturbed samples with low C:N ratios (< 25), which mainly belong to all fen classes and D2B (see Table 2-2). In contrast, samples with a C:N-ratio > 25 were bog samples with low or minimal disturbance, which had clearly lower and less variable SBR rates of 5.4 ± 3.4 µg CO_2-C g SOC^{-1} h^{-1}. In detail, there was a strong negative correlation between SBR rates and the C:N-ratio for D2F samples and moderate negative correlations were found for D0F, D1F, D4F, D0B and D1B, although none of these correlations were significant (Fig. 2-4, Table S4).

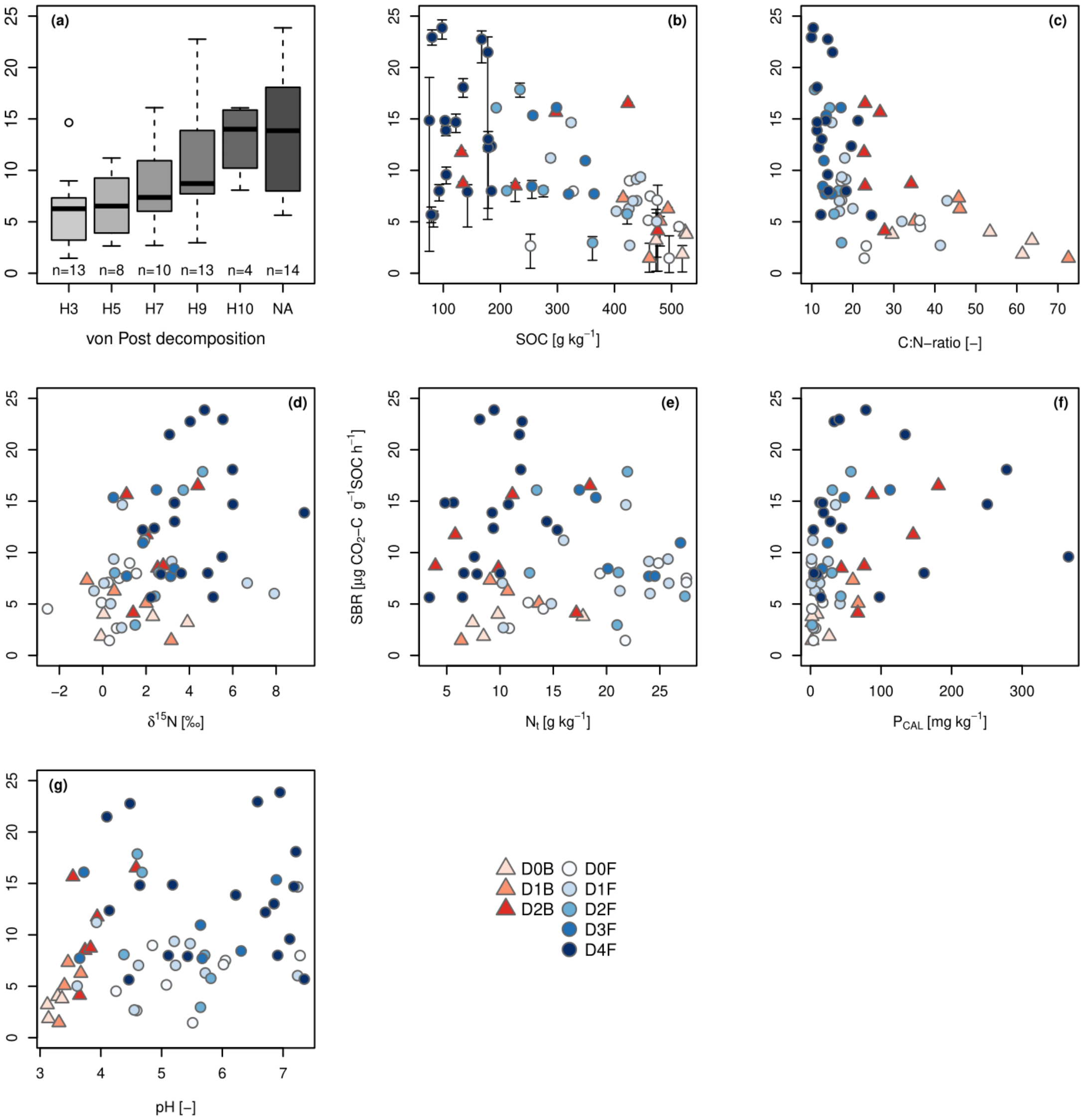

Figure 2-3: Specific basal respiration (SBR) rates of all samples classified in disturbance classes (F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance) versus (a) decomposition degree after von Post (H1 = least decomposed, H10 = most decomposed, NA = "not applicable" as the von Post scale cannot be applied for low C organic soils deriving from peat), (b) soil organic carbon content, (c) carbon to nitrogen ratio, (d) δ^{15}N, (e) total nitrogen content, (f) calcium acetate lactate (CAL) extractable phosphorus content, (g) pH value. Bars in (b) show 2.5 and 97.5% quantiles of the DREAM-fit.

There was a clear difference in δ^{15}N values between samples from undisturbed and disturbed horizons (Fig. 2-3d). The values for undisturbed or slightly disturbed horizons were 1.5 ± 1.9‰ (D0B), 1.2 ± 1.7‰ (D1B), 0.3 ± 1.2‰ (D0F) and 2.2 ± 2.9‰ (D1F) respectively. All the other disturbance classes showed higher δ^{15}N values up to 9.3‰, and a significant overall increase in SBR rates with increasing δ^{15}N (Fig. 2-2). There were positive correlations between δ^{15}N and SBR rates for D0F and D2F (Fig. 2-4, Table S4). In contrast to the overall trend (Fig. 2-2), there was a significant negative correlation between $\delta^{15}N$ and SBR rates in the case of slightly disturbed D1B samples.

Even though there was no significant correlation between N_t and SBR rates (Fig. 2-2), N_t contents were positively correlated with the SBR rates of the disturbance classes D0F, D4F and D0B (Fig. 2-4, Table S4). In contrast, the SBR rates of D3F were negatively correlated with N_t contents.

Overall, P_{CAL} showed significant positive correlations with the SBR rates (Fig. 2-2, Table S3) and, furthermore, P_{CAL} was the explanatory variable with the highest number of positive correlations with SBR over all disturbance classes. This can also be derived from the increase of SBR with P_{CAL} in Fig. 2-3f. In the case of bogs, the correlation increased with increasing disturbance (Fig. 2-4, Table S4). When combining all bog peat samples and all fen peat samples, respectively, there was also a stronger correlation of P_{CAL} and SBR rates for bog peat ($r_s = 0.84$, $p < 0.05$) than for fen peat ($r_s = 0.53$, $p < 0.01$). The effect of the disturbance class was less consistent in the case of fens compared to bogs, with the strongest correlation in D3F.

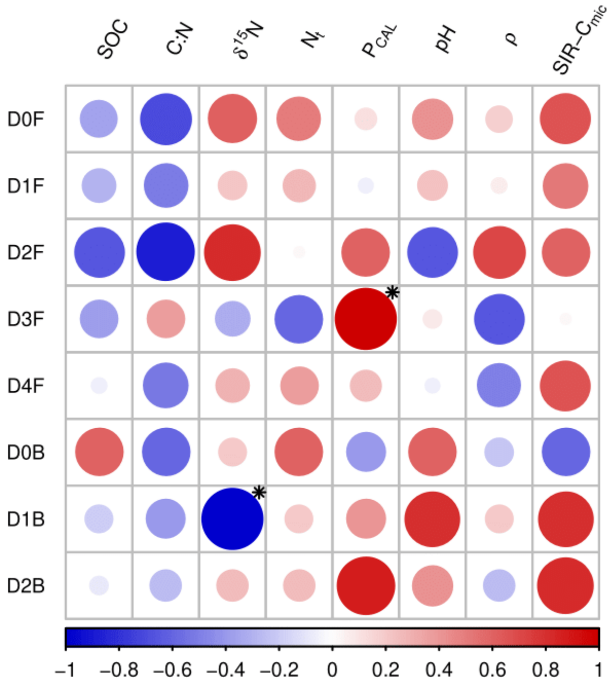

Figure 2-4: Correlation coefficients after Spearman (significant correlations ($p < 0.05$) are marked with asterisks) for the specific basal respiration rates separated into the disturbance classes (F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance) and soil properties: SOC: soil organic carbon content, C:N-ratio: carbon to nitrogen ratio, $\delta^{15}N$, N_t: total nitrogen content, P_{CAL}: calcium acetate lactate (CAL) extractable phosphorus content, pH-value, ρ: bulk density and the specific microbial biomass ($SIR\text{-}C_{mic}$).

Considering all samples, SBR rates and pH did not show a significant correlation, but the general differences between bogs and fens were visible (Fig. 2-3g). Even though bog samples covered only a small range (3.6 ± 0.4) of the overall pH values compared to fen samples (5.5 ± 1.1) the increase in SBR was most distinctive for all disturbance classes of bog samples D0B, D1B and D2B. The correlation between D2F samples and pH values was moderately negative (Fig. 2-4, Table S4).

As texture was only measured for those samples with SOC < 174 g kg^{-1}, correlations could only be determined for n=16 samples. There was neither a significant correlation between sand content and SBR nor between clay content and SBR or BR rates (data not shown).

2.3.3 Microbial biomass and mineralisation rates

The specific microbial biomass (SIR-C_{mic}) was significantly and strongly correlated with SBR (r_s = 0.79, the highest correlation coefficient for the complete data set). SIR-C_{mic} and SBR thus showed similar relationships with explanatory variables (Fig. 2-2, Table S3) as well as comparable patterns across disturbance classes (Fig. 2-1b, Fig. 2-5a). Overall, SIR-C_{mic} was highest for D4F samples followed by D2B, D2F and D3F samples. Values of SIR-C_{mic} were higher for fen peat samples than for bog peat samples and tended to increase with increasing disturbance, especially in the case of bog peat samples. With a closer look to individual disturbance classes, there were still moderate to strong positive correlations between SIR-C_{mic} and SBR, except for D0B and D3F (Fig. 2-4, Table S4). Samples of the classes D1B and D2B showed the highest correlations.

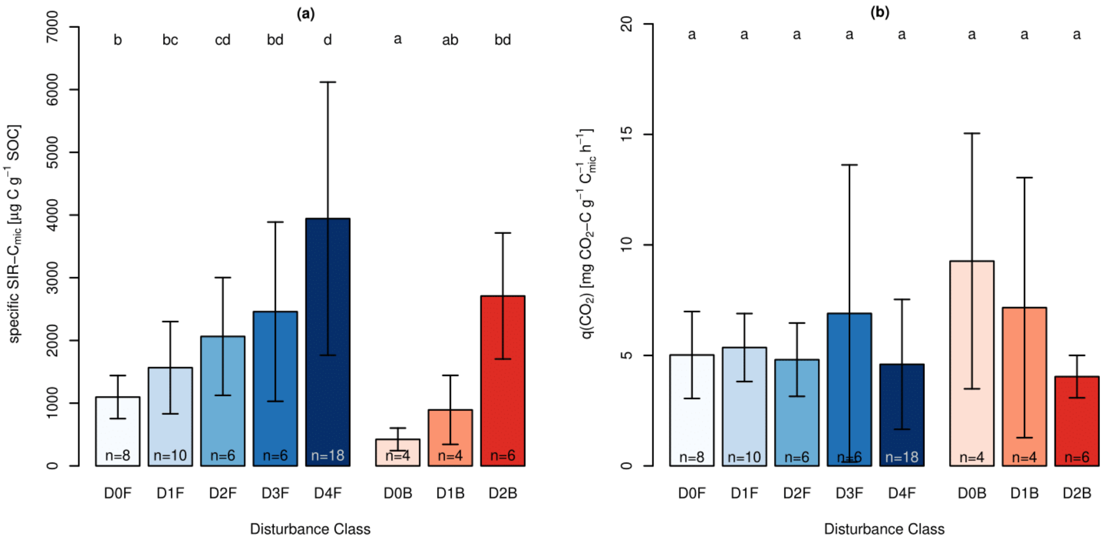

Figure 2-5: Mean of a) specific microbial biomass (SIR-C_{mic}) determined via substrate induced respiration (SIR) and b) metabolic quotient ($q(CO_2)$) for different disturbance classes: F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance. Bars show the standard deviation. Different letters represent significant differences (Tukey's test, $p < 0.05$).

The metabolic quotient was significantly negatively correlated with P_{CAL} and pH values and positively with C:N-ratios (data not shown). There were no significant differences in the metabolic quotient between disturbance classes (Fig. 2-5b, Table S2). Samples of class D0B showed the highest values. All other classes had lower values in similar range. However, there was a slight tendency for decreasing metabolic quotients with increasing disturbance for bog samples.

2.4 Discussion

2.4.1 Methodological aspects

Sieving and drying obviously affects soil structure and microorganisms. Given that the samples cover country-scale variability and originate from a large inventory (Jacobs et al., 2018), they were only available in dried form. The dried soil samples were adjusted to standardised water content and aerobically incubated in the laboratory after pre-incubation. The usage of rewetted soil samples might be seen as a shortcoming of the present study, however, it allowed for an analysis of a sample set of organic soils of unprecedented coverage of land use variability in Germany. Rewetting dried samples is a common approach for soil incubation experiments and numerous studies have shown that effects of drying and rewetting are minor (Grover and Baldock, 2012; Haney et al., 2004; Meisner et al., 2013). Even when samples have been dry for more than three decades respiration rates of rewetted samples matched fresh samples already after some hours for Alfisols and Vertisols (Jones et al., 2019). Unfortunately, there is to our best knowledge no comparable study for organic soils available in literature for which effects might be different. If a sufficient pre-incubation time of the soil samples is maintained such as in our study, rewetting effects will be minimized (Jones et al., 2019), and we assume that this will also be the case for organic soils. Furthermore, the incubation time of this study was based on the standard procedure for this kind of incubation experiment which is 24 to 40 h (Blagodatskaya et al., 2014; Böhme et al., 2005; Dilly and Munch, 1998; Kautz et al., 2004; Müller and Höper, 2004). As pre-experiments have shown that this is too short for some samples to reach quasi-steady state respiration rates we increased the incubation time up to 90 h for SOC rich samples. The range of SBR rates measured in our study (0.03 to 0.6 mg CO_2-C g SOC^{-1} d^{-1}) agreed well with Bader et al. (2018) who provided a literature review on respiration rates from incubation experiments on mineral and peat soil samples, which also stresses the validity of our results.

Thus, our approach allowed to simulate the potential effects of (ongoing) drainage and to compare under standardised and controlled conditions basal respiration rates of samples that experienced different degrees of anthropogenic disturbance comprising both pedogenetic transformation and addition of mineral soil material.

2.4.2 Enhanced variability of respiration rates with increasing disturbance of peat

The most striking result of the present experiment was that specific basal respiration (SBR) rates increased both in magnitude and variability with increasing disturbance of the peat soils, irrespectively of whether this transformation was expressed as a von Post value, a disturbance class or C:N-ratio (Figs. 2-3 and 2-4). Second, while overall SBR rates of fen peat exceeded those of bog peat, SBR of moderately disturbed bog peat was comparable to moderately, strong and heavily disturbed fen peat (Fig. 2-1b), indicating a strong vulnerability of bog peat to decomposition. Third, in contrast to less disturbed peat samples, it proved to be practically impossible to describe SBR or specific microbial biomass (SIR-C_{mic}) for heavily disturbed fen samples with the set of available explanatory variables (Fig. 2-4). Fourth, in contrast to SBR, the basal respiration (BR) rates did not show any consistent patterns (Fig. 2-1a, Fig. S2).

Several previous studies also tried to relate respiration rates to different measures of disturbance. Brake et al. (1999), for example, conducted a study on drained bog peat. As in our study, they found higher SBR rates for disturbed peat samples. In contrast, Glatzel et al. (2004) measured lower rates of aerobic respiration for stronger decomposed bog peat samples, i.e. those with higher von Post values. In this context, it is important to stress that the von Post scale was originally developed for natural peatlands, where strong decomposition is caused by age as well as climatic conditions during peat formation and peatland development, and not by anthropogenic impacts. Due to the lack of better, widely accepted indicators, the von Post scale is frequently (and also in the present study) applied to drained peatlands as well. When taking into account the occasional problematic nature of the von Post value, the results of Glatzel et al. (2004) only contradict our results at first view: Their undecomposed samples are fresh peat from the acrotelm, while samples with a higher degree of decomposition originate from deeper soil layers. Thus, the latter samples are rather comparable with our D0B samples, which also showed low SBR (and BR) rates. This is also consistent with further studies on managed and unmanaged organic soils which found lower SBR rates for samples from deeper soil layers (Bader et al., 2018; Brake et al., 1999; Hardie et al., 2011; Hogg et al., 1992; Säurich et al., 2019a). Reasons might be lower abundance of fresh plant biomass, lower nutrient levels and decreasing availability of labile compounds with depth (see section 2.4.4).

Ilnicki and Zeitz (2003)) reported on highly disturbed fen peat and found lower CO_2 production rates for samples with a high degree of decomposition, especially for moorshy peat soils. In our study, the high variability of SBR, especially of strongly and heavily disturbed fen peat, also comprise samples with such low respiration rates (Fig. 2-3b). However, these samples are rarely pure moorshy peat, but always contain mineral soil, which might improve aeration of the soil and thus increase respiration rates. Physical disturbance of peat, i.e. the destruction of the original structure and mixing with mineral soil, has been previously found to increase CO_2 release in laboratory experiments (Ross and Malcolm, 1988; Rovdan et al., 2002). Similarly, Säurich et al. (2019a) measured SBR rates for peat-sand mixtures and strongly decomposed peat in a long-term incubation experiment with intact soil cores, indicating comparable or even increased SOM vulnerability to decomposition with sand addition.

As mentioned above, strong correlations between soil properties and SBR or SIR-C_{mic} for these heavily disturbed fen samples (D4F, Fig. 2-4) were not found. Since these soils have a comparably low SOC content (127 ± 41 g kg^{-1}, Table 2-2), they have become increasingly similar to mineral soils. It could therefore be expected that stabilisation mechanisms for SOM become more similar to mineral soils. Numerous studies have shown SOM stabilisation on clay minerals (Hassink, 1997; Saidy et al., 2012; Six et al., 2016). However, there was no correlation between clay content and SBR in the present set of samples, despite the wide range of clay content in the heavily disturbed samples (5 to 50%).

The generally higher SBR rates of fen peat compared to bog peat have already been observed in previous studies (Bridgham and Richardson, 1992; Urbanová and Bárta, 2015) and was expected here. Usually, faster decomposition processes occur under minerotrophic conditions and in peat dominated by vascular plants (Blodau, 2002). Undisturbed bogs are characterised by a lack of nutrients, strong acidity and peat substrates that hinder rapid mineralisation due to their chemical composition (Urbanová and Bárta, 2014; Verhoeven and Liefveld, 1997). Urbanová and Bárta (2015) found that the microbial communities in bogs increased in richness and diversity upon drainage, but decreased in fens, indicating high sensitivity of bogs to anthropogenic impacts. The same authors also found that fens and bogs became more similar after long-term drainage as their characteristic differences in biogeochemical properties and microbial composition decreased upon drainage. This is in line with our results: We found significantly lower SIR-C_{mic} in undisturbed bog peat than in fen peat, but under disturbed conditions SIR-C_{mic} became comparable. This points – together with the stronger increase of SBR with disturbance – to a higher vulnerability of bog peat. All these previous findings corroborate our results that SBR rates of bog and fen peat become more similar, but generally higher with stronger degree of disturbance.

Overall, the structural and chemical changes of the peat properties seem to induce destabilising positive feedback processes.

2.4.3 SOM quality as an indicator for respiration rates

While SOM quality is closely linked to the mineralisation of SOM, there is no commonly accepted quality index for SOM (Reiche et al., 2010). To characterize SOM quality, C:N-ratio, degree of decomposition and δ^{15}N stable isotope values were available for this study, as they are all indicators of the transformation stage of organic matter (Bohlin et al., 1989; Glatzel et al., 2004; Krüger et al., 2014; Reiche et al., 2010). The results pointed to a faster turnover of SOM in samples with a narrow C:N-ratio. SBR rates increased rapidly with lower C:N-ratios, at least over a threshold value of 25 (Fig. 3-3c). However, this may only be an effect of preferential C release during decomposition at sufficient N supply (Kuhry and Vitt, 1996), i.e. a narrow C:N-ratio is also a product of fast turnover. In contrast, wider C:N-ratios seem to indicate a more stable SOM pool. This indicates that there seems to be surprisingly no increased stabilisation with increased degradation due to selective preservation of more stable SOC components (Lehmann and Kleber, 2015) that are unattractive for decay, such as waxes, polyphenols, lignins and tannins (Verhoeven and Liefveld, 1997). Low δ^{15}N values appear to be a good indicator of undisturbed or fresh SOM, especially in bog peat, due to the lack of SOM turnover processes that usually result in ^{15}N enrichment (Nadelhoffer et al., 1996). The positive correlation between specific basal respiration and δ^{15}N (Fig. 2-2, Fig. 2-3e) indicated that increased microbial transformation under aerobic conditions altered the stable N isotope signature of SOM. Mineralisation will therefore result in both increased δ^{15}N values and increased respiration rates, making it difficult to distinguish between cause and effect.

The greater the disturbance, the harder it was to find possible correlative patterns of SOM quality parameters and SBR, especially in the case of fen peat samples. One reason for this could be that chemical and physical changes during decomposition differed between peat-forming plants (Bohlin et al., 1989). These are generally more diverse in fens than in bogs, but could no longer be identified. Furthermore, the class of heavily disturbed fen samples combined samples that have been amended by mineral soil by different processes (e.g. ploughing, application from external sources, or natural sedimentation in riverine fens). This adds another level of complexity (see section 2.4.2), which might contribute to the high variability of SBR rates. Finally, the DREAM-fits showed the largest uncertainty for some of the samples of the class D4F (Fig. 2-3b), which might have added to the difficulty in finding appropriate explanatory variables. However, even when excluding those samples with large uncertainties, the general picture of high SBR rates and a high variability remained valid. Explaining respiration rates from disturbed organic soils thus remains challenging, especially when moving beyond samples from one peatland or one region. This problem is not unique to our study, as other authors faced similar problems when trying to relate respiration rates to soil properties. For example, the incubation study on disturbed fen peat by Bader et al. (2018) only found weak relationships between CO_2 fluxes and soil chemical and physical properties, even though they incubated fresh samples for a much longer time (6 months).

2.4.4 Nutrient availability and acidity as indicators for respiration rates

Agriculturally used peat soils drained for a long time are often enriched in N and (labile) P contents (Laiho et al., 1998; Schlichting et al., 2002; Sundström et al., 2000) due to ongoing mineralisation of SOM, fertilisation and, in the case of P, sorption of the resulting inorganic P forms to Fe(III) compounds (Zak et al., 2010). Such enrichment is also visible in the present sample set (Table 2-2). As P is needed for microbial growth, a lack of labile phosphorus limits the decomposition of SOM. Due to the low pH and low iron contents, natural bogs are frequently P-limited (Verhoeven et al., 1990), which is reflected by the low content of plant-available phosphorus (P_{CAL}) of the undisturbed bog peat samples. However, disturbed bog samples showed much higher P_{CAL} contents than the respective fen classes, which likely originated from past fertilisation. Results of the present study showed that P_{CAL} was indeed the most important explanatory variable for SBR rates across all disturbance classes. This confirms the results of Brake et al. (1999) who also found that P strongly correlates with the respiration rates of disturbed bog samples. Furthermore, an incubation experiment with undisturbed peat cores also showed both surprisingly high P_{CAL} contents of bog peat and P_{CAL} as a major explanatory variable for CO_2 fluxes across peat types and sampling depths (Säurich et al., 2019a).

Nitrogen contents of all disturbance classes were comparable (except for D4F) and higher in fen peat than in bog peat (Table 2-2), while C:N-ratios decreased with disturbance. As indicated by Fig. 2-4, SBR rates seem to be positively influenced by N contents in the case of undisturbed samples only. This might indicate a shift from N to P limitation in the course of degradation processes since ongoing mineralisation increases the N supply. Furthermore, Toberman et al. (2015) found a positive correlation between N and P content in Sphagnum peat, pointing to the important role of P availability in N fixation.

Especially in the case of bogs, there was also a positive correlation between SBR rates and pH values (Fig. 2-3g), probably reflecting lower microbial activity in an undisturbed acidic environment (D0B, Fig. 2-5a). Earlier studies have, counterintuitively, sometimes detected a negative correlation (Ausec et al., 2009; Fisk et al., 2003) between pH and respiration. The authors explain the negative relationship by a restricted efficiency of C metabolism of the microbial biomass in bogs due to the acidic environment, which, however, contradicts the common observation that fens show higher respiration rates than bogs (Bridgham and Richardson, 1992; Urbanová and Bárta, 2015). However, with increasing disturbance any influence of the pH-value vanishes in the present sample set, possibly due to better nutrient availability and increased overall pH-values.

2.4.5 Microbial biomass and activity

The specific microbial biomass (SIR-C_{mic}) increased with the increasing degree of anthropogenic disturbance for both fen and bog samples (Fig. 2-5a). While topsoils frequently show higher microbial activity than subsoils (Brake et al., 1999; Fisk et al., 2003; Preston et al., 2012; Säurich et al., 2019a), it is surprising that heavily degraded topsoils (D4F) had higher SIR-C_{mic} than less disturbed topsoils (D2F) since the remaining SOM of such degraded peat should be energetically less attractive for microorganisms than better preserved peat (Fisk et al., 2003). One reason might be the improved availability of nutrients due to long-term aerobic decomposition (and possibly fertilisation), which might cause changes in the community and in the amount of microbial biomass (Amador and Jones, 1993; Brouns et al., 2016). This is reflected in positive correlations of specific SIR-C_{mic} with pH value and P_{CAL} as well as negative correlations with C:N-ratios (Fig. 2-2).

