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REGULAR ARTICLE

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.

KEYWORDS
bog, fen, fibre analysis, mineralisation, NMR, peat, radiocarbon age

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 & 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, Tiemeyer, Dettmann et al., 2019). 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., 2016; Reiche et al., 2010), with phosphorus (P) potentially playing a decisive role (Brake et al., 1999; Säurich, Tiemeyer, Dettmann et al., 2019).

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 & 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 microorganisms 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 mineralization, peat soils undergo secondary pedogenetic processes (Heller & Zeitz, 2012; Ilnicki & Zeitz, 2002). 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 & Bárta, 2016). 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, Tiemeyer, Don et al., 2019) 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 & 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 & 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 & 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 & Radu, 2018; Heller & 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 for 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, Tiemeyer, Dettmann et al., 2019).

2 | MATERIALS AND METHODS

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 1). At each site the soil profile was classified according to the German manual of soil mapping (Ad-Hoc-AG 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 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, Tiemeyer, Dettmann et al., 2019 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 6 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, Tiemeyer, Dettmann, et al., 2019). 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.

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 and N-alkyl C, 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 1h 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

TABLE 1 Sampling sites divided into topsoil (top) and subsoil (sub) with according depths of the 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

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

Note: The degree of decomposition, on the von Post scale (H), was determined according to Ad-Hoc-AG 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.

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 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.

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 van 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).

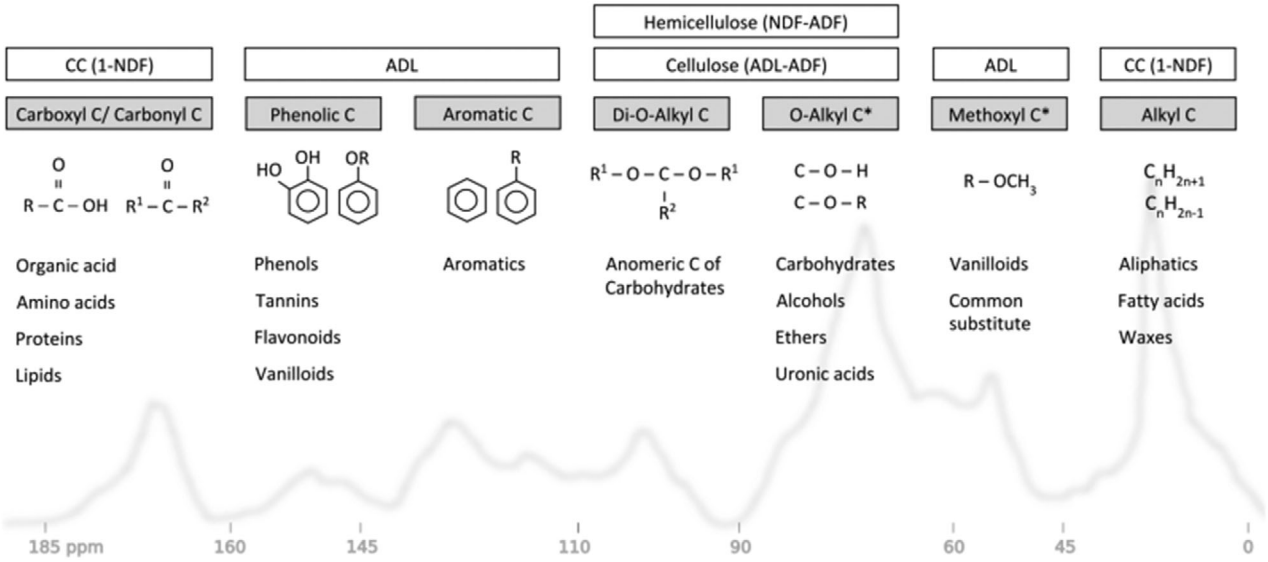

FIGURE 1 Simplified schematic overview of chemical C fractions determined on neutral detergent fibre (NDF), acid detergent fibre (ADF), acid detergent lignin (ADL), cell components (CC) and chemical shift regions of the ^{13}C MAS NMR (grey boxes) with representatives of the main compounds and functional 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

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 Supplementary Table S1.

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 & 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 10 subsoil samples only [Equation (1)]. This relationship is used to derive a theoretical difference in aromatics between topsoils and subsoils depending on their difference in age.

$$Aromatic\ \ (\%\ of\ SOC) = 0.0005 \times age\ (a) + 152. \quad (1)$$

3 | RESULTS

3.1 | Chemical composition of peat substrate

The PCA based on NMR products, fibre analyses, ^{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 (