The metabolic quotient, i.e. the ratio of basal respiration to microbial biomass, indicates the efficiency of microorganisms to transform SOM into microbial biomass. Overall, there were no significant differences in the metabolic quotient between disturbances classes (Fig. 2-5b). The slight tendency towards lower metabolic quotients of strongly disturbed bog and fen samples compared to undisturbed samples might indicate that these microorganisms are more efficient at using SOM for growth, possibly due to better nutrient availability.

2.4.6 Implications for peatland management

Both the high basal respiration and the high specific basal respiration rates of heavily disturbed samples confirm the vulnerability of “low C organic soils” to decomposition that has already been identified in field studies (Leiber-Sauheitl et al., 2014; Tiemeyer et al., 2016). Potential emissions do not reach a constant level, and do not always decrease or stop with increasing disturbance. We expected that below some unknown SOC content such former peat soils would behave like mineral soils, i.e. with respiration rates related to SOC or clay content. However, this threshold does not seem to be within the studied SOC range of 76 to 526 g kg^{-1}. Additionally, the high variability of respiration rates of heavily disturbed samples (Fig. 2-3b) also agrees with the finding that the variability of CO_2 emissions from “low C organic soils” field studies is high (Tiemeyer et al., 2016). Therefore, mixing organic soil with mineral soil does not seem to mitigate respiration rates, but on average increases the vulnerability of SOM to decomposition. Similar effects have been found in field studies (Maljanen et al., 2004) as well as in laboratory studies with intact cores (Säurich et al., 2019a). However, for specific samples the respiration rates remains still rather unpredictable. By mixing peat with mineral soil, a whole new soil horizon develops that may include modified microbial communities and potentially fresh SOM due to aggregate destruction (Ross and Malcolm, 1988). Increased availability of nutrients (especially of P) by fertilisation might also contribute to increased respiration rates (Fig. 2-3f, Amador and Jones, 1993; Brake et al., 1999). However, it should be stressed that we did not carry out fertilisation experiments here. Liming of acidic peat soils might have a similar effect because increasing the pH value generates favourable microbial conditions for decomposition (Andersson and Nilsson, 2001; Fuentes et al., 2006). Finally, degradation of the topsoil might even influence the mineralisation of deeper peat layers due to leaching of nutrients and dissolved organic matter. Raising the water table may prevent further decomposition and, under optimum conditions, reinstate the typical peatland environment, however, severe disturbance might have a long-lasting effect on the biogeochemistry of rewetted peatlands.

2.5 Conclusions

This study examined the vulnerability of SOM of organic soils to decomposition by determining the basal respiration and specific basal respiration (SBR) rates under aerobic conditions in the laboratory. It could be shown that SBR increased in magnitude and variability with increasing disturbance, and that it was highest and most variable at the boundary between mineral and organic soils. Thus, there was a trend towards higher SBR with lower SOC content. Furthermore, bog peat samples seemed to be more sensitive to anthropogenic disturbance than fen peat samples as indicated by a stronger increase of SBR rates with increasing disturbance. Overall, the most important indicators for the vulnerability of SOM to decomposition identified in the present study were narrow C:N-ratios, low SOC content, high pH-values, and – most important – high contents of plant-available phosphorus. There seems to be a positive feedback loop of disturbance and increased mineralisation. However, we could not explain the very high variability of SBR rates of heavily disturbed samples with the available soil properties. Given the continued drainage and disturbance of peatlands and the considerable potential of high CO_2 emissions even from heavily disturbed organic soil presented here, future research needs to be concentrated on identifying hotspots within these very heterogeneous soils for correctly targeting mitigation measures. Furthermore, mixing peat with mineral soils does not seem to be a promising mitigation option.

Acknowledgements

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3 How do sand addition, soil moisture and nutrient status influence greenhouse gas fluxes from drained organic soils?

Säurich, A., Tiemeyer, B., Dettmann, U., Don, A. (2019): How do sand addition, soil moisture and nutrient status influence greenhouse gas fluxes from drained organic soils? Soil Biology and Biochemistry 135, 71-84

Abstract

Drainage turns peatlands from natural carbon sinks into hotspots of greenhouse gas (GHG) emissions from soils due to alterations in hydrological and biogeochemical processes. As a consequence of drainage-induced mineralisation and anthropogenic sand addition, large areas of former peatlands under agricultural use have soil organic carbon (SOC) contents at the boundary between mineral and organic soils. Previous research has shown that the variability of GHG emissions increases with anthropogenic disturbance. However, how and whether sand addition affects GHG emissions remains a controversial issue. The aim of this long-term incubation experiment was to assess the influence of hydrological and biogeochemical soil properties on emissions of carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). Strongly degraded peat with sand addition (peat-sand mixtures) and without sand addition (earthified peat) was systematically compared under different moisture conditions for fen and bog peat. Soil columns originating from both the topsoil and the subsoil of ten different peatlands under grassland use were investigated. Over a period of six months the almost saturated soil columns were drained stepwise via suction to −300 hPa. The CO_2 fluxes were lowest at water-saturated and dry soil moisture conditions, resulting in a parabolic dependence of CO_2 fluxes on the water-filled pore space (WFPS) peaking at 56–92% WFPS. The highest N_2O fluxes were found at between 73 and 95% WFPS. Maximum CO_2 fluxes were highest from topsoils, ranging from 21 to 77 mg C m^{-2} h^{-1}, while the maximum CO_2 fluxes from subsoils ranged from 3 to 14 mg C m^{-2} h^{-1}. No systematic influence of peat type or sand addition on GHG emissions was found in topsoils, but CO_2 fluxes from subsoils below peat-sand mixtures were higher than from subsoils below earthified peat. Maximum N_2O fluxes were highly variable between sites and ranged from 18.5 to 234.9 and from 0.2 to 22.9 µg N m^{-2} h^{-1} for topsoils and subsoils, respectively. CH_4 fluxes were negligible even under water-saturated conditions. The highest GHG emissions occurred at a WFPS that relates – under equilibrium conditions – to a water table of 20–60 cm below the surface in the field. High

maximum CO_2 and N_2O fluxes were linked to high densities of plant-available phosphorus and potassium. The results of this study highlight that nutrient status plays a more important role in GHG emissions than peat type or sand addition, and do not support the idea of peat-sand mixtures as a mitigation option for GHG emissions.

3.1 Introduction

Globally, peatlands hold more than one third of the soil organic carbon (SOC) store (Scharlemann et al., 2014; Yu et al., 2010), although they cover just 330 to 463 million ha (2.2–3%) of the global terrestrial surface (Leifeld and Menichetti, 2018; Tubiello et al., 2016). A total of 22.5–50.9 million ha of peatlands worldwide have been drained for agricultural use (Leifeld and Menichetti, 2018; Tubiello et al., 2016), 60% of which are located in Europe alone (Tubiello et al., 2016). Intact peatlands are a net sink of carbon dioxide (CO_2) but release methane (CH_4) (Wilson et al., 2016). Drainage, however, turns peatlands into sources and hotspots for CO_2 and nitrous oxide (N_2O) emissions from soils while, at the same time, they are either minor sources or even small sinks of CH_4 (Maljanen et al., 2010; Tiemeyer et al., 2016).

Besides increased mineralisation of soil organic matter (SOM) by aerobic decomposition, drainage causes soil consolidation due to the loss of buoyancy. Both processes lead to the subsidence of the soil surface and the initiation of secondary pedogenetic processes in peat. With this formation of aggregates, shrinkage cracks and earthification, the peat structure gradually changes (Ilnicki and Zeitz, 2003). As a consequence, soil physical properties of drained organic soils differ from undisturbed peat soils. For example, macroporosity and total porosity are lower while bulk density (ρ) is higher in drained organic soils (Dettmann et al., 2014; Schwärzel et al., 2002; Zeitz and Velty, 2002).

As a consequence of both the preferential release of CO_2 by mineralisation and fertilisation, the chemical composition of peat changes and N, phosphorus (P) and potassium (K) contents increase in topsoils of agriculturally used peatlands (Holden et al., 2004; Laiho et al., 1998). The increase in nutrient densities is even greater, partly due to the simultaneous increase in bulk density. In agricultural peatlands, nutrients are furthermore added as fertilizer. Field studies have shown that the CO_2 emissions depend on N densities in the aerobic zone (Tiemeyer et al., 2016). Previous studies on N, P and K addition have demonstrated an increase in microbial respiration with increasing nutrient content (Larmola et al., 2013; Pinsonneault et al., 2016a; Sundström et al., 2000). The availability of P has a positive influence on CO_2 (Amador and Jones, 1993; Brake et al., 1999) and N_2O fluxes (Liimatainen et al., 2018; Regina et al., 1996).

In addition to drainage, peat soils may have been covered by mineral soil (mainly sand) (Göttlich, 1990) to enhance trafficability and increase yields. Under ideal circumstances the sand layer should only be ploughed shallowly, however at most sites the underlying peat has subsequently been mixed with the sand which creates peat-sand mixtures (Fig. S3). These topsoils are not to be confused with the “German sand-mixing culture” by which deep ploughing into the mineral subsoil has created alternating tilted bars of sand and peat (Fig. S3). Mixing peat with sand adds to and intensifies the alteration of soil physical parameters and soil structure. As a result the soil hydraulic properties are also changed which is reflected by the percentage of different pore sizes (Rovdan et al., 2002; Walczak and Rovdan, 2002). Soil hydraulic properties are crucial for the response of soil moisture to boundary conditions (groundwater level, precipitation, evapotranspiration) as the same boundary conditions will result in different water contents. Furthermore, changes in the physical structure of peat affect decomposition rates and nutrient mobilisation (Ross and Malcolm, 1988).

As a joint consequence of drainage-induced mineralisation and peat-sand mixing, peatlands under agricultural use can have SOC contents at the boundary between mineral and peat soils (> 300 g SOM kg^{-1} according to the German classification system, Ad-Hoc-Arbeitsgruppe Boden, (2005)). Studies on SOC dynamics of such “low C organic soils” are rare, but a synthesis study on 48 drained grasslands has shown that emissions of CO_2 and N_2O from “low C organic soils” are as high as emissions from “true” peat soils (Tiemeyer et al., 2016). Tiemeyer et al. (2016) also reported that there is a large variability in GHG emissions from these soils, which cannot easily be explained due to the interaction of soil properties, hydro-meteorological conditions and management in field studies. Field studies, however, have shown that SOC content in the topsoil does not influence CO_2 emissions (Leiber-Sauheitl et al., 2014) or that CO_2 emissions actually increase when peat is mixed with mineral soil (Maljanen et al., 2004). Others have found that the German sand-mixing culture (Bambalov, 1999) as well as sand cover on peat (Höper, 2015; Zaidelman and Shvarov, 2000) may reduce CO_2 emissions. Therefore, laboratory studies with defined boundary conditions such as temperature and moisture can help identify to factors that control GHG emissions and allow a systematic evaluation of the hydrological, biogeochemical and management-induced drivers.

There are multiple laboratory studies on GHG fluxes from peat soils. These studies have frequently used constant water content (Ausec et al., 2009; Hardie et al., 2011) or studied the influence of soil moisture on GHG emissions using disturbed samples (Hogg et al., 1992; Moore and Dalva, 1997; Moore and Knowles, 1989). Under such circumstances, the effects of soil physical parameters cannot be captured. However, there are some studies on GHG emissions that have incubated intact samples at different water contents, but the samples only came from one or two sites (Berglund and Berglund, 2011; Brouns et al., 2016; Kechavarzi et al., 2010; Norberg et al., 2018; van Lent et al., 2018) or GHG sampling only occurred sporadically (Berglund and Berglund, 2010; Norberg et al., 2018; van Lent et al., 2018). There is a lack of a systematic evaluation of hydrological and biogeochemical factors, such as peat type and nutrient availability, influencing GHG fluxes on a broader basis using intact samples. Furthermore, an investigation of “low C organic soils” in such laboratory experiments is missing. As sand addition on peatlands is a common practice e.g. in northern Germany (Schulz and Waldeck, 2015) and Norway (Sognnes et al., 2006) and is sometimes proposed as an emission mitigation measure (Bambalov, 1999; Zaidelman and Shvarov, 2000), the focus of the present study was on peat-sand mixtures.

Soil columns originating from six fen and four bog peatlands under grassland use were investigated. Half of these peatlands have anthropogenic peat-sand mixtures as topsoils. The aim of this long-term incubation experiment was to assess the influence of hydrological and biogeochemical soil properties on GHG emissions from drained organic soils with and without sand addition. Accordingly, we had four major objectives: (i) to identify the optimum soil moisture for the occurrence of maximum GHG fluxes, (ii) to assess the impact of sand addition to the peat topsoil on GHG fluxes, (iii) to analyse the sensitivity to drainage of different peat types by comparing topsoils and subsoils as well as fen and bog peat, and (iv) to determine the importance of nutrient contents for GHG fluxes.

3.2 Material and methods

3.2.1 Sampling sites

The choice of sampling sites was based on profile descriptions and soil properties acquired within the German Agricultural Soil Inventory, in which agricultural soils of Germany were sampled in an 8×8 km grid (Vos et al., 2018). The selection criteria included grassland use, the presence of a well-preserved peat horizon in the soil profile and the best possible coverage of the SOC, C:N ratio and pH value ranges. Six fen peat and four bog peat sites were sampled. All the sites have a well-preserved peat subsoil horizon that is permanently below groundwater level and either a strongly degraded (“earthified”) topsoil horizon or sand added and mixed to different degrees into the topsoil (“peat-sand mixture”; Table 3-1; Fig. 3-1). Around 2200 to 2500 t sand ha^{-1} (bog peat-sand mixtures) or 600 to 800 t sand ha^{-1} (fen peat-sand mixtures) were added 35–60 years before sampling. For sampling, a soil pit was opened at each site down to 1m to take intact soil columns (n=3 each) from both the topsoil and the subsoil (upper limits between 5 to 15 and 20–140 cm, respectively, Table S5). Intermediate temporarily water-saturated horizons between strongly decomposed topsoils and well-preserved subsoils were not sampled. Prior to sampling, approximately 5 cm of topsoil including vegetation and roots were removed to avoid artefacts by living biomass and germinating plants during incubation. After digging to the intended depth, the soil was pre-cut with a knife, and plexiglas cylinders (18 cm high, 14.5 cm i.d.) were gently pushed vertically into the soil until the soil column within the cylinder reached a height of 10 cm. Afterwards, the cylinders were carefully dug out. The soil profile was classified according to the German manual of soil mapping (Ad-Hoc-Arbeitsgruppe Boden, 2005).

Table 3-1: Sampling sites and their main soil characteristics. The degree of decomposition in accordance with von Post (H) was determined according to Ad-Hoc-AG Boden (2005), but it is not applicable (NA) for peat-sand mixtures. All topsoils are amorphous peat (partially mixed with sand) without any recognisable plant remains. Sample identifiers: s – peat-sand mixture in the topsoil, e – earthified peat in the topsoil, B – bog, F – fen.

ID	Peatland type	Peat-sand mixture topsoil	Degree of decomposition topsoil|subsoil	Peat composition subsoil
sB1	Bog	yes	NA|H3	*Sphagnum spp., Eriophorum vaginatum* L.*, Ericaceae*
sB2	Bog	yes	NA|H2	*Sphagnum spp., Scheuchzeria palustris* L.*, Ericaceae*
eB1	Bog	no	H10|H4	*Sphagnum spp., Scheuchzeria palustris* L.*, Ericaceae*
eB2	Bog	no	H10|H2	*Sphagnum spp., Ericaceae (*i.a. *Vaccinium oxycoccos* L.*)*
sF1	Fen	yes	NA|H6	*Carex spp., Alnus glutinosa* (L.) Gaertn.
sF2	Fen	yes	NA|H6	*Carex spp., Eriophorum vaginatum* L.*, Sphagnum spp., Ericaceae*
sF3	Fen	yes	NA|H6	*Carex spp., Alnus glutinosa* (L.) Gaertn.
eF1	Fen	no	H10|H2	*Carex spp., Phragmites australis* (Cav.) Trin. ex. Steud.
eF2	Fen	no	H10|H3	*Carex spp., Phragmites australis* (Cav.) Trin. ex. Steud.
eF3	Fen	no	H10|H3	*Carex spp.*

3.2.2 Microcosm incubation experiment

The columns were stored in darkness at 6 °C until the commencement of the incubation experiment. Before starting the experiment, the samples were saturated from the bottom until constant weight over a period of three weeks. All 60 soil columns were installed in a microcosm system (Fig. S4; Hantschel et al. (1994)) at a constant temperature of 10 °C that approximates the mean annual temperature of Germany. The headspace of the soil columns was permanently flushed with 10 mL min^{-1} synthetic CO_2 free air (20% O_2, 80% N_2) that was humidified using gas-washing bottles. The use of this gas mixture improves the accuracy of CO_2 measurements, but precludes the determination of any N_2O or CH_4 uptake. An automatic flow meter switching every 3 min measured flow rates for each column separately, resulting in one measurement per column every 3 h. The initially water-saturated soil columns were drained via suction plates at the bottom of the columns by increasing the suction step by step, starting at 0 hPa (−20, −30, −60, −150, −300 hPa). Each suction step was continued until soil hydrological equilibrium was achieved and CO_2

fluxes showed quasi-constant values. The resulting suction steps took 3, 8, 12, 18, 46 and 108 days, respectively.

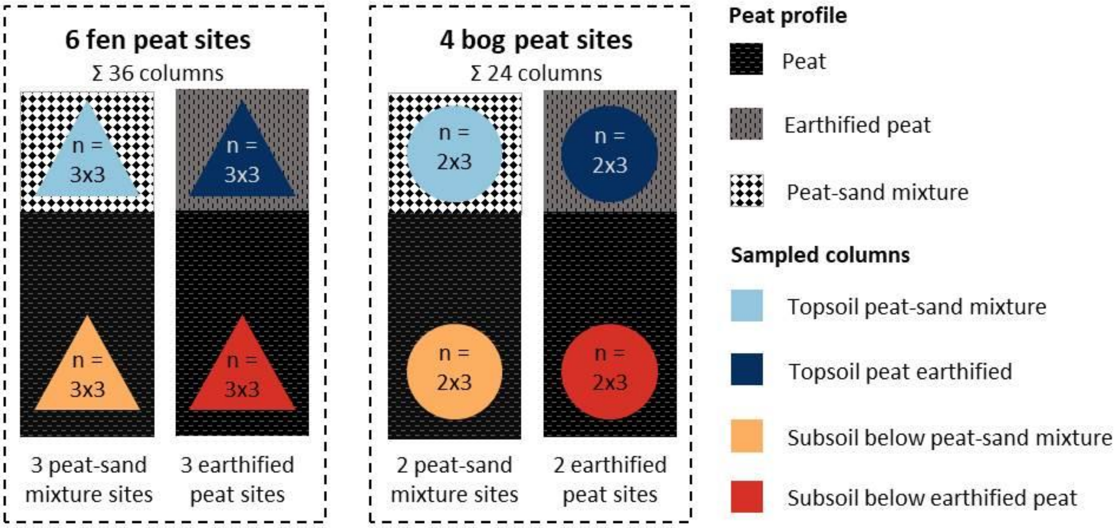

Figure 3-1: Schematic overview of the sampling design: 60 soil columns collected from ten different peatland sites.

3.2.3 Analytical methods

Concentrations of CO_2, N_2O and CH_4 in the headspace gas of each column were measured automatically every 8 h via online gas chromatography (GC-2014, Shimadzu, Kyoto, Japan). The percolate was sampled from the suction bottles when reaching an amount of at least 5 mL and was stored in darkness at 6 °C until further analysis. As the water had passed the membrane of the suction plate (0.2 µm), no further filtration was necessary. The dissolved organic carbon (DOC) concentrations were measured using a DimaTOC 2000 (DIMATEC, Essen, Germany). Total dissolved carbon (TDC) and dissolved inorganic carbon (DIC) were measured separately by combustion (TDC 850 °C; DIC 165 °C) to calculate DOC as the difference between TDC and DIC.

After the final suction step, the soil columns were dried at 80 °C, sieved to < 2 mm and soil properties were determined for each individual column. The bulk density (ρ) was determined by drying the soil columns at 80 °C until constant mass and subsequent weighing. The porosity was calculated from the weights of the fully saturated soil at the start and the dried soil at the end of the experiment. The texture of the peat-sand mixtures was determined by sieve-pipette analysis (Sedimat 4–12, UGT, Müncheberg, Germany) after aggregate destruction and the removal of salt and soil organic matter using H_2O_2 (DIN ISO 11277, 1998).

The pH values were measured with a glass electrode after an extraction with a 0.01 mol L^{-1} $CaCl_2$ solution. Total SOC and total N contents (N_t) were measured by dry combustion (RC 612, LECO Corporation, St. Joseph, USA). Plant-available concentrations of P and K were determined by calcium acetate lactate extraction (P_{CAL} and K_{CAL} respectively) (Schüller, 1969; VDLUFA, 2012). The P_{CAL} concentrations were measured using the molybdenum blue method (Murphy and Riley, 1962) and K_{CAL} concentrations via atomic emission spectroscopy. Calcium acetate lactate extraction is commonly used in agronomics. It mostly determines easily available P and is comparable to Olsen P values (Neyroud and Lischer, 2003). For further data analyses, SOC, N_t, P_{CAL} and K_{CAL} concentrations were converted into densities (mg cm^{-3} or µg cm^{-3}).

3.2.4 Data analyses

Data analyses were performed using the R software environment (R Core Team, 2018). To compare the results of samples with different porosities, the water-filled pore space (WFPS [-]), i.e. the ratio of volumetric water content at the end of each suction step and saturated volumetric water content, was used as a measure of soil moisture. Despite efforts to minimise loss of water due to gravitation during the installation process, the soil columns had WFPS of between 0.83 and 0.96 at the start of the experiment.

DOC losses for each suction step were calculated by multiplying the amount of percolate by the average DOC concentration of the respective suction step. It was assumed that DOC would largely be mineralised at some point and DOC concentrations were converted into CO_2 and thus named CO_{2DOC} (IPCC (Intergovernmental Panel on Climate Change), 2014).

With Eq. 3.1 the measured gas concentrations c (ppm) of CO_2, N_2O and CH_4 in the headspace of each column were converted to fluxes for each time step:

$$F = \frac{M}{V_m}\, c\, \frac{273.15}{273.15+T}\, v\, 10^{-6}\, 60\, \frac{1}{A}, \tag{3.1}$$

where *F* is the flux in mg C m^{-2} h^{-1} or µg N m^{-2} h^{-1} respectively, *M* is the molecular mass in g mol^{-1}, V_m is the ideal gas mole volume (22.4 L mol^{-1}), *T* is the air temperature of the microcosm system (10 °C), *v* is the flow rate in mL min^{-1} and *A* is the cross-sectional area of the soil column in m^2. The mean and standard error of the last 10 values of each replicate (30 values) of each suction step were used to determine the equilibrium CO_2 fluxes. N_2O and CH_4 fluxes are given as the mean and standard error of the triplicates over of each suction step due to the erratic behaviour of N_2O.

The GHG balance was compiled for the −60 hPa suction step. At this point most of the peat's macropores are drained, field capacity is reached (Dettmann et al., 2014) and conditions for microbial activity are favourable. The N_2O and CH_4 concentrations were converted into CO_2 equivalents by multiplying them by the 100-year time horizon global warming potential of 298 and 25 respectively (Forster et al., 2007).

Spearman's rank correlation coefficient *r* (n=10 when topsoils or subsoils tested separately; n=20 for the whole sample set) was calculated for the fluxes and all measured soil properties using the R package *Hmisc* (Harrell, 2016). This approach allows for nonlinear monotonic relationships. The *p* values were adjusted using the Bonferroni method. All the correlation coefficients given in this paper have *p* values < 0.001 unless stated otherwise. Differences between the CO_2 and N_2O fluxes of the different treatments were determined using linear mixed effects models with the sampling site as random factor (R package *lme4*, Bates et al. (2015)) and Tukey's honest significant difference test (α=0.05) for linear mixed effect models implemented in the R package *emmeans* (Lenth, 2018).

3.3 Results

3.3.1 Soil properties

Fig. 3-2 summarises the soil properties of the four different classes: topsoil of peat-sand mixture, earthified peat topsoils, subsoil below peat-sand mixture and subsoil below earthified peat (see Table S5 for details). It is important to bear in mind that the subsoils were neither mixed with sand nor earthified, but were well-preserved peat.

The mean SOC content covered a broad range from peat-sand mixtures to well-preserved subsoil peat. Due to having higher bulk densities than subsoils, the highest mean SOC densities were found in the topsoils. Nutrient densities were also generally much higher in topsoils than in subsoils. The densities of N_t followed a similar pattern as SOC. The C:N ratios in the topsoils were much narrower than in the subsoils, while the opposite was found for pH values. The P_{CAL} and KC_{AL} densities of the topsoils were 6–145 times (P_{CAL}) and 3 to 45 times (K_{CAL}) greater than in the subsoils.

The SOC density of peat-sand mixtures was lower than that of earthified topsoils, but still as high as the subsoil values (bog peat) or even higher (fen peat). Surprisingly, subsoils below the peat-sand mixtures differed from the other subsoils. Particularly in the case of bog peat, they showed higher N_t contents, lower C:N ratios, slightly higher bulk densities, and higher pH values (bog peat only). These might all be indicators of anthropogenic influence. P_{CAL} and K_{CAL} (fen peat only) densities in peat-sand mixture topsoils were also higher than in earthified peat topsoils.

As expected, fen peat had higher values of N_t than the equivalent bog peat class. Thus the C:N ratio was higher in bog peat than in fen peat, while pH values followed an opposite pattern with more variable pH values in fen peat than in bog peat. Surprisingly, P_{CAL} and K_{CAL} densities were clearly higher in bog peat topsoils than in fen peat topsoils. In contrast, mean K_{CAL} and P_{CAL} densities of bog and fen peat subsoils were similar.

3.3.2 Time series of GHG fluxes

Fig. 3-3 shows class-wise mean CO_2 fluxes from fen peat (a) and bog peat (b). Average CO_2 fluxes from all topsoil classes showed an increase with the start of drainage, but fluxes slowly decreased over the whole experiment with decreasing soil moisture. During the first suction steps in particular, initial flux peaks occurred immediately after increasing the suction, but fluxes levelled out after several days. Significantly lower flux rates were measured for the subsoils of all sites. Flux peaks from subsoils following increased suction events were also less distinctive. In contrast to the behaviour of topsoils, fluxes from subsoils did not decrease over the course of the experiment, but actually steadily increased until the −150 hPa suction step in the case of peat-sand mixtures. CO_2 fluxes from earthified topsoils of bog peat were approximately 1.8 times higher than fluxes from all the other topsoil classes, which all showed similar ranges. Thus, in contrast to the bog peat, there were only minor differences between fluxes from peat-sand mixtures and earthified topsoils for the fen peat sites.

Mean N_2O fluxes (Fig. S5) from topsoils peaked early during the experiment under slight drainage. Afterwards, N_2O slowly decreased until the suction step of −150 hPa. With further drying, only minimal N_2O fluxes occurred. N_2O fluxes from the subsoils were negligible except for some slightly elevated values in the case of earthified bog peat subsoils. Fen peat-sand mixtures and earthified bog peat topsoils showed the highest N_2O fluxes.

CH_4 fluxes were generally negligible for all samples (< 1 µg CH_4-C m^{-2} h^{-1}) even at the start of the experiment under quasi-saturated conditions. Due to the use of CH_4-free air, we could not determine any potential uptake of CH_4 by the soil.

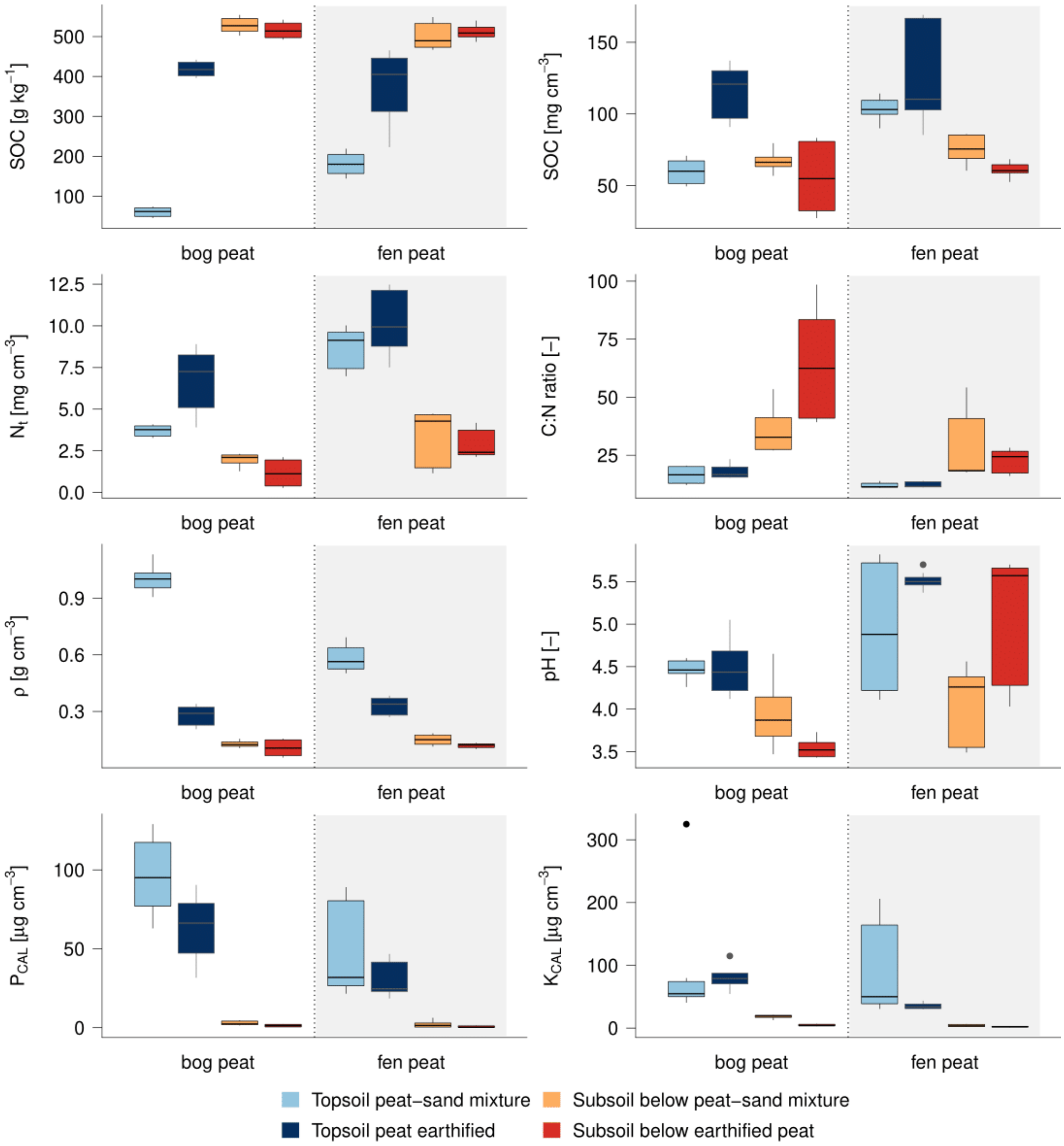

Figure 3-2: Properties of the soil columns: soil organic carbon (SOC) content, SOC density, total nitrogen (N_t) density, C:N ratio, bulk density (ρ), pH value, calcium acetate lactate extractable phosphorus (P_{CAL}) density, calcium acetate lactate extractable potassium (K_{CAL}) density. Sample size: bog peat n=6, fen peat n=9.

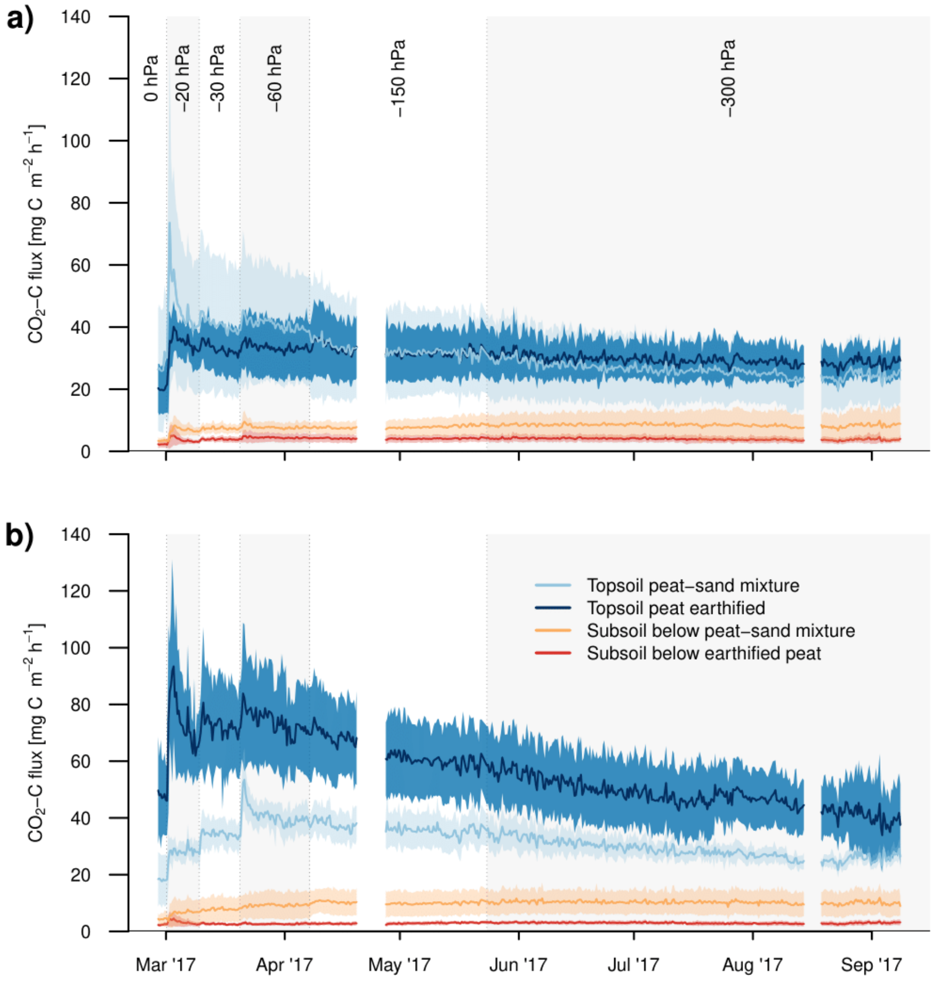

Figure 3-3: CO_2-C fluxes (mean values and standard deviations) over the course of the experiment and suction steps for (a) fen peat and (b) bog peat.

3.3.3 Influence of water-filled pore space, peat type and peat-sand mixing

A distinct parabolic dependence was detected between WFPS and CO_2 fluxes for all topsoils (Fig. 3-4a) and all subsoils (Fig. 3-4b), except for one fen peat and one bog peat subsoil. At the start of the experiment, soils had a mean WFPS (±standard error) of 0.93 ± 0.01. The CO_2 fluxes increased to their maxima at a mean WFPS of 0.84 ± 0.02 (topsoils, Fig. 3-4a) and 0.83 ± 0.05 (subsoils, Fig. 3-4b). Subsequently, they decreased until minimal mean WFPS of 0.68 ± 0.02 (topsoils, Fig. 3-4a) and 0.76 ± 0.04 (subsoils, Fig. 3-4b) at the −300 hPa suction step. Maximum CO_2 fluxes were up to four times higher than those under quasi-saturated conditions, but there were no significant differences between sample groups regarding the ratios of maximum CO_2-C fluxes and CO_2-C fluxes under water saturation (Table 3-2). Maximum CO_2 fluxes (mean ± standard error) from topsoils covered a range from 21.4 ± 0.3 to 77.3 ± 1.4 mg C m^{-2} h^{-1}, whereas subsoils showed a high variability (2.7 ± 0.1 to 14.0 ± 2.0 mg C m^{-2} h^{-1}, Table S6). An influence of peat-sand mixing on CO_2 fluxes was observed for bog peat only, with significantly lower CO_2 fluxes from peat-sand mixtures. No general influence of peat-sand mixing was detected for fen peat topsoils. For subsoils, considerably, but not significantly, higher fluxes occurred from peat-sand mixture sites compared to earthified sites. Although there was no general dependence of CO_2 fluxes on peat type, CO_2 fluxes from earthified bog peat topsoils were significantly higher than those from earthified fen peat topsoils.

N_2O fluxes showed sudden peaks and distinctive differences in maximum N_2O fluxes (Fig. 3-4c and d; Table 3-2). The highest N_2O fluxes occurred at WFPS between 0.78 and 0.95 (topsoil, Fig. 3-4c) and 0.73 and 0.95 (subsoils, Fig. 3-4d). Overall, bog peat topsoils showed lower but more variable maximum N_2O fluxes than their fen peat counterparts. The high variability was mainly caused by high fluxes from one site (eB2, Table S6). The opposite pattern was observed for subsoils, with fen peat sites having lower fluxes than bog peat sites. The impact of sand addition was also ambiguous as fen peat-sand mixtures showed higher N_2O fluxes, but bog peat-sand mixtures lower N_2O fluxes than the respective earthified peat samples. The maximum values of N_2O fluxes from peat-sand mixtures tended to occur at lower WFPS than those of earthified peat. No other patterns were identified.

Table 3-2: Maximum CO_2-C and N_2O-N (mean ± standard error) fluxes per group with the respective water filled pore space (WFPS, mean ± standard error) at the occurrence of maximum fluxes and ratio of maximum CO_2-C fluxes and CO_2-C fluxes under water saturation (start). Different letters represent significant differences ($p < 0.05$). sF: fen peat-sand mixture in the topsoil, eF: fen peat site with earthified topsoil, sB: bog peat-sand mixture in the topsoil, eB: bog peat site with earthified topsoil.

		Max. CO_2-C ($mg\ C\ m^{-2}\ h^{-1}$)	**WFPS (-)**	**Max. N_2O-N ($\mu g\ N\ m^{-2}\ h^{-1}$)**	**WFPS (-)**	**Ratio of max. CO_2-C to start CO_2-C (-)**
top	sB	39.3 ± 4.2 ^{a}	0.77 ± 0.03	35.6 ± 17.1 ^{abcde}	0.85 ± 0.02	2.31 ± 0.47 ^{a}
	eB	72.1 ± 5.2 ^{b}	0.83 ± 0.01	127.2 ± 60.0 ^{bde}	0.88 ± 0.01	1.53 ± 0.16 ^{a}
	sF	41.5 ± 12.9 ^{a}	0.85 ± 0.03	149.0 ± 43.0 ^{e}	0.85 ± 0.05	1.64 ± 0.20 ^{a}
	eF	35.3 ± 3.8 ^{ac}	0.88 ± 0.01	78.7 ± 28.1 ^{cde}	0.92 ± 0.01	1.87 ± 0.29 ^{a}
sub	sB	10.6 ± 1.2 ^{cd}	0.88 ± 0.02	10.1 ± 2.4 ^{abcd}	0.95 ± 0.00	2.54 ± 0.71 ^{a}
	eB	3.2 ± 0.5 ^{d}	0.72 ± 0.16	15.5 ± 8.3 ^{ac}	0.90 ± 0.05	1.36 ± 0.02 ^{a}
	sF	9.3 ± 2.4 ^{d}	0.79 ± 0.12	3.7 ± 0.3 ^{abcd}	0.88 ± 0.07	2.80 ± 0.20 ^{a}
	eF	4.5 ± 0.8 ^{d}	0.90 ± 0.00	0.6 ± 0.4 ^{ab}	0.85 ± 0.06	2.41 ± 0.78 ^{a}

For all subsequent analyses, except for GHG balance which was compiled for the −60 hPa suction step, the maximum fluxes of CO_2 and N_2O were used, i.e. the highest equilibrium flux of every sample during the six suction steps of the experiment (maximum values of Fig. 3-4a–d, Table S6). Cumulative fluxes over the course of the experiment were also calculated, which strongly correlated with maximum fluxes (r=0.99 and 0.91 for CO_2 and N_2O, respectively). Therefore, all the results are also valid for cumulative fluxes.

The normalised soil moisture expressed as WFPS and the suction steps of the present experiment could be used to approximate water retention characteristics, which describe the relationship between suction and soil moisture. As these characteristics determine the reaction of the sites to hydrological boundary conditions, the locations of the maximum fluxes within the WFPS-suction-space are shown in Fig. 3-5. The occurrence of maximum CO_2 fluxes differed greatly between subsoils and topsoils (Fig. 3-5a): the corresponding suction of maximum CO_2 fluxes was between −20 and −60 hPa for topsoils and −20 and −300 hPa for subsoils, while WFPS were similar. Except for one site, the peat-sand mixture topsoils tended to have a lower WFPS at the same suction than the earthified topsoils. In other words, peat-sand mixture sites drained to the same depth as earthified sites will be drier. Nonetheless, the earthified topsoils and peat-sand mixtures showed maximum CO_2 fluxes at the same suction, but not at the same WFPS. Similarly, earthified bog peat was slightly drier than fen peat at the same suctions (not shown).

Most of the maximum N_2O emissions already occurred at low suctions between initial saturation and −30 hPa (Fig. 3-5b). On average, fen peat subsoils proved to be drier than bog peat when maximum N_2O fluxes occurred.

3.3.4 Influence of soil properties and nutrient status on fluxes

SOC content was negatively correlated (r=−0.78) with maximum CO_2 fluxes, while SOC density (r=0.54) showed an – although non-significant positive correlation (Fig. 3-6a, Table S6). However, these (and other) correlations mainly reflected the differences both in terms of fluxes and soil properties between topsoils and subsoils: when only topsoil samples were considered, there was no correlation either in SOC content or in SOC density (Table S6). A similarly strong dependence of r=0.68 was observed for N_t density, but again this mainly highlighted the general differences between topsoils and subsoils and had only some explanatory power for CO_2 fluxes of the topsoils. Maximum CO_2 fluxes showed an exponential increase with decreasing C:N ratios less than or equal to 25 (r=−0.63), but as in the case N_t, there was only a weak correlation for topsoil samples. In contrast, strong positive correlations between K_{CAL} and P_{CAL} and maximum CO_2 fluxes (r=0.87 and 0.86 respectively) covered both the whole data range and the individual layers, although the moderate to strong correlations for subsoils were not significant.

Fig. 3-6b shows the correlation between maximum N_2O fluxes and soil properties. As in the case of CO_2 fluxes, there was a negative correlation with SOC content (r=−0.70) and a strong positive correlation with SOC density (r=0.70) (Table S6). Compared to CO_2, there were stronger positive correlation between maximum N_2O fluxes and SOC density for both the whole data set and the individual layers, although the latter correlations were not significant. The N_2O fluxes showed a positive correlation with N_t (r=0.74), while the correlation with the C:N ratio again reflected differences between topsoils and subsoils. Despite one obvious outlier (topsoil of sample sB2), there were also strong correlations of K_{CAL} and P_{CAL} and maximum N_2O fluxes (r=0.70 and 0.73, respectively).

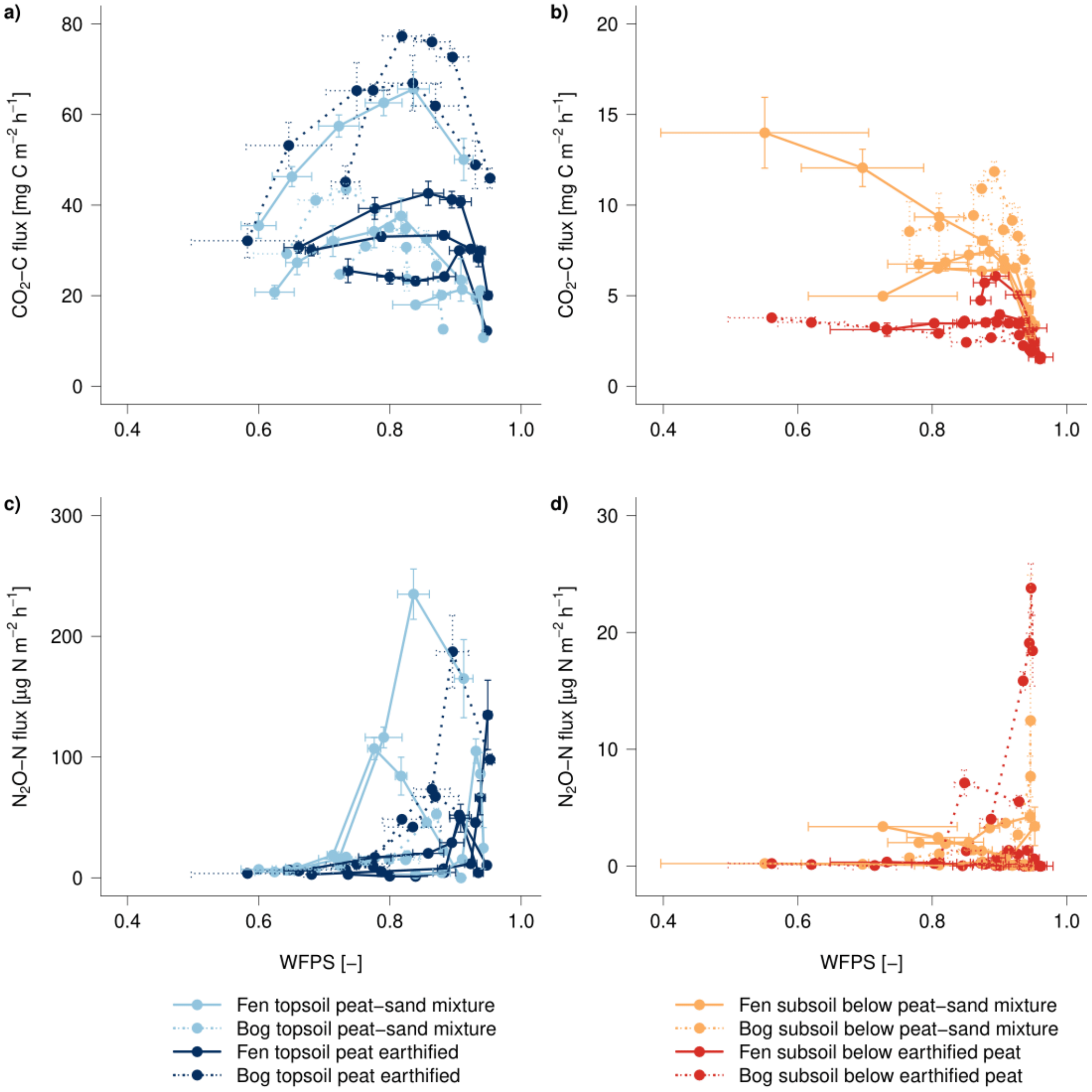

Figure 3-4: Greenhouse gas fluxes and water-filled pore space (WFPS) at the end of each suction step: (a) CO_2-C fluxes of topsoil samples, (b) CO_2-C fluxes of subsoil samples, (c) N_2O-N fluxes of topsoil samples, (d) N_2O-N fluxes of subsoil samples. Means and standard errors are displayed. Lines in (a) and (b) represent fitted quadratic polynomial functions.

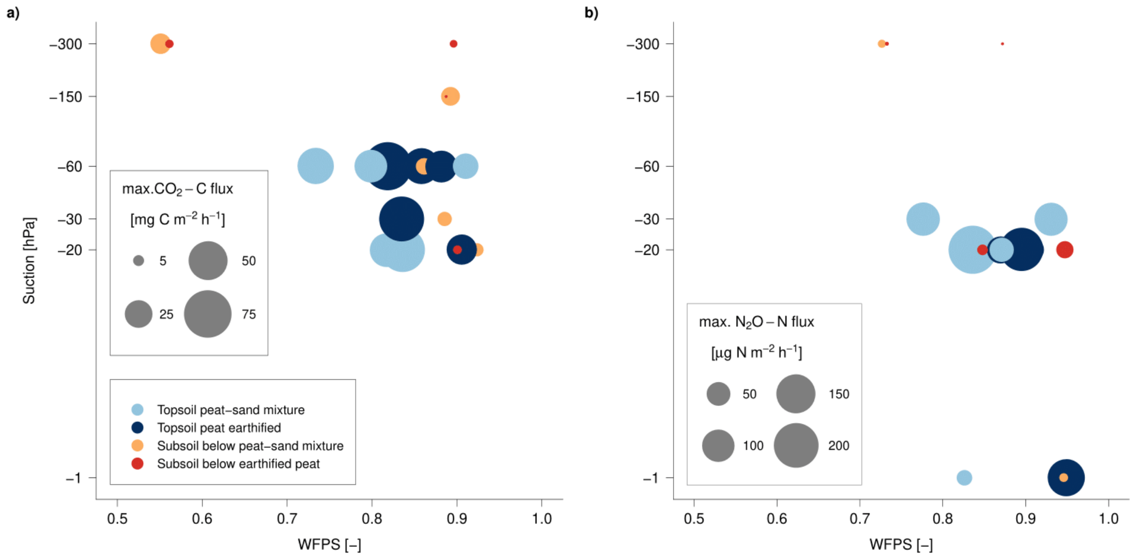

Figure 3-5: Soil hydraulic conditions (water-filled pore space (WFPS) versus suction) of all topsoil and subsoil samples at the occurrence of (a) maximum CO_2-C fluxes and (b) maximum N_2O-N fluxes.

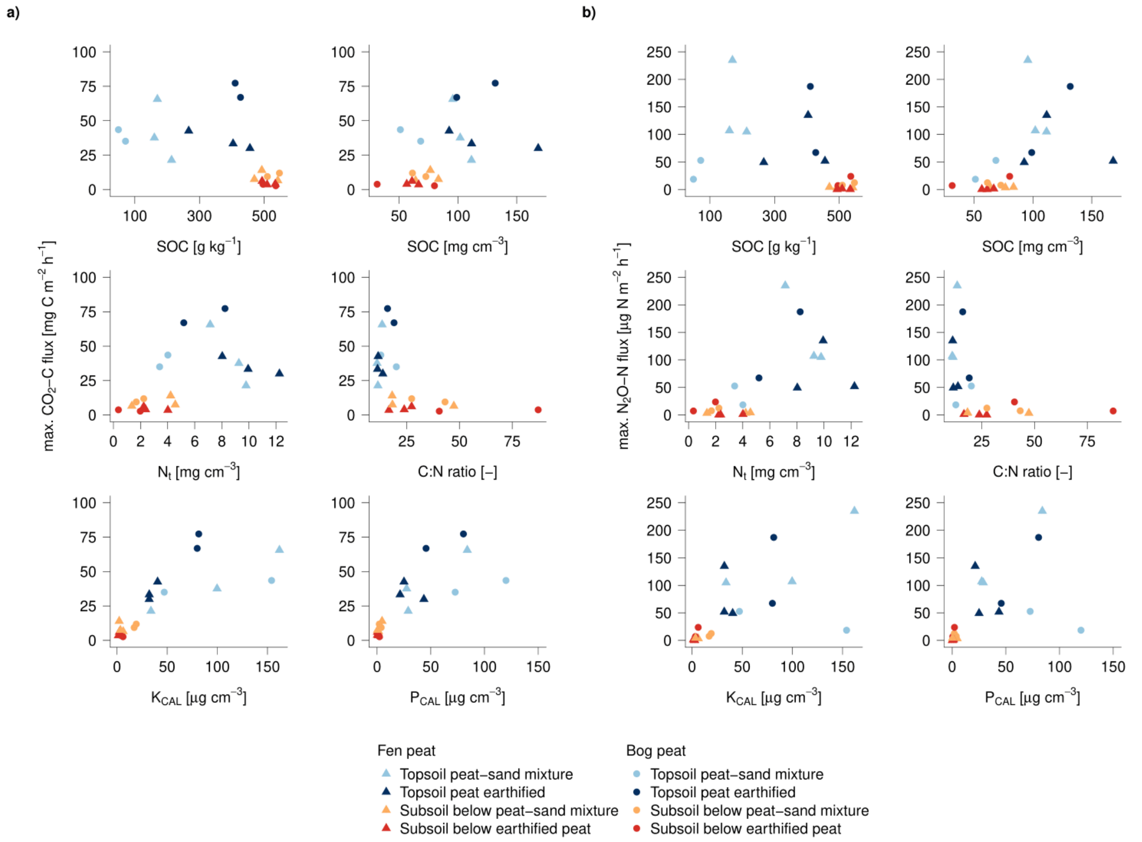

Figure 3-6: Relations between (a) maximum CO_2-C fluxes and (b) maximum N_2O-N fluxes and soil properties: soil organic carbon (SOC) content and density, total nitrogen (N_t) density, C:N ratio, calcium acetate lactate extractable phosphorus (P_{CAL}) density, calcium acetate lactate extractable potassium (K_{CAL}) density.

3.3.5 Specific CO_2 flux and GHG balance

While absolute values of CO_2 fluxes (Fig. 3-7a) showed higher fluxes from topsoils of earthified bog peat sites compared to peat-sand mixture sites, specific CO_2 fluxes (Fig. 3-7b), i.e. fluxes normalised by the samples' SOC stock, hardly showed any differences between the peat-sand mixture and earthified sites. For both peat types' topsoil and subsoil samples, the ratio of CO_2 fluxes of peat-sand mixture sites to CO_2 fluxes of earthified peat sites was higher for specific than for normalized values.

The GHG balance of topsoils (78–311 mg CO_2 eq. m^{-2} h^{-1}) showed much higher values than that of subsoils (14–39 mg CO_2 eq. m^{-2} h^{-1}, Fig. 3-8). The highest emissions were observed for topsoils of the earthified bog sites and peat-sand mixture site sF2. The main component of the GHG balance at the −60 hPa suction step were CO_2 emissions comprising 51–94% of total GHG emissions, followed by similar shares of N_2O and CO_{2DOC} fluxes. CH_4 emissions were negligible for all sites, contributing on average 0.01% to total GHG fluxes. Contributions for N_2O and CO_{2DOC} in topsoils were both 1–8%. In subsoils the proportion of CO_2 was slightly lower than in topsoils and mainly CO_{2DOC} showed an increase in relative importance. While in eight out of ten subsoils CO_{2DOC} and N_2O fluxes contributed 2–14% and 0.1–4% respectively to overall GHG emissions, two bog peat subsoils displayed an immense share of CO_{2DOC} (45%, eB1) and N_2O (46%, eB2). With the exception of these two subsoils, the differences between bog and fen peat were minor regarding each component's individual contribution to the GHG balance. However, higher emissions were observed from earthified topsoil bog peat than from any other group.

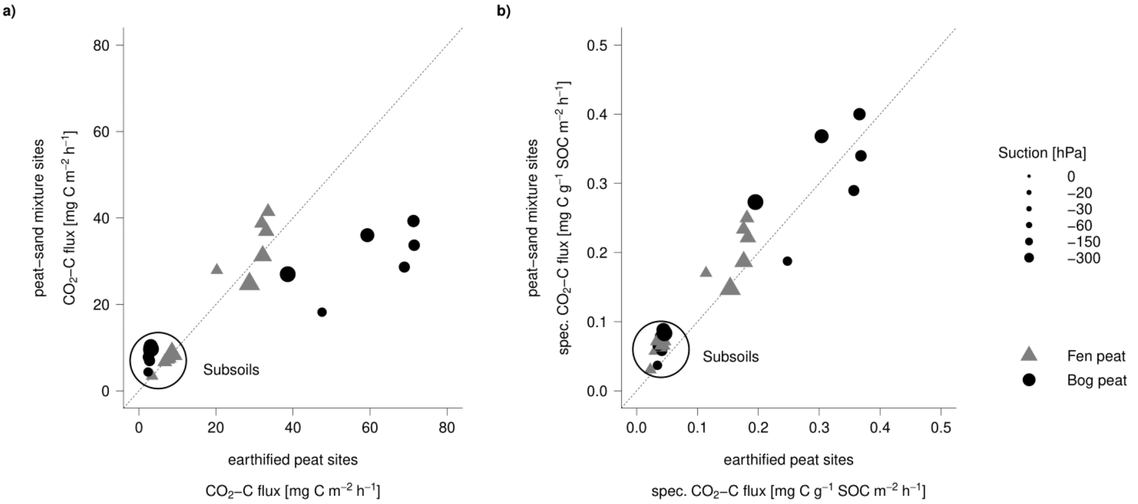

Figure 3-7: Means of peat-sand mixture sites and earthified peat sites (topsoil and subsoil) for six suction steps separated into fen (n=3) and bog (n=2) peat (a) CO_2-C fluxes and (b) specific CO_2-C fluxes.

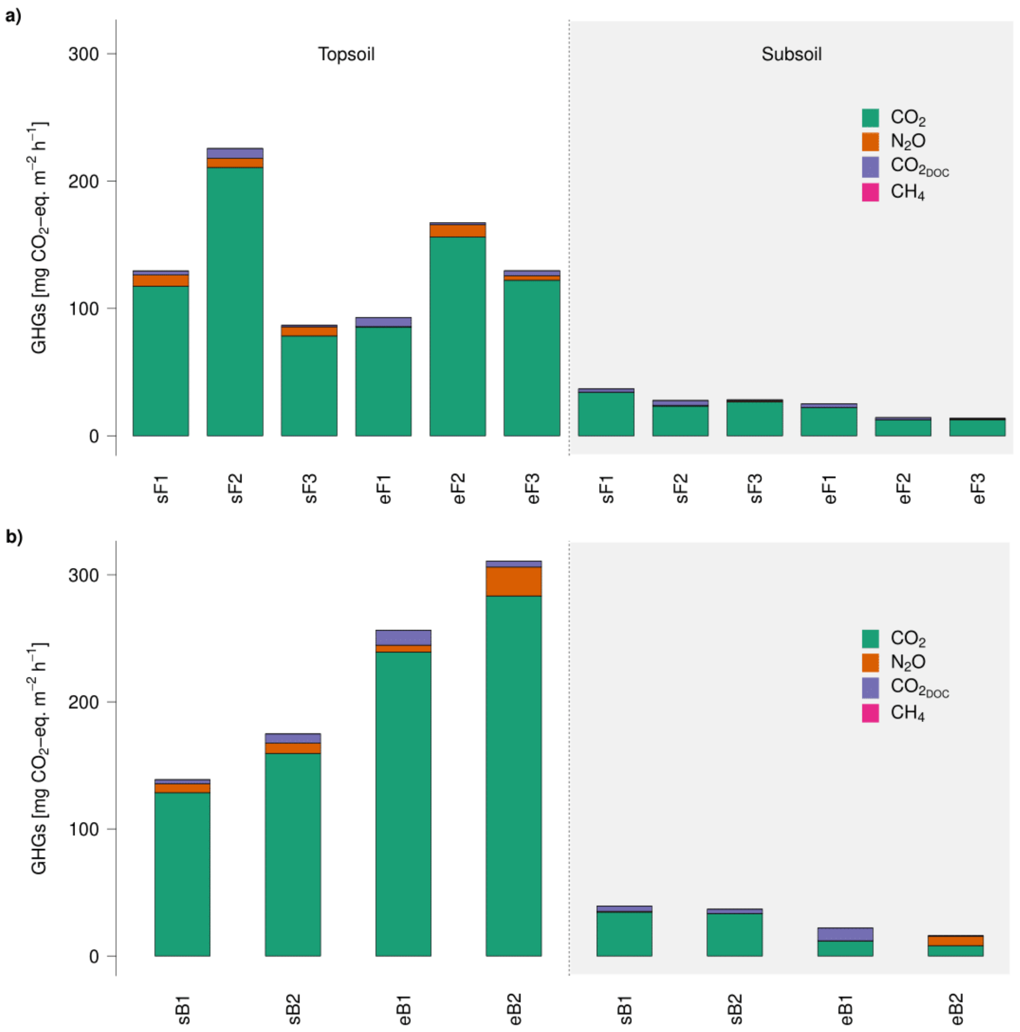

Figure 3-8: Greenhouse gas (GHG) emissions and DOC export as CO_2 (CO_{2DOC}) at the suction step of −60 hPa of (a) fen peat sites and (b) bog peat sites. sF: fen peat-sand mixture in the topsoil, eF: fen peat site with earthified topsoil, sB: bog peat-sand mixture in the topsoil, eB: bog peat site with earthified topsoil**.**

3.4 Discussion

The discussion follows our main objectives, i.e. the identification of the effects of soil moisture, sand addition, peat types as well as nutrient contents on the fluxes of CO_2 and N_2O. Interaction of the different drivers necessitate that some topics overlap as, for example, the reaction of CO_2 fluxes on water-filled pore space depended on peat type.

3.4.1 Influence of water-filled pore space on GHG fluxes

Drainage of the different peat soils increased CO_2 fluxes drastically up to four-fold compared to nearly water-saturated conditions (Table S6). Overall, maximum CO_2 fluxes were measured at WFPS that, under equilibrium conditions (Fig. 3-5), corresponded to groundwater levels of 20–

60 cm below the soil surface, which are typical values for grassland on peat soils (Bechtold et al., 2014).

The stepwise reduction of WFPS in the soil columns resulted in a parabolic response curve of CO_2 fluxes with an "optimum" WFPS at the suction step with maximal CO_2 fluxes (Fig. 3-4). This general shape is in accordance with results reported for both mineral soils (Linn and Doran, 1984; Moyano et al., 2012) and peat soils (Kechavarzi et al., 2010; Norberg et al., 2018; van Lent et al., 2018). Under water-saturated conditions, available oxygen limits microbial activity and CO_2 fluxes. After the WFPS falls below the optimum for CO_2 fluxes (Table 3-2), limitation is caused by the lack of water availability as also observed in field studies where some sites have become very dry in summer (Tiemeyer et al., 2016). Nonetheless, dry conditions in the topsoil under field conditions still expose thicker peat layers than incubated here to drainage and therefore to mineralisation. For the soils in the present study, maximum CO_2 fluxes were observed at 84 ± 2% WFPS. Maximum CO_2 fluxes in mineral soils were reached at 50–60% WFPS, while other incubation studies with intact soil samples of managed peatlands also showed optimum WFPS at around 80% (Kechavarzi et al., 2010; Norberg et al., 2018). The latter study reports, possibly due to errors in units, unrealistically high average CO_2 fluxes (36–167 mg g^{-1} min^{-1}), but the relationship between CO_2 fluxes and WFPS is plausible. While at maximum CO_2 fluxes, topsoils of peat-sand mixtures tended to be drier than earthified peat topsoils (Fig. 3-4, Table 3-2), the influence of WFPS on CO_2 fluxes in peat-sand mixture topsoils was still more similar to organic soils than to mineral soils. Overall, the results of the present study emphasize that peat soils need to be very wet to reduce emissions, while moist conditions might even increase emissions compared to very dry conditions.

The reaction of microbial activity towards soil moisture might depend on the peat type. In contrast to our results, Kechavarzi et al. (2010) found more pronounced parabolic response curves for fibrous peat subsoil than for amorphous peat topsoil, concluding that deeper, fibrous peat has greater oxidation potential, while Norberg et al. (2018) found hardly any differences between topsoil and subsoil samples. The hydrological reaction of our subsoils to drainage was surprising given that other studies have reported that less decomposed peat already loses a large percentage of water at low suctions (Boelter, 1968; Rovdan et al., 2002; Schwärzel et al., 2002; Zeitz and Velty, 2002). However, the slightly higher capability of subsoil peat to retain water can only explain their slower reaction compared to the topsoils, but not the lower CO_2 fluxes, as optimum values of WFPS were still reached in all but one case (Fig. 3-4).

Nitrification and denitrification are the major pathways producing N_2O in soil. Among other factors, depending on soil moisture and concomitantly the amount of oxygen in the soil, N_2O is either produced by ammonium oxidation or nitrate reduction (Butterbach-Bahl et al., 2013). As denitrification is limited by water availability whereas nitrification is limited by aeration, early studies on mineral soil suggest that the highest N_2O fluxes should occur at approximately 60% WFPS when both processes occur simultaneously (Davidson et al., 2000; Linn and Doran, 1984). The influence of WFPS on N_2O fluxes in the present study varied considerably between samples, however the majority of increased N_2O fluxes were observed at WFPS over 80% (Fig. 3-4). This optimum for N_2O fluxes diverges from the theory of Davidson et al. (2000) as do the results of other studies (Berglund and Berglund, 2010; Liimatainen et al., 2018; van Lent et al., 2018) and the meta-analysis of Butterbach-Bahl et al. (2013), which also found an optimum of 80–90% WFPS. The fact that N_2O fluxes predominantly occurred at WFPS > 80% indicates that the N_2O primarily originated from denitrification.

3.4.2 Influence of sand addition on GHG fluxes

In contrast to other studies (Bambalov, 1999; Zaidelman and Shvarov, 2000), mixing sand into the topsoil and thus reducing the SOC content did not systematically reduce either CO_2 or N_2O fluxes. In fen peat topsoils, there was no difference in absolute and specific CO_2 fluxes from peat-sand mixtures and earthified peat (Fig. 3-7). In contrast, absolute CO_2 fluxes from earthified peat bog topsoils were significantly higher than from bog peat-sand mixtures, but the specific CO_2 fluxes of both classes did not differ (Fig. 3-7, Table 3-2). This indicates that soil organic matter of the peat-sand mixtures in the present study was not stable.

To interpret the effects of anthropogenically changed peat properties, it is crucial to distinguish between SOC content and SOC density. While the peat-sand mixtures showed much lower SOC content, the SOC density was only slightly lower than in the respective earthified topsoils due to their higher bulk densities (Fig. 3-2). Furthermore, all topsoils showed lower SOC contents, but mostly higher densities than the subsoils. Ross and Malcolm (1988) measured the respiration rates of artificial peat-sand mixtures for different sizes of peat cubes and detected increasing CO_2 fluxes with a decreasing peat cube size. The effects of physical disturbance might compensate for the lower SOC densities since mixing destroys the intrinsic peat structure and increases the available surface area of the organic matter.

Mixing sand into the topsoil peat was accompanied by higher CO_2 fluxes from well-preserved and unmixed subsoils (Fig. 3-4b). As in Zaidelman and Shvarov (2000), the 23% higher dry bulk densities of subsoil peat below peat-sand mixtures could have been caused by the extra load from the relatively heavy sandy topsoil and are the reason for the higher SOC densities (Fig. 3-2). This and higher specific CO_2 fluxes than from subsoil below earthified sites (Fig. 3-7b) might indicate more favourable microbial conditions. Given the higher hydraulic conductivity of peat-sand mixture topsoils compared to earthified peat more of the topsoils' nutrients might have leached into deeper layers and increased amounts of N, P and K there, which in turn increased microbial activity (Fig. 3-3, see section 3.4.4).

In theory, ploughing the underlying peat layer into the topsoil sand layer should be avoided to minimise peat mineralisation (Göttlich, 1990). However, in practice, the SOC contents of covered peat soils are highly variable, and ideal sand covers are much rarer than peat-sand mixtures (Wittnebel, pers. comm.). This was also the case here: the peat-sand mixtures had lower SOC contents than the earthified peat sites (Fig. 3-2), however only the two bog peat topsoils with the lowest SOC content (49 and 71 g kg^{-1}) come close to an ideal sand cover (Fig. S3). Although these two topsoils did show lower CO_2 fluxes compared to their earthified peat counterparts, the values are still four-fold higher than those of the subsoils and in the same range as all the fen topsoils. Furthermore, the comparable specific fluxes of earthified peat and peat-sand mixtures indicated ongoing soil organic matter transformation in the latter soils (Fig. 3-7). These results corroborate field studies which have observed similar or even increased CO_2 or GHG emissions from peat-sand mixtures (Leiber-Sauheitl et al., 2014; Maljanen et al., 2004), from a bog peat site covered with sand (88 g SOC kg^{-1}) and a neighbouring peat soil (Beyer, 2014) or from "low C organic soils" compared to peat soils (Tiemeyer et al., 2016).

The influence of sand addition on N_2O fluxes was ambiguous as fens and bogs showed opposite reactions, i.e. fluxes from earthified bog peat tended to be higher than from bog peat-sand mixtures, while the opposite was true for the fen peat sites. The reasons for this are not entirely clear, but this pattern might be explained by the higher bulk density and lower pH values of fen peat-sand mixtures compared to earthified topsoils, while N_t density was higher for earthified bog peat than for bog peat-sand mixtures. Leiber-Sauheitl et al. (2014) and Maljanen et al. (2004) observed no clear differences between N_2O emissions from true peat and peat-sand mixtures under grassland use.

3.4.3 Influence of sampling depth and peat type on GHG fluxes

Fluxes of CO_2 and N_2O displayed immense differences between topsoil and subsoil peat (Figs. 3-4 and 3-7). All sites have been under agricultural use and drained for many decades. It could be assumed that, as a result, the peat topsoils would be of poor organic matter quality (Leifeld et al., 2012), with lower decomposability (Urbanová and Bárta, 2015) and are therefore less suitable for microbial use than “freshly drained” subsoils. However, physically disturbed peat-sand mixture topsoils that are under intensive management could have more accessible organic matter surfaces that enhance microbial activity and concurrently increase nutrient mobilisation (Ross and Malcolm, 1988). Furthermore, nutrient availability was much higher in the topsoils (see section 3.4.4).

Lower CO_2 fluxes from samples from deeper peat layers have also been found in other studies on both managed and unmanaged peatlands (Bader et al., 2018; Brake et al., 1999; Glatzel et al., 2004; Hardie et al., 2011; Hogg et al., 1992). These lower CO_2 fluxes have been explained by lower nutrient levels, a smaller abundance of fresh plant biomass and poorer substrate quality of subsoil horizons. Therefore, topsoil horizons have been shown to generally have higher microbial activity than subsoil horizons (Brake et al., 1999; Fisk et al., 2003; Preston et al., 2012). Although the uppermost centimetres of the soil were intentionally removed before sampling, remaining roots in the peat topsoils cannot be excluded as a possible source of CO_2. For managed grassland topsoils, Bader et al. (2017) showed that crop residues were accountable for 40% of the CO_2 emissions. The sites in the present study showed a few fine roots even down to 50 cm. However, even if it were assumed that 50% of the CO_2 emissions came from roots, this would not explain the on average nine-fold greater values of the topsoils.

As in the present study, lower N_2O fluxes from subsoil samples were observed in Berglund and Berglund (2011). Well et al. (2005) also showed that denitrification capacity decreases with depth. The reasons for higher maximum N_2O fluxes from topsoils were probably a combination of higher nutrient availability, higher pH values, narrower C:N ratios and higher bulk densities (see section 3.4.4).

Surprisingly, no consistent differences could be found between fen and bog peat, i.e. peat composition in terms of peat genesis and peat-forming plants had a marginal influence on GHG fluxes. Under natural conditions faster decomposition processes occur in fens under minerotrophic conditions (Blodau, 2002). Natural bogs however are characterised by low pH values, ombrotrophic conditions and recalcitrant peat substrates (Urbanová and Bárta, 2014; Verhoeven and Liefveld, 1997). Consistent with expectations, the fen peat subsoils in the present study did contain more nitrogen and showed narrower C:N ratios and higher pH values than bog peat subsoils (Fig. 3-2). Due to drainage, the biogeochemical characterisation and microbial composition of bogs and fens become more similar (Urbanová and Bárta, 2015). However, for the sites in the present study that were all drained, differences between the topsoils of bog and fen peat were still visible in terms of wider C:N ratios and lower pH values in bog peat topsoils compared to fen peat topsoils (Fig. 3-3). Nevertheless, higher CO_2 fluxes were found from bog peat than from fen peat, which contrasts with a large number of field studies that have been summarised by IPCC (2014). A reason might be the high sensitivity of bog peat to anthropogenic effects: Urbanová and Bárta (2015) found that after drainage the microbial community decreases in fen peat but increases in richness and diversity in bog peat. Furthermore, the bog peat sites of our study were more intensively used than many sites in IPCC (2014), which is probably the reason for the high nutrient contents (section 3.4.4.).

3.4.4 Influence of soil properties and nutrient status on GHG fluxes

The increase in oxygen following drainage increases the mineralisation of organically bound nutrients such as N, P and K, which are then enriched in the topsoils (Holden et al., 2004; Laiho et al., 1998) resulting for example in lower C:N ratios. The C:N ratio is commonly used to characterise the quality of soil organic matter as well as microbial availability and turnover (e.g. Reiche et al., 2010; Vos et al., 2018). In the present sample set, the C:N ratio clearly differentiated topsoils and subsoils (Fig. 3-2). When examining topsoils separately, the C:N ratio had no explanatory power for CO_2 fluxes as all samples showed very similar C:N ratios and as earthified bog samples showed surprisingly high CO_2 fluxes (Fig. 3-6a). Although N_t densities had no decisive explanatory power for CO_2 fluxes, the availability of N plays an important role in organic matter stoichiometry and for microbial activity. The non-significant, but slightly positive correlation between CO_2 fluxes from subsoils and N_t densities ($r=0.27$) might indicate that mineralisation processes increase the N supply. This might suggest a shift from N to P limitation. Densities of available P and K correlated strongly with maximum CO_2 fluxes ($r=0.85$ and 0.86 respectively; Fig. 3-6a). Total P is important for microbial turnover of soil organic matter (Brake et al., 1999). Amador and Jones (1993) found that high P amendment increases respiration rates in the long term: after P application the C:P ratio of organic matter decreases and soil microorganisms intensify their catabolism. K is a limiting element in agriculturally used organic soils and is known for its importance for plant growth (Zörb et al., 2014). However, the influence of K on microbial turnover of organic matter is rarely studied. Studies on nutrient addition concentrated on N, P and K amendment simultaneously and reported an increase in microbial respiration, however without specifically separating between the influence of P and K (Larmola et al., 2013; Pinsonneault et al., 2016a; Sundström et al., 2000).

The availability of SOC and N_t had a strong positive influence on N_2O fluxes (Fig. 3-6b), probably as N_t is correlated with denitrification capacity in peat soils (Well et al., 2005). The exponential relationship between C:N ratio and N_2O fluxes is a frequently used estimator for field N_2O emissions (Klemedtsson et al., 2005; Leifeld, 2018). This relationship was generally confirmed in the whole sample set in the present study (Fig. 3-6b). Both in our dataset and Klemedtsson et al. (2005), there were very low N_2O fluxes at C:N ratios > 25, while topsoils displayed large differences in N_2O fluxes despite a narrow range in C:N ratios. This highlights the limitations of the predictive power of the C:N ratio and shows that a C:N ratio of 25 is more of a threshold than a predictor. At low C:N ratios, factors other than N limitation seem to be regulating the high variability in N_2O fluxes (Liimatainen et al., 2018). In contrast to other studies (e.g. Regina et al., 1996; Weslien et al., 2009), there was no correlation between N_2O fluxes and pH values in the present study (data not shown). Densities of plant-available P and K showed very strong influences on N_2O fluxes. Although the exact reasons are unknown, P is known for its important positive role on N_2O fluxes from peat soils (Liimatainen et al., 2018; Regina et al., 1996). P possibly favours nitrification and/or denitrification processes (Mehnaz and Dijkstra, 2016), e.g. the denitrification enzyme activity in wetland soils (White and Reddy, 1999). N and P addition experiments emphasized the importance of the interaction of both nutrients with P possibly becoming the limiting factor (Wang et al., 2014; White and Reddy, 1999). This could be due to the fact that P availability increases the microbial biomass, which in turn increases the potential for N mineralisation (White and Reddy, 2000).

3.4.5 GHG balance

The GHG emissions primarily consisted of CO_2 emissions (Fig. 3-8), which is in accordance with field data from grassland on organic soils (Tiemeyer et al., 2016). Fluxes of CH_4 were negligible at −60 hPa suction as WFPS was beyond the anoxic conditions that favour methanogenesis. Although CH_4 consumption could not be determined with the present experimental setup, there might be uptake of CH_4 by drained organic soils under field conditions (Maljanen et al., 2002). However, this uptake generally plays only a minor role for the GHG balance of drained organic soils. For example, of the 48 drained grassland sites synthezised by Tiemeyer et al. (2016), 17 sites were slight sinks of CH_4, but, in terms of CO_2-equivalents, this amounted to only 0.1–0.8% of the CO_2 emissions.

Only two horizons of each site's profile were incubated in the present study. Even though the earthified peat horizon and the peat-sand mixture horizon displayed most of the anthropogenic disturbance, the contribution of GHG emissions from underlying peat horizons needs to be taken into consideration. These horizons are also drained and soil organic matter continues to mineralise. CO_{2DOC}, as a measure of C that is lost from the soil in the liquid phase, showed similar shares to N_2O. The loss of CO_{2DOC} tends to decrease for subsoils compared to topsoils. This is in agreement with a field study on bog peat under grassland use, which found much higher DOC concentrations in the topsoil than in the subsoil (Frank et al., 2017). Although concentration levels can be compared between the samples within this experiment, it is not advisable to relate actual numbers of CO_{2DOC} losses to values measured in field studies as there had been no input of (rain or irrigation) water for around six months in the present laboratory study.

3.5 Conclusions

The aim of this long-term incubation experiment was to assess the influence of hydrological and biogeochemical soil properties on GHG emissions from drained organic soils with and without sand addition. Although the experiment was conducted under controlled laboratory conditions, there was still an enmeshed interplay of the effects of soil moisture, soil physical and chemical properties, and soil microbial activity.

First and as expected, soil moisture was closely connected to CO_2 and N_2O fluxes. However, this dependence was clearer for CO_2 where parabolic dependencies could be found for most samples. Optimum values of WFPS indicate that, under equilibrium conditions, a water level of 20–60 cm below soil surface in the field provides conditions for the occurrence of maximal CO_2 emissions.

Second, mixing sand into the topsoil peat layer decreased CO_2 emissions from bog peat sites compared to earthified topsoils, but not from fen peat sites. However, the specific CO_2 fluxes of peat-sand mixture sites and earthified sites were similar regardless of peat type, which indicates that the SOM of peat-sand mixtures still is prone to decomposition. Furthermore, mixing sand into the topsoil peat seems to have a negative impact on the well-preserved subsoils, which is apparent both in the soil properties (e.g. bulk density) and in the increased CO_2 fluxes. There was no systematic impact of peat-sand mixtures on N_2O fluxes. The results of the present study do not support peat-sand mixtures to be advanced as a way of mitigating GHG emissions from drained peatlands.

Third, even after decades of drainage and agricultural use, all topsoils were still emitting considerable amounts of CO_2, which was in all cases the major component of the GHG balance. Subsoil fluxes were clearly lower. Surprisingly, sites with bog peat showed higher CO_2 fluxes than their fen counterparts, probably due to higher contents of P and K.

This shows that, fourth and finally, the influence of soil characteristics and nutrients on GHG fluxes was more important than the impact of sand addition or peat type. Increased P and K availability in particular showed a strong positive influence on CO_2 as well as on N_2O fluxes.

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4 Substrate quality of drained organic soils – Implications for carbon dioxide fluxes

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Abstract

Background: Peatlands only cover a minor fraction of the global terrestrial surface, but due to drainage, they are major contributors to carbon dioxide (CO_2) emissions from soils. Previous studies have shown that hydrological conditions, nutrient availability and anthropogenic disturbance play an important role in the mineralisation of organic matter. Furthermore, microbial turnover depends on peat quality, which is determined by its botanical origin and degree of transformation under natural conditions.

Aims: The objective of this study was to shed light on the interdependence between mineralisation rates, secondary transformation of peat and chemical composition by examining the differences between bog and fen peat and between strongly degraded topsoil and well-preserved subsoil.

Methods: Bog and fen peat from ten different peatlands under grassland use in Germany were analysed for their chemical composition using standard ^{13}C nuclear magnetic resonance (NMR) spectroscopy and wet chemical extractions for fibre analysis. The radiocarbon age was determined as well. The results were combined with CO_2 fluxes from a previous incubation study.

Results: Topsoils had higher shares of proteins and lipids, and lower shares of carbohydrates and aromatics than subsoils. Bog peat subsoils were characterised by higher shares of carbohydrates and lower shares of aromatics than fen peat subsoils. Topsoils were more similar to each other in their chemical composition than the subsoils. Considering all samples, aromatics and phenolics were negatively correlated with CO_2 fluxes. Measured CO_2 fluxes from topsoils were significantly higher than from subsoils. However, no influences of chemical composition on CO_2 fluxes were detected when examining topsoils and subsoils separately. Even though aromatics and phenolics showed positive relationships with radiocarbon age, differences in age alone were unable to explain the higher amounts of these compounds in the subsoil.

Conclusions: The results imply that chemical composition of topsoil peat is not the reason for higher mineralisation rates compared to subsoil peat, but rather a consequence of decomposition and transformation. Thus, peat mineralisation of drained organic soils under agriculture might not slow down over time due to gradually decreasing peat quality but could increase further.

4.1 Introduction

Drained peatlands are recognised as a major and increasing anthropogenic source of greenhouse gases (GHG), primarily emitting carbon dioxide (CO_2) (Parish et al., 2008; Smith et al., 2014). Intact peatlands are sinks for carbon (C) due to their inherent processes that slow down decomposition rates, but drainage and agricultural use significantly alter their biogeochemical processes. As soon as peat is drained, decomposition of soil organic matter (SOM) accelerates (Dawson et al., 2010), which changes chemical and physical soil properties (Holden et al., 2004). Despite only covering 2.2–3.0% of the global terrestrial surface, this turns peatlands, of which 10–13% are currently drained, into GHG sources that contribute between 0.9 and 1.9 Gt CO_2 eq. to worldwide GHG emissions every year (Leifeld and Menichetti, 2018; Smith et al., 2014; Tubiello et al., 2016).

Emissions of CO_2 from drained peatlands are controlled by various drivers, including soil properties, hydrology, agricultural practice and climate. Since the microbial community ultimately controls the release of CO_2, environmental factors interact with the peat quality and thus with the decomposability of the peat itself. Here 'peat quality' is defined as the chemical composition of the peat substrate. A higher peat quality indicates increased microbial decomposability, while lower peat quality reflects low decomposability.

Studies have shown that peat in the subsoil is more resistant to mineralisation than peat material in the upper horizon (Bader et al., 2018; Brake et al., 1999; Hardie et al., 2011; Hogg et al., 1992; Säurich et al., 2019a). This reduced decomposability in deep soil is thought to be due to its lower nutrient status, the lower abundance of readily available fresh plant biomass and therefore poorer peat quality. The importance of nutrients for decomposition has been demonstrated in previous studies (Larmola et al., 2013; Pinsonneault et al., 2016a; Reiche et al., 2010), with phosphorus (P) potentially playing a decisive role (Brake et al., 1999; Säurich et al., 2019a).

Natural peat-forming processes lead to a decline in peat quality and a higher degree of decomposition on the von Post scale (von Post, 1922) with depth and age (Hardie et al., 2011; Leifeld et al., 2012; Reiche et al., 2010). All peat-forming plants are rich in both readily degradable carbohydrates (O-alkyl C) and phenolic substances (Reddy and DeLaune, 2008). During anaerobic transformation of peat O-alkyl C is transformed into refractory compounds, which leads to an increase in aromatic C. During this process metabolites are produced by microorganism resulting in increased shares of alkyl C (Hammond et al., 1985; Hopkins et al., 1997). Consequently, Hogg et al. (1992) and Glatzel et al. (2004) have concluded that the degree of decomposition is negatively correlated with CO_2 production and more humified peat in deeper layers is more resistant than fresh peat in the upper horizon.

In the case of agricultural use and thus of drainage, fertilisation, compaction and mineralisation, peat soils undergo secondary pedogenetic processes (Heller and Zeitz, 2012; Ilnicki and Zeitz, 2003). Among other changes, this results in a higher degree of decomposition on the von Post scale (von Post, 1922) in the topsoil than in the subsoil, which makes the topsoil the more decomposed layer. Some authors argue that due to decomposition, primarily recalcitrant material with lower peat quality is selectively preserved, ultimately causing lower mineralisation rates (Leifeld et al., 2012; Urbanová and Bárta, 2015). Lower peat quality might be a reason for the lower decomposability of subsoils but also for lower CO_2 emissions with time. Furthermore, current topsoils might be 'naturally' enriched in recalcitrant organic substrate since the readily decomposable, younger peat layers have already been mineralised (Leifeld et al., 2012). Despite this, degraded organic soils have shown high mineralisation rates both in laboratory (Säurich et al., 2019b) and field studies (Tiemeyer et al., 2016), although, in theory mainly recalcitrant SOM should have been left. Besides the enhanced nutrient availability in agricultural peatlands, one explanation might be that enzymes, which play a key role in peat mineralisation (e.g. phenol oxidase), are activated by drainage, thus reducing the protective effect of phenolic compounds, for example, against decomposition (Freeman et al., 2001).

Besides environmental controls and age, peat quality depends on its botanical origin, which differs between fen and bog peat since they are formed by different plants (Bohlin et al., 1989). Fen peat is mainly formed by *Carex spp.*, *Phragmites australis*, trees such as *Alnus glutinosa* and moss species, which are adapted to minerotrophic conditions, while bog peat is predominately formed by *Sphagnum spp*. under ombrotrophic conditions. The differences in the origins of fen and bog peat might result in differing decomposability. Inhibitory effects of compounds such as polyphenolics protect plants from microbial breakdown (Dunn and Freeman, 2018; Freeman et al., 2001). Fens are often dominated by vascular plants that contain polyphenolics mainly in the form of lignin and tannins (Zak et al., 2019). In contrast to vascular plants, *Sphagnum* does not contain lignin, but synthesises polymeric lignin-like phenolics (e.g. sphagnum acid) and polymerised uronic acid ('sphagnan') (Verhoeven and Liefveld, 1997). Depending on the vegetation composition, even down to species level especially in the case of *Sphagnum*, the chemical composition and therefore peat quality differ (Aerts et al., 2006; Bengtsson et al., 2018; Duval and Radu, 2018).

It is possible to assess peat quality through basic peat properties such as C:N ratio, isotopes or degree of decomposition (Glatzel et al., 2004; Krüger et al., 2014; Reiche et al., 2010). Chemical composition of substrates can be determined via spectroscopy, for example using Fourier-transform infrared (FTIR), visible to near-infrared (Vis-NIR), ^{13}C solid-state nuclear magnetic resonance (NMR) and pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) (e.g. Artz et al., 2008; Daugherty et al., 2019; Hoyos-Santillan et al., 2016; Swails et al., 2018). Another approach is the identification of labile and more recalcitrant compounds by wet chemical fractionation of the soil. Soil fractions can be determined, for example *via* hot-water extracts or fibre analyses, including neutral detergents and acid hydrolysis (Duval and Radu, 2018; Heller and Zeitz, 2012; Hermans et al., 2019). Comparisons of spectroscopic techniques and the chemical extraction of bulk soil samples are uncommon. Secondary reactions, chemical artefacts and losses might occur during wet chemical extraction procedures and therefore, compared with spectroscopy, the results only provide an estimation of chemical composition (Kögel-Knabner, 1997; Schmidt et al., 2011). Even though there is a multitude of methods to determine substrate quality, previous studies have mainly focused on natural peatlands (e.g. Artz et al., 2008; Daugherty et al., 2019; Hermans et al., 2019; Hoyos-Santillan et al., 2016; Tfaily et al., 2014). In comparison, studies on drained organic soils used in agriculture are rare (Heller et al., 2015; Leifeld et al., 2012; Negassa et al., 2019).

The aim of this study was to improve understanding of the interplay between chemical composition, transformation of the peat substrate due to drainage and agricultural use, and CO_2 fluxes. The objectives were to (1) characterise the chemical composition of degraded topsoils and well-preserved subsoils originating from both fen and bog peat, and (2) to assess whether differences in chemical composition due to mineralisation and age influence CO_2 fluxes. Using 20 samples from ten German peatlands, NMR spectroscopy and various fibre analyses were conducted to characterise substrate chemistry, the radiocarbon age was investigated, and the data were combined with results from a previous incubation experiment (Säurich et al., 2019a).

4.2 Material and Methods

4.2.1 Sampling sites and microcosm incubation experiment

Ten sampling sites were chosen from the database of the German Agricultural Soil Inventory (Poeplau et al., 2020). The six fen and four bog peat sites investigated are under permanent grassland use, cover a broad range of soil properties, and have a well-preserved peat subsoil horizon (Table 4-1). At each site the soil profile was classified according to the German manual of soil mapping (Ad-Hoc-Arbeitsgruppe Boden, 2005). Six intact soil columns (18 cm high, 14.5 cm in diameter) were collected per site from the degraded topsoil and the well-preserved subsoil each containing 10 cm of soil (upper limits of the soil column were 5–15 and 20–140 cm respectively, see Table 4-1). To avoid artefacts during incubation, the densely rooted upper centimetres were not sampled. The sampled subsoil peat was supposed to approximate the original peat material of the now degraded topsoils. This requirement resulted in choosing, for example, peat from the same *Sphagnum* section and thus in the broad range of subsoil sampling depths. The topsoils were either heavily degraded (‘earthified’) or had been mixed with applied sand 35 to 60 years prior to sampling (‘peat-sand-mixture’). Bulk soil samples were also taken from both depths (see Säurich et al. (2019a) for further information about sampling and determination of soil properties).

In total, 60 soil columns were incubated in a microcosm device (Hantschel et al., 1994) at 10 °C for six months. Starting at near water saturation, the samples were drained stepwise in six steps until -300 hPa. Every 8 hours an automatic online gas chromatograph (GC-2014, Shimadzu, Kyoto, Japan) measured the headspace CO_2 concentrations of each column. The maximum specific CO_2 fluxes were used as a proxy for peat decomposability (Säurich et al., 2019a). Briefly, after the transformation of CO_2 concentrations into flux rates, equilibrium CO_2 fluxes were determined for each suction step by calculating the mean and standard error of the respective last 30 values (10 values of each replicate). The specific CO_2 flux rates used in this study are the maximum fluxes of each sample during all suction steps normalised by the respective soil organic carbon (SOC) content.

4.2.2 Analytical methods

Standard ^{13}C solid-state cross polarisation magic angle spinning (MAS) NMR spectra were measured at the Institute of Soil Science at the TU Munich, Germany, using a Bruker DSX 200 (Bruker BioSpin GmbH, Karlsruhe, Germany). Finely ground samples were used for this analysis. Spectral regions were selected and separated into seven areas of different C-bonds according to previous studies (Preston et al., 2009; Sarker et al., 2018): 0–45 ppm alkyl C, 45–60 ppm methoxyl C and N-alkyl, 60–90 ppm O-alkyl C, 90–110 ppm di-O-alkyl C, 110–145 ppm aromatic C, 145–160 ppm phenolic C and 160–185 ppm carboxyl C. Results are expressed as percentages of SOC. Further, the ratio of alkyl C and the complete O-alkyl region (45–110 ppm) was calculated as an index for microbial transformation (Baldock et al., 1997).

Ground soil was analysed for neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL), according to the method of Goering and Van Soest (1970). With the NDF treatment, soluble cell wall compounds were dissolved by boiling 1 g soil for 1 h in a neutral detergent solution. The dry weight of insoluble residuals gave the NDF content, which was composed mainly of hemicellulose, cellulose and lignin and lignin-like phenolics, while the difference between NDF and total SOM is referred to as cell components (CC) and included proteins, fats and soluble carbohydrates. The ADF treatment removed cell constituents, carbohydrates, hemicelluloses and proteins. For this treatment, 0.5 g soil was boiled for 1 h in a solution of sulphuric acid (H_2SO_4) and cetyltrymethylammonium bromide. The amount of dry residue equalled the ADF content. The difference between NDF and ADF gave the estimate of the hemicellulose content. Subsequently the ADF residue was subjected to the ADL treatment, that is, stirred with concentrated H_2SO_4 (72%) at room temperature for 3 h to hydrolyse crystalline cellulose. The non-hydrolysable residue of ADL was composed of lignin and lignin-like phenolics. The difference between ADL and ADF provided an estimate for cellulose. All fractions were subsequently ashed and are shown on an ash-free basis. Results are expressed as a percentage of SOM.

Figure 4-1 gives a schematic overview of the products of both NMR spectroscopy and fibre analysis after Goering and van Soest (1970), and their attribution regarding the main chemical compounds.

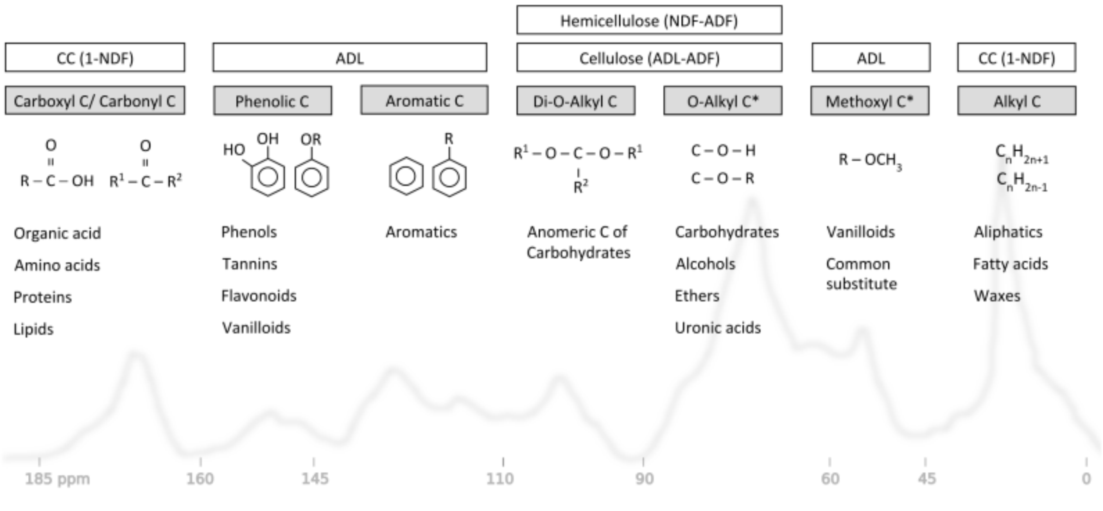


Figure 4-1: Simplified schematic overview of chemical C fractions determined on neutral detergent fibre (NDF), acid detergent fibre (ADF), acid detergent lignin (ADL), cell components (CC) and chemical shift regions of the ^{13}C MAS NMR (grey boxes) with representatives of the main compounds and functional groups. The course of an exemplary NMR spectrum is separated into seven areas based on the displayed ppm values. This scheme is not exhaustive and the attribution of functional groups to fibre analysis products is only approximate. For further reading, see Kögel-Knabner (2002). *Contains N-alkyl; methoxyl is an O-alkyl

Another less expensive and less time-consuming method was also used for fibre analysis to test its applicability in comparison with the method after Goering and von Soest (1970). The soil samples were dissolved in a solution of saturated 5% sodium hexametaphosphate [$(NaPO_3)_6$] for 48 h. The soil was then wet-sieved trough a 1-mm mesh and the dry weight was compared to the bulk soil dry weight (modified after Boelter, 1968).

The radiocarbon dating was conducted at the Leibniz Laboratory for Radiometric Dating and Stable Isotope Research (University of Kiel, Germany) using the type HVE 3MV Tandetron 4130 accelerator mass spectrometer (AMS). The resulting ^{14}C-content was related to the hypothetical atmospheric value of 1950 and reported in pMC (percent modern carbon). The conventional radiocarbon age was calculated using this value according to Stuiver and Polach (1977). The topsoils of sB2 and sF2 were modern samples (younger than 1950) in the sense of ^{14}C dating and contained high levels of bomb-^{14}C. Calibrated radiocarbon ages (years before 2020) were determined with OxCal 4.4 (Ramsey, 2009) using IntCal20 atmospheric data (Reimer et al., 2020). Nearly all samples were attributed more than one calibrated age; therefore mean ages were used for further analysis. Details on the probability distribution can be found in Table S8.

4.2.3 Data analyses

Data analyses were performed using the R software environment (R Core Team, 2018).

The relationship between the properties of the samples was characterised by principal component analysis (PCA) using prcomp (*stats*) with normalised data. For display purposes the *ggbiplot* package (Vu, 2011) was used. The PCA included peat quality (NMR spectral regions, ADL, cellulose, hemicellulose, CC, fibre), radiocarbon age, phosphorus and nitrogen content, C:N ratio, specific CO_2 fluxes and bulk density. Normal probability ellipses (including 68% of distribution) were incorporated for better visualisation.

Spearman's rank correlation coefficient r was evaluated for the interactions between the above-mentioned data *via* the *Hmisc* package (Harrell, 2019). The p values were adjusted using the method after Bonferroni. The *corrplot* package (Wei and Simko, 2017) was used to display the correlation matrix.

Even under natural conditions, topsoils would differ in chemical composition as they had less time for transformation than the subsoils. Therefore, we estimated the theoretical share of aromatics as a function of age by a linear regression ($R^2 = 0.47$) using the ten subsoil samples only (Eq. 4.1).

This relationship is used to derive a theoretical difference in aromatics between topsoils and subsoils depending on their difference in age.

$$\text{Aromatic [\% of SOC]} = 0.0005 * \text{age [a]} + 152 \tag{4.1}$$

Table 4-1: Sampling sites divided into topsoil (top) and subsoil (sub) with according depth of lower end of the soil column, and their main soil properties (mean ± standard error): soil organic carbon (SOC) content, nitrogen (N) content, C:N ratio, bulk density (ρ), calcium acetate lactate extractable phosphorus (P_{CAL}) content, and specific CO_2 flux rates. The degree of decomposition, on the von Post scale (H), was determined according to Ad-Hoc-Arbeitsgruppe Boden (2005). For the topsoil of peat-sand mixtures, H could not be determined (NA). All topsoils were amorphous peat (partially mixed with sand) without any recognisable plant remains. Sphagna of the bog subsoils mainly consisted of the section *cuspidata*. Sample identifiers: s – peat-sand mixture in the topsoil, e – earthified peat in the topsoil, B – bog, F – fen.

Sample	Depth (cm)	Von Post	Peat composition subsoil	SOC (g kg^{-1})	N (g kg^{-1})	C:N ratio (-)	ρ (g cm^{-3})	P_{CAL} (mg kg^{-1})	Spec. CO_2 flux (µg C g^{-1} SOC m^{-2} h^{-1})
Bog peat									
sB1	20 (top)	NA	–	71 ± 2	3.5 ± 0.0	20.1 ± 0.3	0.96 ± 0.04	75.5 ± 3.3	309 ± 5
	70 (sub)	H3	*Sphagnum spp.*, *Eriophorum vaginatum* L., *Ericaceae*	510 ± 4	11.7 ± 1.2	44.5 ± 4.7	0.14 ± 0.01	26.2 ± 5.8	77 ± 14
sB2	20 (top)	NA	–	49 ± 3	3.8 ± 0.1	12.8 ± 0.4	1.05 ± 0.05	114.5 ± 0.4	484 ± 14
	55 (sub)	H2	*Sphagnum spp.*, *Scheuchzeria palustris* L., *Ericaceae*	547 ± 4	20.0 ± 0	27.4± 0.2	0.11 ± 0	17.9 ± 3.1	107 ± 5
eB1	20 (top)	H10	–	427 ± 13	21.8 ± 1.9	19.9 ± 2.2	0.23 ± 0.03	192.3 ± 20.6	413 ± 38
	95 (sub)	H4	*Sphagnum spp.*, *Scheuchzeria palustris* L., *Ericaceae*	496 ± 2	5.6 ± 0.3	88.4 ± 5.0	0.06 ± 0	7.7 ± 0.4	72 ± 2
eB2	15 (top)	H10	–	410 ± 11	25.6 ± 0.5	16.1 ± 0.7	0.32 ± 0.01	249.5 ± 8.9	336 ± 6
	25 (sub)	H2	*Sphagnum spp.*, *Ericaceae (*i.a. *Vaccinium oxycoccos* L.*)*	536 ± 3	13.2 ± 0.2	40.5 ± 0.7	0.15 ± 0	14.6 ± 1.0	20 ± 1
Fen peat									
sF1	15 (top)	NA	–	160 ± 11	14.5 ± 0.8	11.0 ± 0.1	0.64 ± 0.04	42.9 ± 1.6	228 ± 24
	105 (sub)	H6	*Carex spp.*, *Alnus glutinosa* (L.) Gaertn.	493 ± 4	27.1 ± 0.7	18.2 ± 0.3	0.16 ± 0.01	29.7 ± 6.1	128 ± 18
sF2	15 (top)	NA	–	170 ± 11	12.7 ± 0.9	13.4 ± 0.3	0.57 ± 0.04	148.7 ± 7.8	406 ± 23
	80 (sub)	H6	*Carex spp.*, *Eriophorum vaginatum* L., *Sphagnum spp.*, *Ericaceae*	542 ± 5	11.5 ± 0.9	47.9 ± 3.9	0.12 ± 0	11.6 ± 0.5	63 ± 1
sF3	15 (top)	NA	–	214 ± 5	18.7 ± 0.3	11.4 ± 0.1	0.52 ± 0.01	55.6 ± 7.7	114 ± 2
	90 (sub)	H6	*Carex spp.*, *Alnus glutinosa* (L.) Gaertn.	470 ± 2	25.7 ± 0	18.3 ± 0	0.18 ± 0.01	2.2 ± 0	54 ± 4
eF1	25 (top)	H10	–	456 ± 6	33.2 ± 0.4	13.7 ± 0.1	0.37 ± 0	118.0 ± 3.4	107 ± 2
	140 (sub)	H2	*Carex spp.*, *Phragmites australis* (Cav.) Trin. ex. Steud.	493 ± 4	18.0 ± 0.4	27.4 ± 0.4	0.12 ± 0	2.2 ± 0	60 ± 2
eF2	20 (top)	H10	–	267 ± 26	23.1 ± 2.0	11.5 ± 0.1	0.35 ± 0.02	71.8 ± 5.0	282 ± 18
	90 (sub)	H3	*Carex spp.*, *Phragmites australis* (Cav.) Trin. ex. Steud.	534 ± 5	22.4 ± 0.6	23.9 ± 0.5	0.11 ± 0	3.2 ± 1.0	42 ± 1
eF3	15 (top)	H10	–	404 ± 5	35.9 ± 0.3	11.2 ± 0.1	0.28 ± 0	77.3 ± 4.7	185 ± 5
	90 (sub)	H3	*Carex spp.*	509 ± 2	30.6 ± 0.7	16.6 ± 0.4	0.13 ± 0	9.2 ± 0.4	31 ± 1

4.3 Results

4.3.1 Chemical composition of peat substrate

The PCA based on NMR products, fibre analyses, the ^{14}C dating, specific CO_2 fluxes, nutrients (P and N), C:N ratio and bulk density demonstrated clear differences between the topsoil and subsoil samples and the fen and bog peat samples (Fig. 4-2). There was a strong clustering in the topsoil and subsoil samples on the axis of PC1, while PC2 mainly separated the bog peat samples from the fen peat samples. The differences between bog and fen peat were most distinctive in the subsoil samples. In contrast, the topsoil samples converged both between and within the peat types. However, two subsoil samples of a fen and a bog peat site were in close vicinity. The bog peat (sB2, lowermost dark green triangle) consisted of vascular plants next to *Sphagnum*, while the fen peat (sF2, purple dot outside the ellipse) contained *Sphagnum* and thus showed signs of a transition bog (Table 4-1). Together, PC1 and PC2 explained 73% of the variation in the sample set. Here cellulose, cell components (CC) and C:N ratio had the strongest effects on PC1 and O-alkyl, radiocarbon age and aromatics mainly influenced PC2.

Figure 4-3 shows the partitioning of the organic matter of the different peat types (fen and bog peat from both topsoil and subsoil) into functional groups (NMR, left-hand side) and fibre types (fibre analysis, right-hand side). Alkyl and O-alkyl were the most abundant functional groups and accounted for half (49 to 56%) of the NMR products together, followed by aromatics (Fig. 4-3a). These three NMR functional groups also showed the greatest variability within each sampling group. With exception of bog peat subsoil, the products of fibre analysis were dominated by the cell components (CC) (Fig. 4-3b).

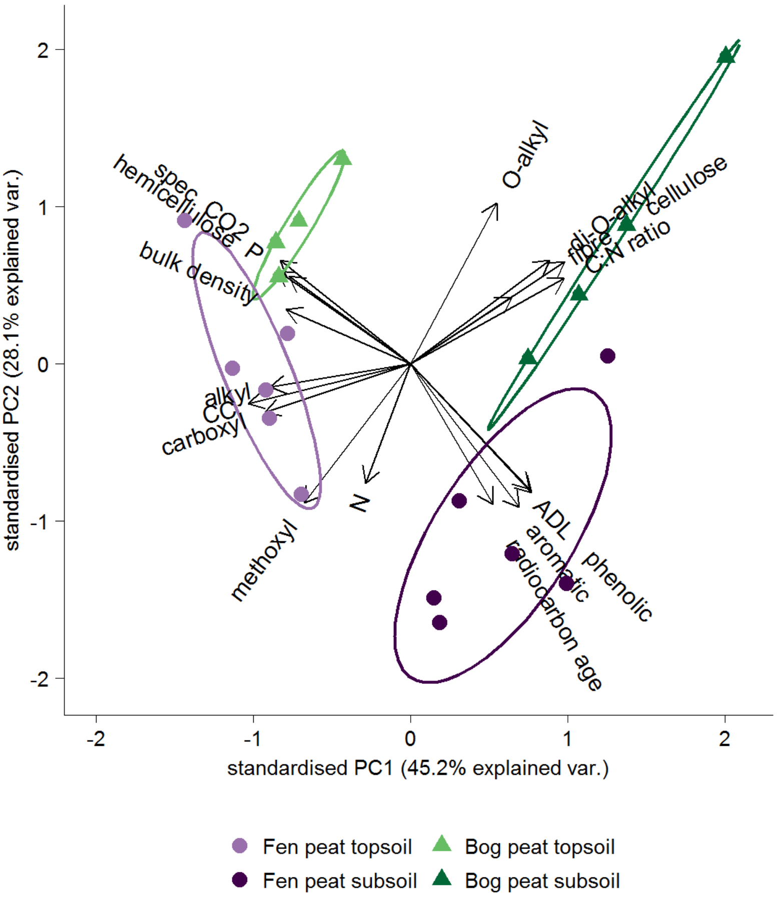


Figure 4-2: PCA biplot based on NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl), fibre analyses products (hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC), fibre), nitrogen (N) content, C:N ratio, bulk density, phosphorus (P) content, radiocarbon age, and specific CO_2 fluxes. Black arrows represent the eigenvectors of the variables. Circles are normal probability ellipses.

In general, that is, for both fen and bog peat together, the shares of alkyl, methoxyl and carboxyl were higher in the topsoil than in the subsoil samples, while the portions of aromatics, di-O-alkyl and phenolics were lower in the topsoil than in the subsoil samples (Fig. 4-3c). Higher shares of certain compounds in the subsoil always meant higher *absolute* contents in the subsoil because SOC content was always higher in the subsoil (Table 4-1). The fibre analysis revealed higher hemicellulose contents in the topsoils, while the cellulose and ADL contents were lower in the topsoil samples than in the subsoil samples (Fig. 4-3d).

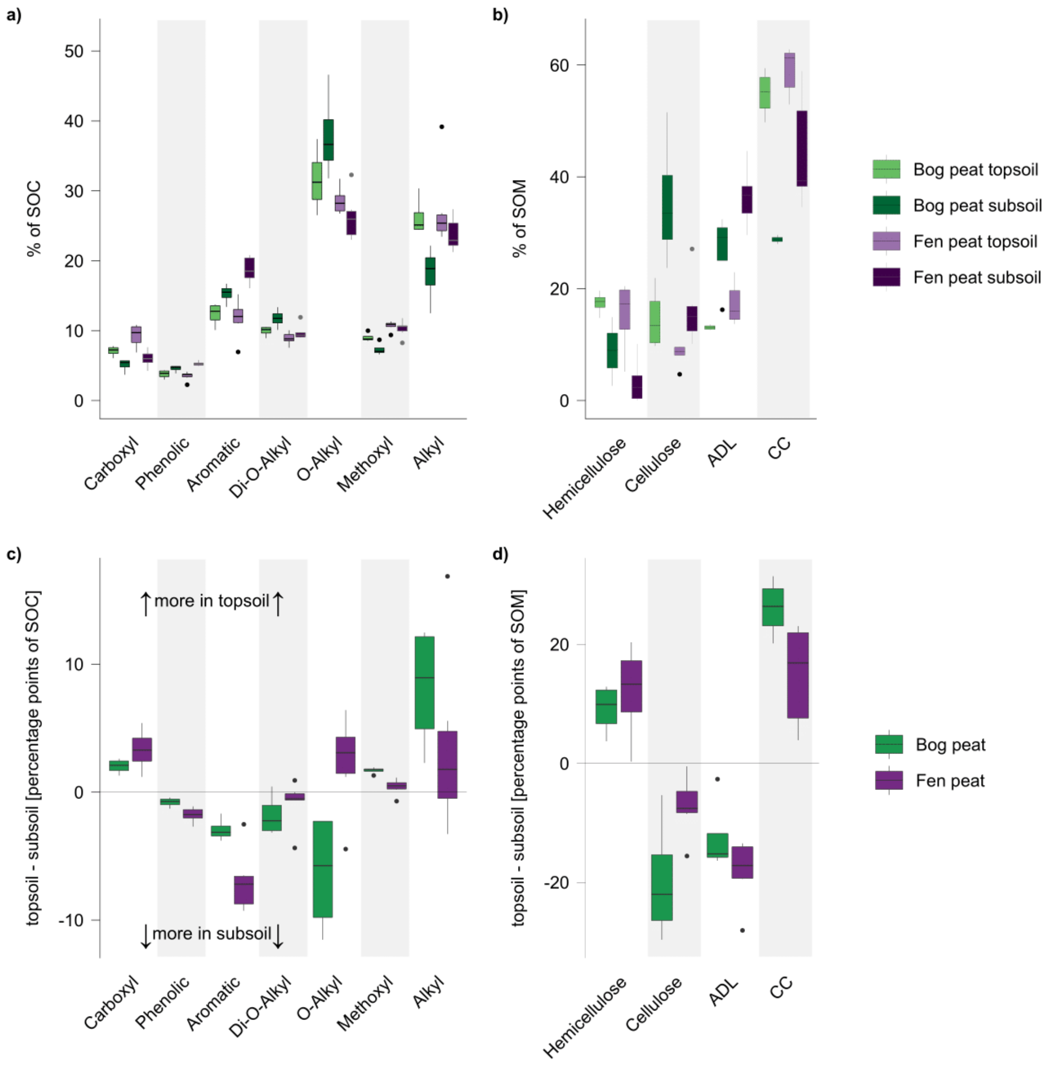


Figure 4-3: (a) NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl) and (b) fibre analysis products (hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC)) of the grouped samples. (c) Respective differences between topsoil and subsoil of fen and bog peat that are displayed in a). (d) Respective differences between topsoil and subsoil of fen and bog peat that are displayed in b). Negative values indicate higher shares in subsoil than in topsoil samples.

When looking at differences between fen and bog peat, slightly larger shares of methoxyl, carboxyl and ADL characterised the fen topsoil samples than was the case with the bog topsoil samples. In contrast, the values of O-alkyl, di-O-alkyl and cellulose were higher in the bog topsoil samples than in the fen topsoil samples. The chemical composition of peat subsoils differed more between bog peat and fen peat samples than the topsoil samples did. Aromatics were more abundant in the fen peat than bog peat subsoils, while shares of phenolic and carboxyl were similar. The abundance of alkyl and methoxyl proved to be higher in fen peat subsoils than in bog peat subsoils. Bog peat subsoils were characterised by higher O-alkyl and di-O-alkyl. This agreed with the higher amounts of cellulose in the bog peat subsoil samples than in the fen peat subsoil samples. In contrast, the fen peat samples showed higher lignin portions than the bog peat samples. In accordance with the PCA results, the amount of chemical compounds of bog and fen peat topsoils, were very similar, especially compared with the clear compositional differences between the subsoils. Only the share of O-alkyl illustrated distinct differences between bog and fen peat. While bog peat topsoil samples had lower amounts of O-alkyl than subsoil samples, the fen peat topsoils had higher values compared with the subsoil samples. The alkyl/O-alkyl ratios of the fen (0.57 ± 0.15) and bog peat (0.53 ± 0.11) topsoils were similar. In the case of subsoils, the ratios differed for the two peat types (fen peat: 0.52 ± 0.08, bog peat: 0.33 ± 0.11).

4.3.2 Peat quality and mineralisation rates

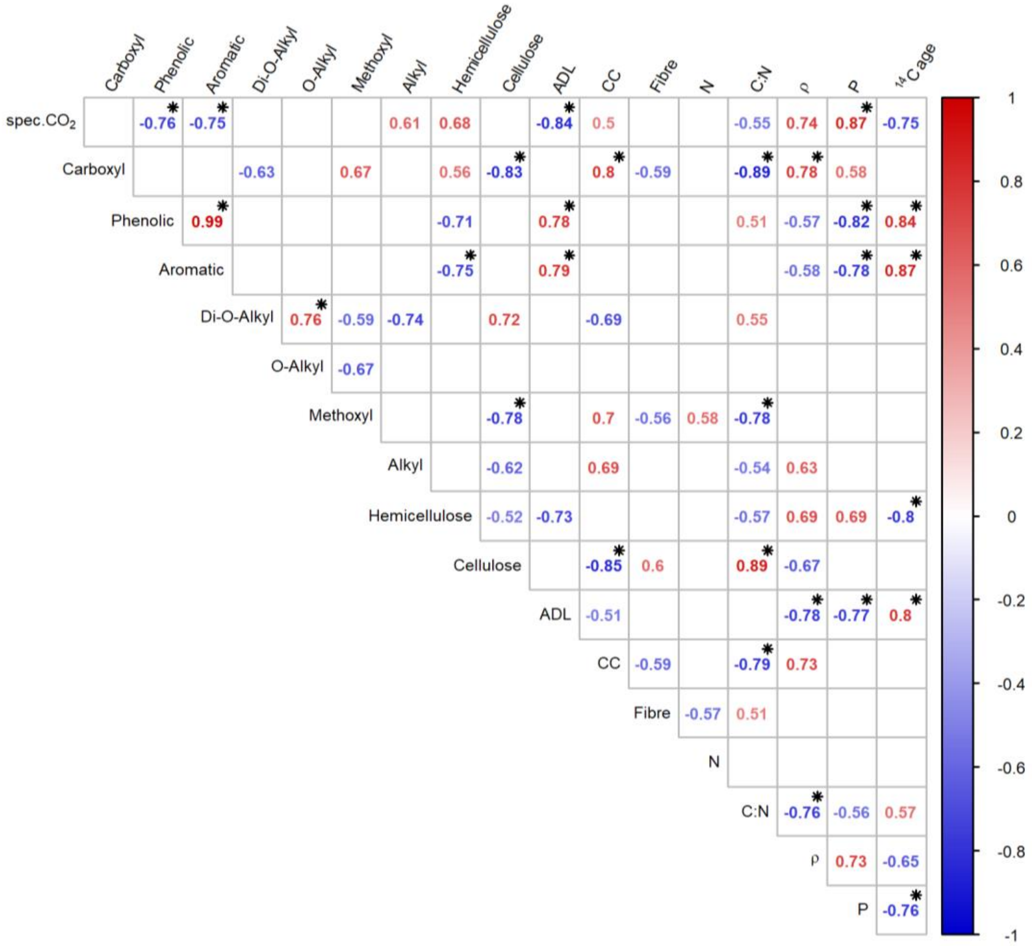
Topsoil samples had nine times higher specific CO_2 fluxes on average than subsoil samples (Table 4-1). This difference was especially pronounced for bog peat samples. Overall, specific CO_2 fluxes were significantly negatively correlated with aromatics, phenolics and ADL, and significantly positively correlated with P content (Fig. 4-4). However, no significant correlations were found when considering topsoil samples and subsoil samples separately. It was also checked whether differences in chemical composition between the topsoil and subsoil at each site had an influence on (differences in) specific CO_2 fluxes, but no correlations could be found (data not shown).

Hemicellulose content was significantly negatively correlated with aromatics, and cellulose content was significantly negatively correlated with methoxyl and carboxyl. The ADL content showed significant positive correlations with aromatics and phenolics. Cell components were significantly positively correlated with carboxyl content and negatively correlated with fibre.

4.3.3 Radiocarbon Analysis

Radiocarbon dating showed that topsoil samples were always younger than subsoil samples (Fig. 4-5a). The age range of topsoils (100 to 2800 a) was smaller than in the subsoil samples (850 to 10,700 a). Topsoils were mostly younger than 1000 years except at two sites (sB1, eF1). Subsoil samples of bog peat all showed similar radiocarbon concentrations, translating into ages of around 1800–2400 years. Fen peat subsoil samples showed a wider range from 850 years to a maximum age at site eF1 at 140 cm depth of around 10,700 years. Despite this huge range, there was no relationship between the ages of the subsoil samples and the corresponding CO_2 fluxes (Fig. 4-5b).

Significant correlations between chemical compounds and carbon age were detected for aromatics, phenolics, hemicellulose and ADL (Fig. 4-4). The strongest correlation was found for aromatics (Fig. 4-5c), but the patterns of phenolics and ADL versus carbon age were similar. From this relationship, using only the subsoil samples, it was possible to estimate the increase of aromatics with age (0.5 percentage points in 1000 years), and thus the theoretical share of aromatics in the topsoil when only induced by aging, that is, anoxic decomposition (Fig. 4-5d). When comparing the measured differences in aromatic compounds with this theoretical line, all but one site (eF1) showed steeper decreases in aromatics. The differences for the bog peat sites were smaller than for fen peat sites, but the share of aromatics in the topsoil was lower than expected from differences in age alone.



	Carboxyl	Phenolic	Aromatic	Di-O-Alkyl	O-Alkyl	Methoxyl	Alkyl	Hemicellulose	Cellulose	ADL	CC	Fibre	N	C:N	ρ	P	^{14}C age
spec.CO$_2$		-0.76*	-0.75*				0.61	0.68		-0.84*	0.5			-0.55	0.74	0.87*	-0.75
Carboxyl				-0.63		0.67		0.56	-0.83*		0.8*	-0.59		-0.89*	0.78*	0.58	
Phenolic			0.99*					-0.71		0.78*				0.51	-0.57	-0.82*	0.84*
Aromatic								-0.75*		0.79*					-0.58	-0.78*	0.87*
Di-O-Alkyl					0.76*	-0.59	-0.74		0.72		-0.69			0.55			
O-Alkyl						-0.67											
Methoxyl									-0.78*		0.7	-0.56	0.58	-0.78*			
Alkyl									-0.62		0.69			-0.54	0.63		
Hemicellulose									-0.52	-0.73				-0.57	0.69	0.69	-0.8*
Cellulose											-0.85*	0.6		0.89*	-0.67		
ADL											-0.51				-0.78*	-0.77*	0.8*
CC												-0.59		-0.79*	0.73		
Fibre													-0.57	0.51			
N																	
C:N															-0.76*	-0.56	0.57
ρ																0.73	-0.65
P																	-0.76*

Figure 4-4: Correlation coefficients after Spearman (r ≥ 0.5) for specific CO$_2$ fluxes, NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl), fibre analyses products (hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC), fibre), nitrogen (N) content, C:N ratio, bulk density (ρ), phosphorus (P) content, and radiocarbon (^{14}C) age. Significant correlations ($p < 0.05$) are marked with asterisks.

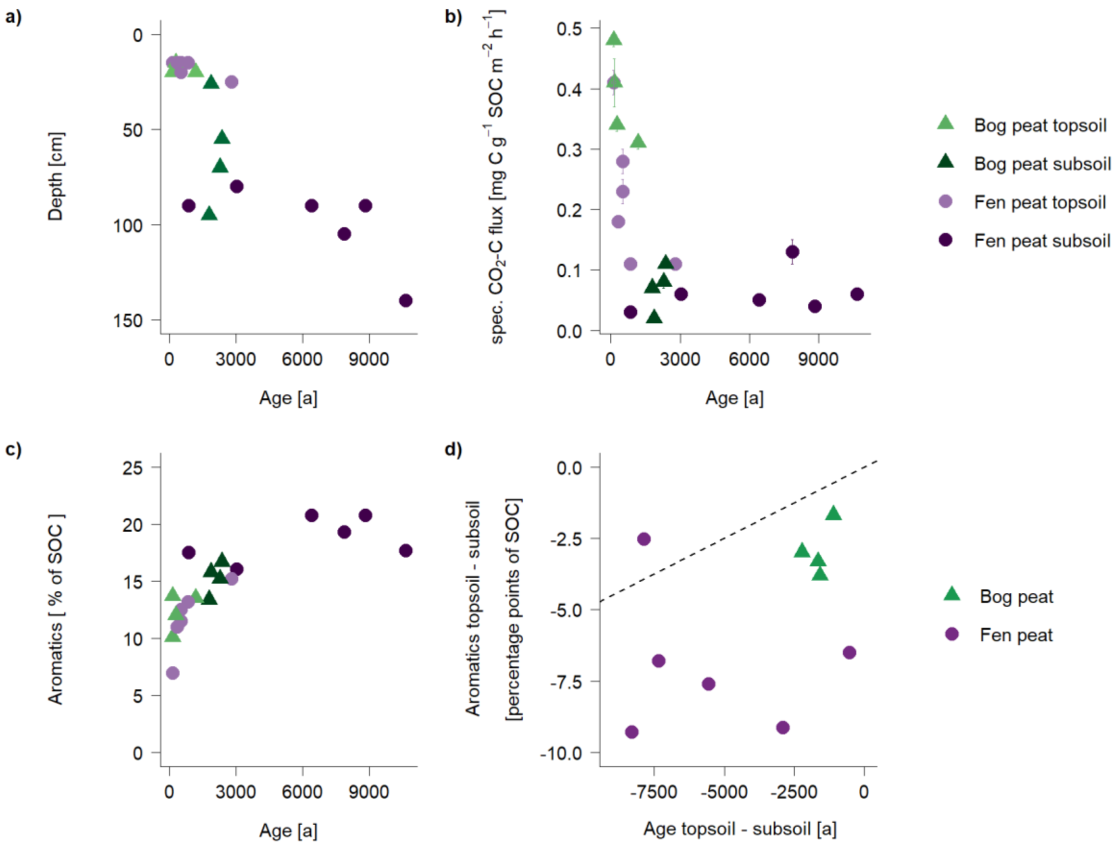


Figure 4-5: Radiocarbon age versus (a) depth of the soil samples, (b) specific CO_2 fluxes including standard errors, and (c) content of aromatics identified by NMR. Standard deviations of ^{14}C dating are too small to be visible on this scale. (d) Differences between radiocarbon age and aromatic content of topsoils and subsoils with theoretical anoxic decomposition based on subsoils from c) (dashed line) respectively.

4.4 Discussion

4.4.1 Chemical composition of peat substrate

Topsoil and subsoil

Under natural conditions, the chemical composition of peat depends strongly on depth, that is, on age and hydro-climatic conditions during peat growth. The acrotelm of both fens and bogs is characterised by fresh peat, which is dominated by O-alkyls and alkyls followed by the fraction of aromatics, phenolics and carboxyl. Predominantly oxic conditions at the surface change to anoxic conditions in the underlying catotelm. With increasing depth, the portion of carboxyl and O-alkyls decreases and the dominance of O-alkyl is replaced by alkyls and aromatics (Daugherty et al., 2019; Tfaily et al., 2014).

The drained peatlands used for agriculture in the present study have undergone secondary pedogenetic processes (Ilnicki and Zeitz, 2003), which has resulted in highly decomposed topsoil peat with no visible plant remains. Mineralisation of organic matter has exposed peat layers today that have been mostly buried deep down before drainage commenced. It was assumed that the topsoil in this study was of a similar botanical origin to the subsoil. While higher shares of aromatics and ADL in subsoils corresponded with findings from natural peatlands, this was not the case with other compounds. The share of alkyl was higher in the topsoil than in the subsoil samples, while shares of di-O-alkyl and cellulose were lower. O-alkyl showed contrasting patterns for fen samples (more in topsoils) and bog samples (more in subsoils) (Fig. 4-3). The higher share of alkyl in the topsoil was surprising because two other studies on drained peatlands have found lower shares of alkyl in the topsoils (Heller et al., 2015; Leifeld et al., 2012). Furthermore, Leifeld et al. (2012) report higher shares of aromatics and O-alkyl in the topsoils of drained bogs, which contradicts our results.

Carbohydrates such as O-alkyl and di-O-alkyl are easily degradable and microbial decomposition results in the production of alkyl C (Hopkins et al., 1997). The surprisingly high share of alkyl in the topsoil compared with the subsoil samples might indicate that the sites in this study are much more degraded than the drained sites studied by Leifeld et al. (2012) and Heller et al. (2015). This effect was especially pronounced in the case of the bog peat, which not only had more alkyl in the topsoil, but also more O-alkyl in the subsoil. he higher alkyl/O-alkyl ratios for bog topsoils compared with subsoils, indicating a high extent of microbial transformation, further support the interpretation of advanced degradation. This might have been caused by differences in peat substrates and sampling depth. The subsoil of bogs was only weakly decomposed ‘white peat’ (H2–H4), while the fen peat subsoils were in part more heavily decomposed (H2–H6, Table 4-1). Furthermore, the samples from the fen peat subsoil came from a greater depth than those from the bog peat. Thus, microorganisms had longer to use O-alkyls as an oxygen source under anoxic conditions. In contrast to fen species, *Sphagnum* does not contain lignin to strengthen cell walls, but polymerised uronic acids (Verhoeven and Liefveld, 1997) that are identified as O-alkyls. This might also explain the high share of these compounds (Fig. 4-3a).

Given that SOC contents in the subsoil are always higher than in the topsoils (Table 4-1), higher shares of aromatics, phenolics and ADL in the subsoil samples compared with the topsoil samples showed that aromatics, like lignin, tannins and lignin-like phenolics, were not selectively preserved during the topsoil peat degradation (see section 4.4.2). Lignin and lignin-like phenolics are considered to be recalcitrant chemical compounds, but their turnover might take place under different velocities, depending on the specific environmental factors (Kleber, 2010). In mineral soils, lignin might not even be preferentially preserved at all (Heim and Schmidt, 2007). Due to access to oxygen in the topsoil peat layer, numerous enzymes, e.g. phenol oxidase, are activated to decompose peat substrate (Freeman et al., 2001). Phenol oxidase oxidises the –OH group of phenolics and turns them into ketons, which explains the increase in carbonyl (which is part of the 'carboxyl' spectral region, Fig. 4-1) and the decrease in phenolics in the topsoil compared with the subsoil samples (Fig. 4-3).

The fibre analysis revealed higher hemicellulose shares in topsoils than subsoils, which is in contrast to the results of the NMR products of O-alkyl and di-O-alkyl (Fig. 4-2 and 4-3) since hemicellulose mainly consists of carbohydrates (Fig. 4-1). Furthermore, the decomposition rates of these compounds should follow the order cellulose > hemicellulose > ADL (Reddy and DeLaune, 2008). Thus, this divergence was probably caused by uncertainties in this analytical method (see section 4.4.4).

Bog and fen

The differences between the bog and fen topsoil samples were minor compared to the differences between the bog and fen subsoil samples (Fig. 4-3). Due to drainage and agricultural use, the microbial community and biogeochemical conditions of fens and bogs converge (Urbanová and Bárta, 2015), hence the similar chemical composition of the topsoils (Fig. 4-2). Obvious differences between fen and bog peat subsoils originate from the different peat-forming plants of the respective peatland type (Bohlin et al., 1989). The subsoils were characterised by several chemical metabolites, which protect cell wall substances against microbial decomposition. The richness of lignins in fen peat, especially woody peat, and polyphenols such as tannins was visible in the higher shares of ADL, methoxyl and aromatics compared with the bog subsoil samples (Fig. 4-3). Phenolic compounds are inhibitors of hydrolase enzymes, which are major agents in the decomposition of organic matter (Dunn and Freeman, 2018). The fen and bog subsoil samples had similar portions of phenolics, but decomposition seems to be dependent on the type of polyphenol rather than on the total amount (Bragazza et al., 2007; Zak et al., 2019). The abundance of lignin in bog peat was low since bogs are predominantly formed by bryophytes such as *Sphagnum* species, that do not synthesise lignin (Kremer et al., 2004; Maksimova et al., 2013). To strengthen its cell walls, *Sphagnum* uses sphagnum acid, for example, a lignin-like phenolic, and polymerised uronic acids called sphagnan (Bengtsson et al., 2018; Verhoeven and Liefveld, 1997). The occurrence of sphagnan, which is a polysaccharide, could have contributed to higher shares of O-alkyl, di-O-alkyl, hemicellulose and cellulose in the bog subsoils than in the fen subsoils. Furthermore, high shares of O-alkyl are common in mosses (Maksimova et al., 2013; Philben et al., 2018), which are the dominant peat-forming plants in bogs.

4.4.2 Radiocarbon analysis

As expected, there was a clear age difference between the topsoil and subsoil samples at each site and a correlation with depth for subsoils (Fig. 4-5a). Given the same depth, intact peat of natural peatlands is generally younger than degraded peat of drained peatlands used in agriculture (Leifeld et al., 2018). It can be assumed that the older the topsoil peat, the more peat has already been lost due to drainage and mineralisation, which was very evident for the 2800-year-old topsoil of site eF1. Based on a mean subsidence rate of 1 cm a^{-1} (Dawson et al., 2010; Leifeld et al., 2011), more than 2.5 m of peat might have been lost at this site due to drainage and agricultural use. This amount of subsidence is reasonable as the 'Friedländer Große Wiese' peatland, where site eF1 is located, has been exposed to drainage since the 18th century, which was further intensified in the 1960s (Succow and Joosten, 2001).

Although the bog subsoil samples came from different depths, they had a similar age of around 1800–2400 years. This fits well with the onset of the development of fibric 'white' peat dominated by well-preserved hummock mosses in north-west Germany during the Subatlantic about 2600 BP (Rydin and Jeglum, 2006). All the bog samples were identified as 'white' peat. In contrast, the fen subsoil samples came from similar depths (with the exception of eF1) but had different ages. Although the subsoil samples had different chemical compositions and large age differences, neither had an influence on the CO_2 fluxes. Aromatics and phenolics were significantly positively correlated with age (Fig. 4-5c), that is, older and deeper peat had a higher share of aromatics. However, the younger topsoils had much lower shares of aromatics than could be expected by the age difference to the subsoils alone. The theoretical difference in aromatics between topsoils and subsoils is indicated by the line in Fig. 4-5d. The measured differences were, however, clearly distinct from the theoretical enrichment in aromatic compounds which could be explained by differences in age. Therefore, peat-aging processes cannot be the only reason for the quantities of aromatics and other chemical compounds diverging between the topsoil and subsoil samples. Hence, the abundance of lower shares of recalcitrant compounds in the topsoil samples indicated increased mineralisation also of 'recalcitrant' SOM due to agricultural use. Even though radiocarbon dating is often used in soil science (Bader et al., 2017; Krüger et al., 2015; Leifeld et al., 2018), it is theoretically designed for closed systems only. Thus, radiocarbon age in subsoil could be underestimated due to possible fresh C-input. However, we did not find any signs of roots in the subsoil indicating minor C-input at sampled subsoil depth and low bias in age estimation. Age determination of the topsoil samples was more uncertain due to their intrinsic high levels of bomb- ^{14}C. Next to this calibration uncertainties however, the topsoils are open systems with a mixture of old peat and younger plant derived C even though fresh roots were deliberately removed from topsoil samples. Still, the current topsoil composition results from the partial transformation of old material, the formation of new microbial products from metabolised organic matter, and new input material such as root exudates or plant residues missed out when removing roots. The latter might have diluted the signature of the old organic material. However, even if the 'younger' topsoils were a few centuries older than estimated here, this would not change the general interpretation of Fig. 4-5.

4.4.3 Peat quality and mineralisation rates

Previous studies on managed and unmanaged peatlands have found strong relationships between peat quality and CO_2 fluxes (Leifeld et al., 2012; Reiche et al., 2010; Sjögersten et al., 2016). Both Leifeld et al. (2012) and Sjögersten et al. (2016) identify O-alkyl as a proxy for higher respiration rates. In the present case, there was no correlation between O-alkyl and CO_2 fluxes, even when separating the bog and fen peat samples due to their contrasting patterns with depth. Instead, negative correlations were found between aromatics, phenolics and ADL and CO_2 fluxes in the present study (Fig. 4-4). However, these relationships mainly reflected the strong differences in CO_2 fluxes and chemical composition between topsoil and subsoil, and were not found when analysing topsoils and subsoils separately. It has been argued that peat decomposition will slow down with time because recalcitrant peat predominantly remains, which hinders mineralisation (Leifeld et al., 2012; Urbanová and Bárta, 2015). In the present study, less 'recalcitrant' substances (aromatics, phenolics, ADL) were found in the topsoil even when considering the age difference between topsoils and subsoils. Another laboratory study, using a broad range of disturbed organic soils, shows the high variability in CO_2 fluxes of heavily disturbed soils, but also demonstrates an overall increase in mineralisation rates with higher anthropogenic disturbance (Säurich et al., 2019b). Even shallow peat remaining after peat extraction, consisting of highly decomposed old peat, has been shown to emit as much CO_2 as deep peat (Leiber-Sauheitl et al., 2014, Tiemeyer et al., 2016). Furthermore, the degradability of aromatics that are generally considered recalcitrant has been shown in natural peatlands (Reiche et al., 2010; Sjögersten et al., 2016). All this strongly points to the decomposition of aromatics and phenolics under aerobic conditions. Overall, the chemical composition of the peat seemed to be more a result from, rather than a driver of, mineralisation in the case of agricultural use involving drainage and fertilisation.

4.4.4 Measurement methods for peat quality

As proposed in Figure 4-1, the shares of functional groups identified by NMR bore a strong resemblance to the wet chemical extraction results of CC (alkyl and carboxyl), cellulose (O-alkyl and di-O-alkyl), and ADL (aromatic and phenolic) (Fig. 4-2 and 4-4). Even though the results of ADL and shares of aromatics and phenolics fit well here, the method after Goering and von Soest (1970) and the similar Klason lignin method were not developed for soils and might include aliphatics in addition to lignin and lignin-like phenolics (Kögel-Knabner, 2002). However, the relative values of the fibre analysis showed higher values of cell components in the form of lipids and proteins than NMR did (Fig. 4-3). This inaccuracy lies in the non-selective nature of the stepwise procedure: soluble carbohydrates and lignins might be removed in the NDF extraction step, leading to an underestimation of polysaccharides and an overestimation of cell components (Veeken et al., 2001). This might also be a reason why the portion of hemicellulose was clearly lower for subsoils than for topsoils, alongside the possible interference of other compounds during the determination of hemicellulose (van Soest, 2018). Generally, wet chemical extractions might be more prone to inaccuracies than NMR spectroscopy due to secondary reactions, losses during the chemical degradation processes or incomplete release of these products (Kögel-Knabner, 1997). Given the merely proximate chemical fractions and uncertainties, and especially the peculiar results for hemicellulose content, a quantitative comparison of both peat quality methods remains difficult.

Cell components and therefore NDF correlated well with fibre content, which was determined using sodium hexametaphosphate. This is surprising since the peat is not boiled in this method, but only soaked in the solution, and the samples are not ground but bulk peat is used. Hence, if solely the overall fibre content is of importance, this determination provides good results with fewer chemicals and less time and effort compared with the NDF method.

4.5 Conclusions

This study examined the peat quality of bog and fen peat sites used for agriculture by means of NMR spectroscopy, wet chemical extractions and radiocarbon dating. Differences in chemical composition were more pronounced between topsoil and subsoil samples than between peatland types. While the composition of topsoils converged, the chemical composition of bog and fen subsoils could be explained by their botanical origin. Recalcitrant compounds such as aromatics and phenolics were not enriched in the topsoil samples. Taking radiocarbon age into account, the lower share of these substances in the topsoils points to their decomposition under aerobic conditions. This implies that a gradual decrease in peat quality might not slow the rate of mineralisation of organic soils used for agriculture. Overall, CO_2 fluxes were negatively correlated with aromatics and phenolics, however a separate examination of topsoils and subsoils was unable to establish any relationship between CO_2 fluxes and peat quality indicators. Thus, it seems that differences in chemical compositions are more a result of peat decomposition than the reason behind increased mineralisation rates.

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5 Synthesis

This thesis aimed at the disclosure of the sensitivity of drained organic soils under agricultural use to decomposition, thereby focusing on low C organic soils and peat-sand mixtures. The goal was to find biogeochemical and hydrological indicators for increased or decreased GHG emissions from these drained organic soils. Studies on drained organic soil under agricultural use are rare compared with studies on (nearly) natural peatlands (e.g. Bridgham and Richardson, 1992; Daugherty et al., 2019; Larmola et al., 2013; Pinsonneault et al., 2016b). The existing studies on the interrelations of drivers for peat mineralisation of anthropogenically disturbed peatlands mostly spotlighted 'true' peat only (e.g. Ausec et al., 2009; Berglund and Berglund, 2011; Brake et al., 1999; Brouns et al., 2016). However, heavily disturbed organic soils, that sometimes are hardly recognizable as such anymore, seem to be disregarded in the current state of research.

In the framework of this thesis two laboratory incubation studies were conducted. In the first experiment, rewetted, processed, dried soil samples covering a broad range of soil properties were incubated at the same optimum soil moisture. In the second experiment, fully water-saturated undisturbed soil columns were stepwise drained. Production rates of CO_2, N_2O and CH_4, and microbial biomass were measured. Next to basic soil properties, plant-available phosphorus and potassium content, DOC, radiocarbon age as well as chemical composition by NMR spectroscopy and wet chemical extractions were determined.

5.1 General findings

With the aerobic incubation experiment in the Heinemeyer device (Heinemeyer et al., 1989; section 2) it has been shown that potential specific basal respiration rates (SBR) increased in magnitude and variability with increasing disturbance of organic soil. Bog peat samples had relatively high SBR rates, which were comparable to the fen peat sample rates. This result disagrees with field studies summarised by the IPCC (2014). Together with a similar microbial biomass for disturbed fen and bog peat samples this pointed towards higher vulnerability of bog peat to drainage. The amount of specific microbial biomass increased with increasing disturbance, although SOM quality should be less attractive for microbial turnover at this point of degradation. There seemed to be no preservation of stable and recalcitrant SOM in the disturbed samples. Anthropogenically induced factors like long-term fertilization and aeration due to drainage might have altered the microbial community and thereby increased the microbial biomass.

Neither SBR nor microbial biomass of heavily disturbed peat samples could be explained by the set of analysed soil parameters. This was most notable for the broad group of different heavily disturbed fen samples. Overlaying processes of decomposition and mineral soil addition moreover increase the complexity of this group. For less disturbed samples, a dependency on soil properties was more visible. Plant-available P was the most important explanatory variable for all disturbance classes, but especially for bog samples. With increasing disturbance there seemed to be a transformation in microbial SOM turnover from N to P limitation. Of all the soil parameters investigated in this study narrow C:N-ratio, low SOC content, high pH-value, and high content of plant-available P were identified as key indicators for increased CO_2 production rates.

In the second experiment of the thesis (section 3 and 4), instead of dried soil samples, undisturbed soil columns were used and long-term incubated in a microcosm device (Hantschel et al., 1994). The first part of this study (section 3) focused on the influence of agricultural management like water regulation and sand addition as well as peat type and nutrient status. All samples showed a parabolic optimum curve with maximum CO_2 fluxes at about 84% water-filled pore space (WFPS). The results displayed a high variability between samples for optimum moisture for maximum N_2O fluxes. However, most of the highest fluxes occurred above 80% WFPS. This indicates that mainly denitrification processes contribute to the maximum N_2O production. Fluxes of CH_4 were negligible throughout the whole experiment and the used synthetic air (20% O_2, 80% N_2) made it impossible to determine potential CH_4 uptake of the soil.

No significant differences in specific CO_2 fluxes were found between earthified peat topsoils and peat-sand mixture topsoils. However, the well preserved subsoils of peat-sand mixtures showed higher CO_2 fluxes than subsoils under earthified topsoils. These subsoils also had higher bulk densities and more nutrients. A consistent pattern for N_2O could not be established: Topsoils of peat-sand mixed fens showed higher N_2O fluxes than earthified fen topsoils and vice versa for bog peat sites.

For both CO_2 and N_2O, topsoil fluxes exceeded subsoil fluxes by far: On average, topsoils had nine fold higher CO_2 fluxes than subsoils. Even though differences were visible in soil properties like C:N ratio and pH-value, there were no consistent differences between GHG fluxes of fen and bog peat. Surprisingly, higher CO_2 fluxes were observed in bog peat than fen peat topsoils. A reason behind this might be the strong influence of plant-available P and K on CO_2 and N_2O fluxes in the case of all samples, which was most pronounced in bog peat.

The second part of the second study (section 4) focused on the chemical characterization and its influence on decomposition. The results showed that the chemical composition converged for bog and fen peat in the topsoils, and clear peat type related distinction by chemical compounds was only evident in subsoils. The chemical composition of subsoil peat correlated with their respective botanical origin: bog peat was characterized by prominent O-alkyl and fen peat by aromatic compounds.

The measured maximum CO_2 fluxes negatively correlated with aromatics and phenolics. However, when separating out topsoils and subsoils no reliable relationships with indicators were detected. There was no visible enrichment of recalcitrant compounds like aromatics and phenolics in the studied topsoil samples. The relationship between radiocarbon age and recalcitrant compounds as differences between topsoil and subsoil implied that mineralisation played an important role next to natural peat-aging processes. The results of NMR and wet-chemical fibre analysis were in good agreement with each other, although wet chemical extraction held high uncertainties due to secondary reactions during the laboratory determination.

5.2 General conclusions and implications

The higher the degree of disturbance the higher were the amount and variability of CO_2 production rates. Both, highest variability and highest amount, was detected for heavily disturbed samples with low SOC values at the boundary to mineral soils. Therefore, the vulnerability to decomposition of low C organic soils is enhanced compared with ‘true’ peat soils. The critical SOM content where these peat-derived soils respond like mineral soils seems to be well below the 150 g kg^{-1} SOM given by the German soil classification, since the lowest sample value of this thesis was 49 g kg^{-1} SOC (~ 85 g kg^{-1} SOM using the conversion factor of 1.72; Ad-Hoc-Arbeitsgruppe Boden, 2005). Drainage and cultivation are important progressing processes that need to be further studied given the high intrinsic potential of peat to emit large amounts of GHGs. Further research should concern the improvement of the GHG quantification by incorporating contributions of these hotspots and possible approaches to mitigation strategies. The fact that nearly 50% of the organic soils under agriculture in Germany cannot be classified as typical peat soil according to the German soil classification anymore (< 30 g kg^{-1} SOM; Ad-Hoc-Arbeitsgruppe Boden, 2005; Jacobs et al., 2018; Wittnebel et al., submitted) illustrates the importance to correctly identify these disturbed organic soils.

Generally, CO_2 production rates from bog peat samples were nearly as high as from fen peat (section 2) or even exceeded them (section 3). This was rather surprising since fen peat is characterized by vascular plants and nutrient rich conditions clearing the way for elevated decomposition rates (Blodau, 2002) compared with bog peat, which is lacking nutrients and acidity, and recalcitrant material hinders on-going decomposition processes (Urbanová and Bárta, 2014; Verhoeven and Liefveld, 1997). Results of previous studies underpin this theory (Bridgham and Richardson, 1992; IPCC (Intergovernmental Panel on Climate Change), 2014; Urbanová and Bárta, 2015). However, Urbanová and Bárta (2015) reported that with increasing drainage bogs and fens become more similar in their biogeochemical properties and microbial composition, in that the microbial community of bogs increased in diversity and richness. The results of increasing microbial biomass with higher disturbance in bog peat samples (section 2) and the convergence of chemical composition in topsoils of fens and bogs (section 4) are in good agreement with the latter study. This again highlights the high sensitivity of bog peat to decomposition triggered by drainage and agricultural use. Hence, even though the share of bogs under agricultural use in Germany (10–18%) is clearly smaller than that of fens (41–53%; Roßkopf et al., 2015), emission from bogs could contribute substantially to overall emissions from this sector.

In both experiments, lowest CO_2 and N_2O emissions were detected for subsoil samples or well preserved peat samples, which is in line with previous studies (Bader et al., 2018; Berglund and Berglund, 2011; Hardie et al., 2011; Hogg et al., 1992). These reduced mineralisation rates of subsoil peat compared with topsoil peat was possibly caused by less microbial biomass (section 2) and persistent chemical compounds (section 4) of the subsoil peat, but primarily by higher nutrient contents (N, P and K) of topsoil peat. The nutrient status, especially P and K, seemed to be more important than the peat type or the chemical composition of the sample. Thus, the intensity of peatland management, including liming and fertilization, might be the main reason behind increased decomposition rates. To utilize bogs for agriculture, a lot more fertilization is necessary compared with fens given their naturally higher nutrient status (Göttlich, 1990). This circumstance was visible in this thesis in much higher P contents of bog than fen samples. The consequences of heavy disturbance and increased degradation of topsoil peat due to intensive agricultural use were noticeable even in the nutrient status of subsoil peat – probably caused by leaching – thereby probably favouring microbial turnover. Unmixed subsoils underneath peat-sand mixture topsoils were affected in particular.

In general, the practice of sand application as uppermost layer of the peatland as a promising mitigation option cannot be supported with the results of this thesis. Actually, CO_2 emissions of peat-sand mixtures indicated quite the contrary, as SOM in peat-sand mixtures seemed to be unstable. The mineralisation rates of these soils appeared to be more similar to organic soils than mineral soils. In addition, corresponding subsoils are negatively impacted by altered soil properties (e.g. nutrient content and bulk density) and are prone for increased decomposition.

Both CO_2 and N_2O emissions were clearly dependent on soil moisture. The distinct parabolic dependence between CO_2 fluxes and WFPS points to the circumstance that peat soils need to be very wet to reduce emissions. Furthermore, moist conditions seemed to increase CO_2 emissions more than very dry conditions. Under equilibrium conditions, the WFPS at maximum CO_2 fluxes match a water-table depth of 20 to 60 cm below surface. Therefore, it is highly questionable that most German grasslands on organic soil are near this optimum water-table (Bechtold et al., 2014). Raising the water-table might already considerably decrease mineralisation rates and even reinstate a functioning peatland environment under optimum conditions. However, rewetting can be aggravated by long-lasting biogeochemical and hydraulical changes in these heavily disturbed organic soils and it is going to take several decades until rewetted peatlands are comparable to their natural matches once again (Urbanová and Bárta, 2020; van Diggelen et al., 2020; Zak et al., 2010).

It appears that increased disturbance and increased mineralisation rates form a destabilizing positive feedback loop and the chemical composition of heavily disturbed organic topsoils results from rather than drives mineralisation. The results of this thesis did not indicate a preferential preservation of recalcitrant compounds like aromatics and phenolics in the topsoils, but instead unfold their apparent decomposition under aerobic conditions. The gradual decrease in peat quality with time might not slow the mineralisation of organic soils used for agriculture as proposed by Leifeld et al. (2012).

5.3 Limitations and outlook

While the first experiment included organic soil under grassland and cropland use, samples of the second experiment were collected under grassland use only. This way field sampling was eased, comparability was given and the major land use of organic soil in Germany (53%; Tiemeyer et al., 2020) was depicted. However, future studies should inquire organic soils under cropland use, as these management practices are even more intensive than grassland use. Although in this thesis, low C organic soils were intensively studied and their high vulnerability to drainage and variability in GHG emissions was revealed, it still remains unclear at which point low-C organic soils behave rather like mineral soils in terms of GHG emissions.

In this thesis, only one or two soil horizons were investigated per site. The most obvious consequences of anthropogenic disturbance are visible in the uppermost peat layer. Although this horizon is examined thoroughly in the second experiment, all other horizons above the water-table are prone to increased mineralisation, too. Taking all peat horizons into account as well as the interplay between them, the reported GHG emissions in this thesis are only the tip of the iceberg. However, it needs to be stressed that all of the measured GHG production rates and fluxes are potential production rates and fluxes under laboratory conditions.

The results of this thesis imply that availability of P and K is an indicator of major importance for the vulnerability of organic soils to SOM decomposition. The positive effect of P on CO_2 and N_2O production from peat has already been studied (Amador and Jones, 1993; Brake et al., 1999; Liimatainen et al., 2018; Regina et al., 1996). A fertilization experiment on disturbed organic soils could further investigate the relationships of N, P and K, since this was not conducted in the frame of this thesis.

To properly examine factors that influence mineralisation of peat and to determine which sites are sources or maybe sinks for GHGs, a monitoring approach is essential. A combination of monitoring and long-term experiments in laboratory and field is beneficial. With a repeated sampling after 5 to 10 years, when changes in SOC content are measurable, it may be investigated which factors influence possible changes in the SOC content, e.g. climate conditions, location or management practices.

The von Post scale is the standard procedure to determine the peat's degree of decomposition as was done in this thesis. This procedure was developed for natural peatlands where increased decomposition is caused by climatic conditions during peat development and age only. Anthropogenic impacts are not considered. Here, a classification system for the degree of disturbance under anthropogenic impact was proposed (Table S1) using the mapped soil horizons (Ad-Hoc-Arbeitsgruppe Boden, 2005), information on secondary pedogenetic processes (Ilnicki and Zeitz, 2003; Succow and Joosten, 2001) and soil properties. Unfortunately, the experiment is lacking a uniform distribution of samples between the different disturbance classes since the classification was developed after the sample set was selected.

Even though this thesis takes a major step forward in terms of magnitude and diversity of sampled sites compared with previous studies, the heterogeneous nature of organic soils under agriculture can be presented but not fully be explained. The naturally occurring variety of peat types with different biochemical composition and peat evolution is manifold.

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Appendix A

Drained organic soils under agriculture — The more degraded the soil the higher the specific basal respiration

Table S1: Classification of the degree of disturbance with corresponding soil horizons and description (Ad-Hoc-AG Boden, 2005; TGL 24300/04 in Succow and Joosten, 2001); abbreviations of soil horizons according to KA5 (Ad-Hoc-AG Boden, 2005)

Degree of disturbance	Disturbance class	Soil horizons*	Description
No disturbance	D0F/D0B	Hr	Permanently saturated and anaerobic ("reduced") conditions, not altered by secondary pedogenetic processes, peat substrates can be identified. "Undisturbed horizons" may not be confused with "undisturbed peatlands" as such horizons may appear at greater depth of drained sites.
Slight disturbance	D1F/D1B	Hw	Alternating saturated-unsaturated conditions and thus temporarily subjected to aerobic conditions, subsoil horizon of drained sites, peat structure not yet altered by secondary pedogenetic processes.
Moderate to strong disturbance	D2F/D2B	Hv, Hm	Topsoil horizon of moderately drained sites, earthified (Hv), crumbly structure caused by aerobic decomposition, plant residuals not visible anymore. One sample was classified as "Mulm" (Hm, topsoil horizon of heavily drained sites), i.e. showed a "moorshy", dusty or small-grained structure when dry, intensive aerobic decomposition, plant residuals not visible anymore.
Strong disturbance	D3F	Ht, Ha	Subsoil horizon of intensively drained sites, polyhedral aggregates caused by swelling and shrinkage, crumbly when dry (Ha) OR prismatic aggregates with vertical cracks (Ht) as transition horizon to underlying peat. Aggregate and shrinkage horizons have been combined in this class due to the very low number (n = 2) of shrinkage horizons in our sample set. This class occurred only in fen peat samples.
Heavy disturbance	D4F	rHv, rHm	Topsoil horizon of intensively drained fen peat sites which cannot be classified as peat anymore. The low SOC content may have been caused by ploughing, mineralisation, anthropogenic addition of mineral soil material from external sources, addition of mineral soil material from natural sources (sedimentation in riverine fens or translocation by wind) or a combination of several factors. In the field, horizons have frequently either shown attributes of earthified or moorshy peat. Due to the strongly disturbed conditions of these topsoils, it was impossible to distinguish between the underlying different processes. The only 2 respective bog samples were classified as D2B.

*Examples of fairly basic horizon symbols without additional geogenetic or pedogenetic attributes or combined horizons, for details see data supplement (data.xlsx)

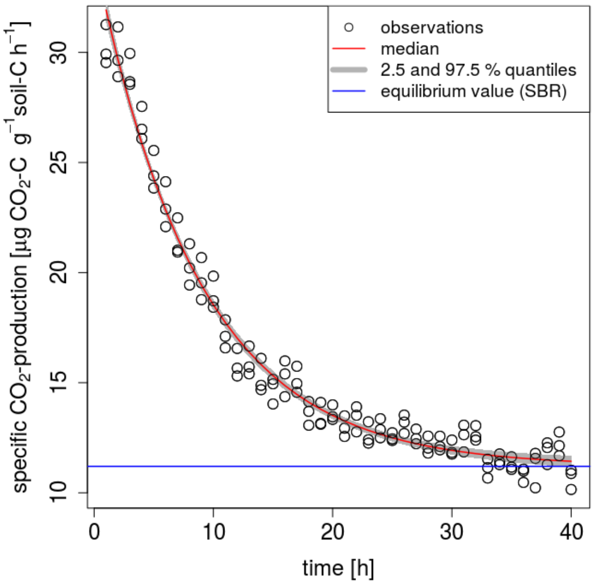

Figure S1: Specific CO_2 production of three incubation replicates over time. Corresponding median including quantiles (2.5 and 97.5 %) and the equilibrium value of the SBR, as determined by the exponential model.

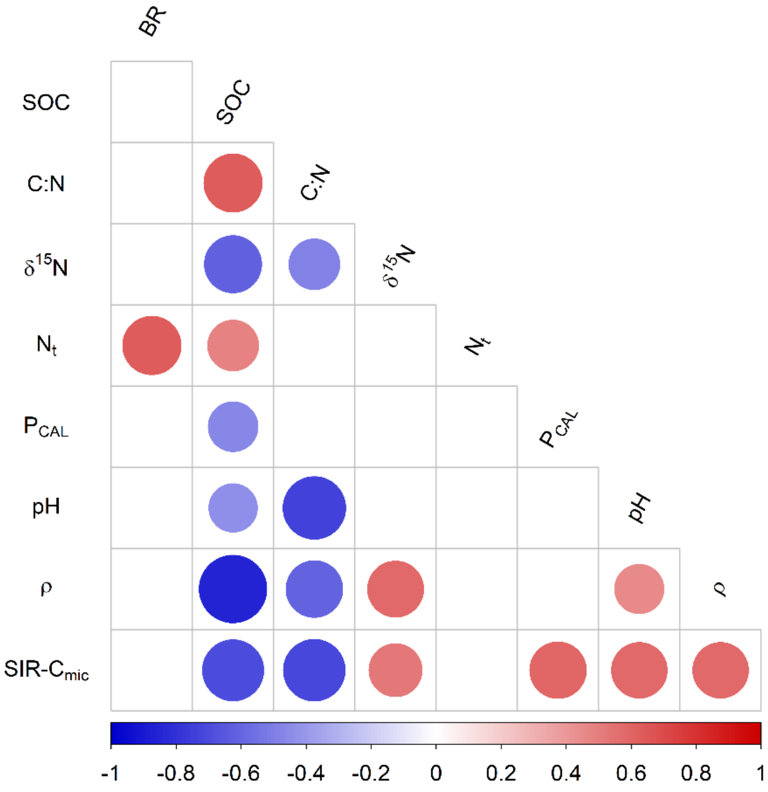

Figure S2: Significant ($p < 0.05$) correlation coefficients after Spearman for basal respiration rates (BR) with soil properties (SOC: soil organic carbon content C:N-ratio: carbon to nitrogen ratio, $\delta^{15}N$, N_t: total nitrogen content, P_{CAL}: calcium acetate lactate (CAL) extractable phosphorus content, pH-value and ρ: bulk density) and specific microbial biomass (SIR-C_{mic}).

Table S2: Mean and standard deviation of basal respiration rates (BR), specific basal respiration rates (SBR), microbial biomass (SIR-C$_{mic}$) and microbial quotient (q(CO$_2$)) for all disturbance classes: F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance.

Disturbance class	BR (µg CO$_2$-C g soil^{-1} h^{-1})	SBR (µg CO$_2$-C g SOC^{-1} h^{-1})	SIR-C$_{mic}$ (µg C g^{-1} SOC)	q(CO$_2$) (mg CO$_2$-C g^{-1} C$_{mic}$ h^{-1})
D0F	2.4 ± 1.2	5.7 ± 2.7	1097 ± 344	5.0 ± 2.0
D1F	3.1 ± 1.0	7.8 ± 3.4	1566 ± 735	5.4 ± 1.5
D2F	2.5 ± 1.1	9.8 ± 5.9	2064 ± 939	4.8 ± 1.7
D3F	3.3 ± 1.0	11.0 ± 3.8	2459 ± 1429	6.9 ± 6.7
D4F	1.8 ± 1.0	13.9 ± 6.0	3942 ± 2177	4.6 ± 2.9
D0B	1.7 ± 0.5	3.2 ± 1.0	423 ± 180	9.3 ± 5.8
D1B	2.3 ± 1.1	5.0 ± 2.6	893 ± 551	7.2 ± 5.9
D2B	3.1 ± 2.3	10.9 ± 4.7	2709 ± 1005	4.0 ± 1.0

Table S3: Correlation coefficients after Spearman for basal respiration rates (BR) and specific basal respiration rates (SBR) with soil properties (SOC: soil organic carbon content, C:N: carbon to nitrogen ratio, δ^{15}N, N$_t$: total nitrogen content, P$_{CAL}$: calcium acetate lactate (CAL) extractable phosphorus content, pH-value and *ρ*: bulk density) and specific microbial biomass (SIR-C$_{mic}$). Levels of statistical significance: *p <0.05, **p <0.01 and ***p <0.001.

	BR	SBR	SOC	C:N	δ^{15}N	N$_t$	P$_{CAL}$	pH	ρ
SOC	0.28	-0.65***							
C:N	-0.13	-0.65***	0.63***						
δ^{15}N	-0.16	0.47**	-0.61***	-0.49**					
N$_t$	0.64***	-0.04	0.48**	-0.24	-0.32				
P$_{CAL}$	0.09	0.51**	-0.47**	-0-26	0.38	-0.31			
pH	-0.01	0.31	-0.44*	-0.73***	0.32	0.24	0.14		
ρ	-0.30	0.49**	-0.85***	-0.60***	-0.59***	-0.35	0.41	0.46*	
SIR-C$_{mic}$	0.16	0.79***	-0.70***	-0.71***	-0.53***	-0.11	0.60***	0.58***	0.58***

Table S4: Correlation coefficients after Spearman for the specific basal respiration rates (SBR) separated into the disturbance classes (F=fen, B=bog, D0=no disturbance, D1=slight disturbance, D2=moderate disturbance, D3=strong disturbance, D4=heavy disturbance) and soil properties: SOC: soil organic carbon content, C:N: carbon to nitrogen ratio, δ^{15}N, N$_t$: total nitrogen content, P$_{CAL}$: calcium acetate lactate (CAL) extractable phosphorus content, pH-value, *ρ*: bulk density and the determined specific microbial biomass (SIR-C$_{mic}$). Levels of statistical significance: *p <0.05, **p <0.01 and ***p <0.001.

Disturbance class	SOC	C:N	δ^{15}N	N$_t$	P$_{CAL}$	pH	ρ	SIR-C$_{mic}$
D0F	-0.36	-0.69	0.62	0.50	0.12	0.43	0.18	0.67
D1F	-0.30	-0.50	0.21	0.27	-0.05	0.23	0.06	0.53
D2F	-0.66	-0.89	0.83	0.03	0.60***	-0.66	0.71	0.60
D3F	-0.37	0.37	-0.31	-0.60	1.00	0.09	-0.66	0.03
D4F	-0.06	-0.53	0.29	0.37	0.25	-0.05	-0.49	0.66
D0B	0.60	-0.60	0.20	0.60	-0.40	0.60	-0.21	-0.60
D1B	-0.20	-0.40	-1.00***	0.20	0.40	0.80	0.20	0.80
D2B	-0.09	-0.26	0.26	0.26	0.89	0.43	-0.26	0.83

Appendix B

How do sand addition, soil moisture and nutrient status influence greenhouse gas fluxes from drained organic soils?

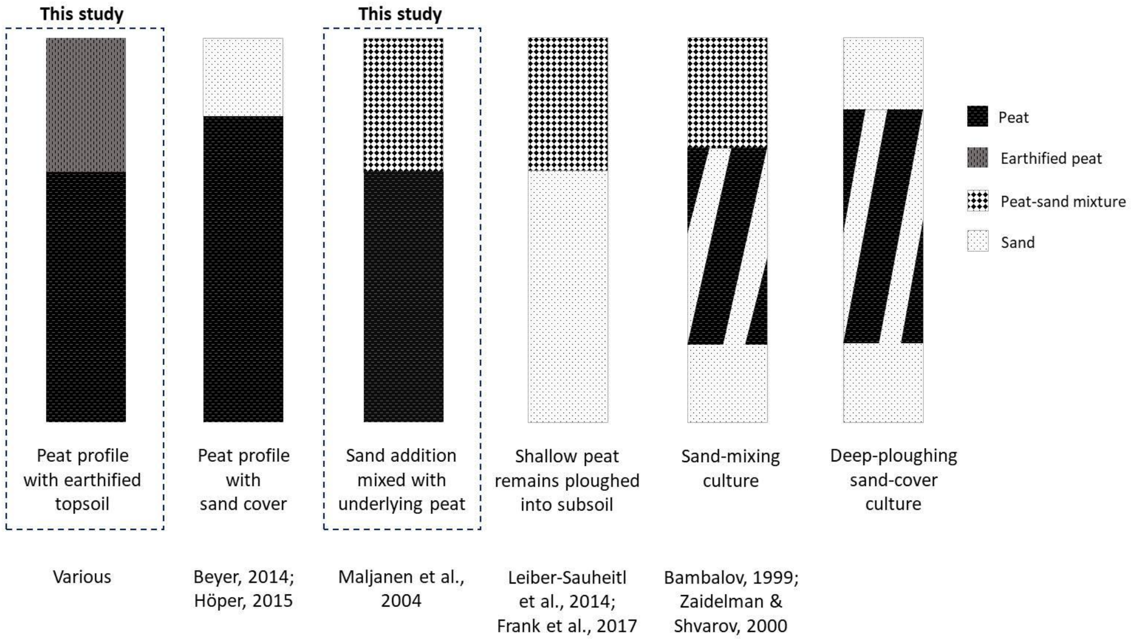

Figure S3: Anthropogenically modified peat profiles (schematic) and corresponding field studies.

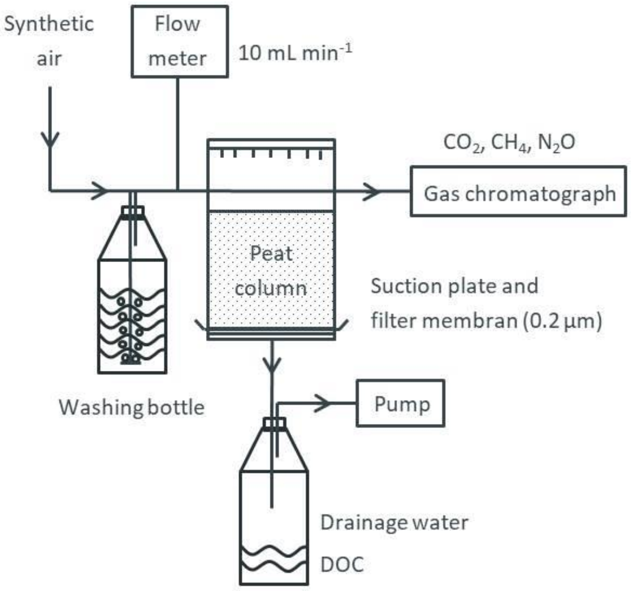

Figure S4: Schematic diagram of the microcosm system

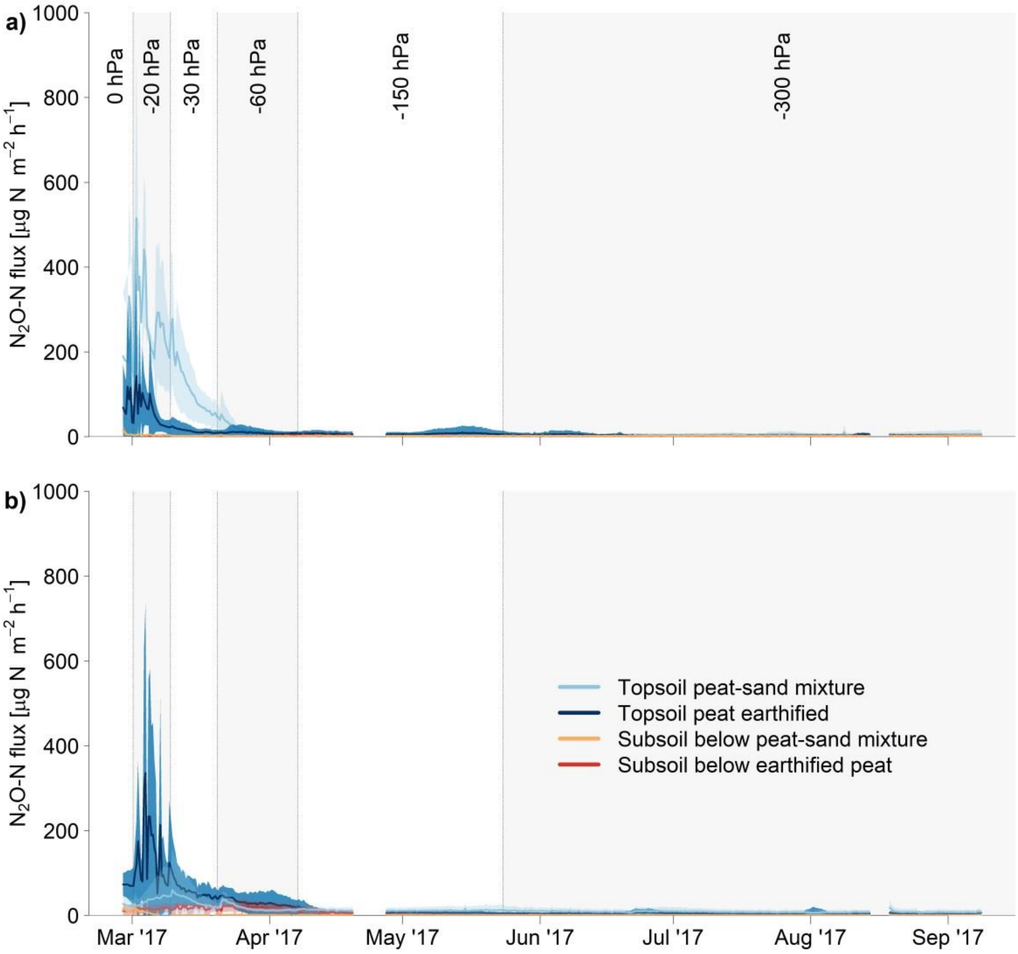

Figure S5: N_2O-N fluxes (mean values and standard deviations) over the course of the experiment and suction steps for (a) fen peat and (b) bog peat.

Table S5: Sampling sites divided into topsoil (top) and subsoil (sub) and their soil properties (mean ± standard error) of soil organic carbon (SOC) content, SOC density, total nitrogen (N_t) density, C:N ratio, bulk density (ρ), pH value, calcium acetate lactate extractable phosphorus (P_{CAL}) density, calcium acetate lactate extractable potassium (K_{CAL}) density, sand, clay contents and depth of lower end of the soil column. Latitude and longitude are given in decimal degrees for the WGS84

		SOC (g kg^{-1})	SOC (mg cm^{-3})	N_t (mg cm^{-3})	C:N (-)	ρ (g cm^{-3})	pH (-)	P_{CAL} (µg cm^{-3})	K_{CAL} (µg cm^{-3})	Sand (%)	Clay (%)	Depth (cm)	Lat (°)	Long (°)
Bog peat														
sB1	top	71 ± 2	68.4 ± 1.2	3.4 ± 0.1	20.1 ± 0.3	0.96 ± 0.04	4.4 ± 0.1	72.7 ± 4.9	47.1 ± 3.5	89.3	3.6	20	53.22	8.33
	sub	510 ± 4	72.8 ± 3.5	1.7 ± 0.2	44.5 ± 4.7	0.14 ± 0.01	4.2 ± 0.3	3.8 ± 0.9	17.0 ± 2.3	-	-	70		
sB2	top	49 ± 3	51.1 ± 1.0	4.0 ± 0.0	12.8 ± 0.4	1.05 ± 0.05	4.6 ± 0.0	120.0 ± 5.0	154.1 ± 85.3	91.0	4.4	20	53.08	7.77
	sub	547 ± 4	61.4 ± 2.3	2.2 ± 0.1	27.4± 0.2	0.11 ± 0.00	3.7 ± 0.2	2.0 ± 0.4	19.1 ± 1.3	-	-	55		
eB1	top	427 ± 13	99.0 ± 8.1	5.2 ± 1.1	19.9 ± 2.2	0.23 ± 0.03	4.8 ± 0.1	45.6 ± 9.4	80.0 ± 18.1	-	-	20	53.21	8.31
	sub	496 ± 2	31.4 ± 2.3	0.4 ± 0.0	88.4 ± 5.0	0.06 ± 0.00	3.5 ± 0.1	0.5 ± 0.0	3.2 ± 0.1	-	-	95		
eB2	top	410 ± 11	131.7 ± 3.1	8.2 ± 0.5	16.1 ± 0.7	0.32 ± 0.01	4.2 ± 0.1	80.5 ± 6.2	81.5 ± 5.7	-	-	15	53.06	7.77
	sub	536 ± 3	80.2 ± 2.9	2.0 ± 0.1	40.5 ± 0.7	0.15 ± 0.00	3.6 ± 0.0	2.2 ± 0.1	6.1 ± 0.5	-	-	25		
Fen peat														
sF1	top	160 ± 11	102.0 ± 1.4	9.3 ± 0.2	11.0 ± 0.1	0.64 ± 0.04	4.9 ± 0.0	27.5 ± 1.7	99.7 ± 53.2	81.2	11.3	15	53.63	12.09
	sub	493 ± 4	76.6 ± 4.8	4.2 ± 0.3	18.2 ± 0.3	0.16 ± 0.01	4.2 ± 0.3	4.6 ± 1.0	2.2 ± 0.2	-	-	105		
sF2	top	170 ± 11	95.7 ± 3.9	7.1 ± 0.1	13.4 ± 0.3	0.57 ± 0.04	4.2 ± 0.0	84.0 ± 5.9	161.8 ± 7.1	71.2	10.8	15	53.22	8.83
	sub	542 ± 5	64.1 ± 2.6	1.4 ± 0.1	47.9 ± 3.9	0.12 ± 0.00	3.5 ± 0.0	1.4 ± 0.1	6.2 ± 0.2	-	-	80		
sF3	top	214 ± 5	111.5 ± 1.4	9.8 ± 0.1	11.4 ± 0.1	0.52 ± 0.01	5.8 ± 0.0	28.9 ± 3.7	33.8 ± 2.5	66.1	12.6	15	53.73	14.16
	sub	470 ± 2	83.4 ± 2.2	4.6 ± 0.1	18.3 ± 0.0	0.18 ± 0.01	4.4 ± 0.1	0.4 ± 0.0	3.4 ± 0.3	-	-	90		
eF1	top	456 ± 6	168.2 ± 0.7	12.2 ± 0.1	13.7 ± 0.1	0.37 ± 0.00	5.5 ± 0.1	43.6 ± 1.6	32.1 ± 1.7	-	-	25	53.67	13.79
	sub	493 ± 4	61.0 ± 0.7	2.2 ± 0.0	27.4 ± 0.4	0.12 ± 0.00	4.1 ± 0.1	0.3 ± 0.0	2.3 ± 0.1	-	-	140		
eF2	top	267 ± 26	92.6 ± 5.2	8.0 ± 0.4	11.5 ± 0.1	0.35 ± 0.02	5.5 ± 0.1	25.0 ± 1.3	40.5 ± 1.6	-	-	20	53.58	11.34
	sub	534 ± 5	56.6 ± 2.0	2.4 ± 0.1	23.9 ± 0.5	0.11 ± 0.00	5.6 ± 0.0	0.3 ± 0.1	2.4 ± 0.3	-	-	90		
eF3	top	404 ± 5	111.7 ± 1.8	9.9 ± 0.2	11.2 ± 0.1	0.28 ± 0.00	5.5 ± 0.0	21.4 ± 1.5	32.1 ± 0.9	-	-	15	53.74	13.44
	sub	509 ± 2	66.7 ± 1.1	4.0 ± 0.1	16.6 ± 0.4	0.13 ± 0.00	5.7 ± 0.0	1.2 ± 0.1	1.3 ± 0.1	-	-	90		

Table S6: Maximum CO_2-C and N_2O-N (mean ± standard error) fluxes with the respective water filled pore space (WFPS, mean ± standard error) at the occurrence of maximum fluxes and ratio of maximum CO_2-C fluxes and CO_2-C fluxes under water saturation (start). Sample identifiers: s – peat-sand mixture in the topsoil, e – earthified peat in the topsoil, B – bog, F – fen.

		Max. CO_2-C (mg C m^{-2} h^{-1})	**WFPS (-)**	**Max. N_2O-N (µg N m^{-2} h^{-1})**	**WFPS (-)**	**Ratio of max. CO_2-C to start CO_2-C (-)**
Bog peat						
top	sB1	35.1 ± 0.6	0.80 ± 0.01	58.2 ± 6.3	0.87 ± 0.01	2.8 ± 0.2
	sB2	43.5 ± 1.3	0.73 ± 0.02	18.5 ± 3.9	0.83 ± 0.02	1.8 ± 0.2
	eB1	66.9 ± 6.2	0.83 ± 0.04	52.7 ± 4.8	0.87 ± 0.04	1.4 ± 0.2
	eB2	77.3 ± 1.4	0.82 ± 0.03	187.2 ± 30.1	0.90 ± 0.02	1.7 ± 0.1
sub	sB1	9.4 ± 1.7	0.86 ± 0.02	7.7 ± 1.7	0.95 ± 0.01	1.8 ± 0.5
	sB2	11.9 ± 0.6	0.89 ± 0.02	12.5 ± 12.5	0.95 ± 0.01	3.3 ± 0.3
	eB1	3.8 ± 0.1	0.56 ± 0.06	7.1 ± 1.1	0.85 ± 0.02	1.3 ± 0.1
	eB2	2.7 ± 0.1	0.89 ± 0.02	23.8 ± 2.1	0.95 ± 0.00	1.4 ± 0.1
Fen peat						
top	sF1	37.6 ± 3.9	0.82 ± 0.01	107 ± 9.2	0.78 ± 0.01	1.6 ± 0.4
	sF2	65.6 ± 3.8	0.84 ± 0.02	234.9 ± 20.8	0.84 ± 0.02	1.3 ± 0.1
	sF3	21.4 ± 0.4	0.91 ± 0.00	105.0 ± 10.1	0.93 ± 0.00	2.0 ± 0.2
	eF1	30.0 ± 0.6	0.91 ± 0.02	51.8 ± 3.6	0.91 ± 0.02	2.5 ± 0.1
	eF2	42.6 ± 2.7	0.86 ± 0.02	49.3 ± 11.5	0.91 ± 0.02	1.5 ± 0.1
	eF3	33.3 ± 1.0	0.88 ± 0.01	134.9 ± 28.7	0.95 ± 0.01	1.7 ± 0.1
sub	sF1	14.0 ± 2.0	0.55 ± 0.15	3.4 ± 1.6	0.95 ± 0.01	4.2 ± 0.6
	sF2	6.5 ± 0.1	0.92 ± 0.00	3.4 ± 0.1	0.73 ± 0.11	1.3 ± 0.1
	sF3	7.4 ± 0.6	0.89 ± 0.01	4.2 ± 0.5	0.95 ± 0.01	2.7 ± 0.2
	eF1	6.1 ± 0.2	0.89 ± 0.02	0.2 ± 0.01	0.87 ± 0.02	3.8 ± 0.2
	eF2	4.0 ± 0.1	0.90 ± 0.01	0.3 ± 0.01	0.73 ± 0.08	1.1 ± 0.0
	eF3	3.5 ± 0.1	0.90 ± 0.01	1.4 ± 0.1	0.94 ± 0.01	2.3 ± 0.2

Table S7: Spearman's rank correlation coefficient (r) of maximum CO_2-C and N_2O-N fluxes and soil properties: soil organic carbon (SOC) content, SOC density, total nitrogen (N_t) density, C:N ratio, calcium acetate lactate extractable potassium (K_{CAL}) and calcium acetate lactate extractable phosphorus (P_{CAL}) density, where determined for all samples (r, n=60), topsoils only ($r_{topsoil}$, n=30) and subsoils only ($r_{subsoil}$, n=30). Asterisks indicate the level of significance (*p<0.05, **p<0.01, ***p<0.001).

	max. CO_2-C			**max. N_2O-N**		
	r	$r_{topsoil}$	$r_{subsoil}$	r	$r_{topsoil}$	$r_{subsoil}$
SOC (g kg^{-1})	-0.76***	0.04	-0.12	-0.68***	0.08	0.17
SOC (mg cm^{-3})	0.57***	0.11	0.20	0.72***	0.31	0.35
N_t	0.63***	-0.50**	0.27	0.66***	0.22	-0.27
C:N	-0.63***	0.45*	-0.15	-0.64***	-0.25	0.35
K_{CAL}	0.87***	0.66***	0.27	0.80***	0.1	0.46*
P_{CAL}	0.85***	0.49**	0.31	0.73***	-0.24	0.29

Appendix C

Substrate quality of drained organic soils – Implications for carbon dioxide fluxes

Table S8 Sampling sites divided into topsoil (top) and subsoil (sub), and their $F^{14}C$ signatures, calibrated ages in years before 2020 (mean ± 1σ) and the composition of the 95.4% probability range of the calibrated ages using the OxCal tool (*Ramsey*, 2009). Sample identifiers: s – peat-sand mixture in the topsoil, e – earthified peat in the topsoil, B – bog, F – fen.

Sample	**Depth**	**$F^{14}C$ [-]**	**Calibrated Age [a BP]**	**95.4% probability [a BP]**
Bog peat				
sB1	top	0.857 ± 0.003	1175 ± 56	1270 – 1205 (39.4%) 1191 – 1071 (56.0%)
	sub	0.7516 ± 0.003	2284 ± 63	2356 – 2300 (61.3%) 2240 – 2158 (34.2%)
sB2	top	0.9955 ± 0.003	131 ± 77	255 – 226 (29.4%) 140 – 111 (28.4%) 104 – 99 (0.7%) 74 – 34 (36.9%)
	sub	0.7474 ± 0.003	2361 ± 50	2486 – 2480 (0.5%) 2467 – 2311 (94.1%) 2222 – 2214 (0.8%)
eB1	top	0.9798 ± 0.003	154 ± 87	287 – 252 (16.8%) 229 – 165 (36.3%) 158 – 136 (9.8%) 116 – 65 (12%) 41 – present (20.6%)
	sub	0.7895 ± 0.002	1799 ± 37	1872 – 1850 (10.0%) 1843 – 1737 (85.4%)
eB2	top	0.9695 ± 0.003	274 ± 75	425 – 392 (8.4%) 320 – 275 (63.6%) 208 – 200 (0.6%) 185 – 150 (22.8%)
	sub	0.7855 ± 0.002	1863 ± 35	1933 – 1819 (92.5%) 1809 – 1792 (2.1%) 1759 – 1750 (0.9%)
Fen peat				
sF1	top	0.9423 ± 0.003	517 ± 10	540 – 497 (95.4%)
	sub	0.4166 ± 0.002	7867 ± 49	7960 – 7781 (94.7%) 7763 – 7755 (0.7%)
sF2	top	0.9893 ± 0.003	129 ± 76	258 – 224 (26.3%) 140 – 32 (69.2%)
	sub	0.6969 ± 0.002	3038 ± 48	3149 – 3091 (13.6%) 3080 – 2958 (81.9%)
sF3	top	0.8917 ± 0.003	839 ± 47	915 – 771 (90.7%) 761 – 744 (4.8%)
	sub	0.4961 ± 0.002	6402 ± 48	6488 – 6386 (63.6%) 6377 – 6313 (31.8%)
eF1	top	0.7165 ± 0.002	2785 ± 29	2848 – 2809 (24.3%) 2794 – 2750 (71.1%)
	sub	0.3094 ± 0.001	10647 ± 46	10732 – 10575 (95.4%)
eF2	top	0.9441 ± 0.003	511 ± 11	536 – 491 (95.4%)
	sub	0.3717 ± 0.001	8820 ± 99	8985 – 8822 (49.6%) 8816 – 8689 (37.1%)

				8680 – 8646 (8.8%)
eF3	top	0.9671 ± 0.003	333 ± 68	430 – 372 (35.4%)
				327 – 283 (54.2%)
				168 – 154 (5.8%)
	sub	0.8867 ± 0.003	857 ± 40	926 – 896 (23.1%)
				890 – 793 (72.3%)

Selbstständigkeitserklärung

Ich erkläre, dass ich die hier vorgelegte Arbeit selbständig und ohne fremde Hilfe verfasst, andere als die von mir angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Mainz, August 2021 Annelie Säurich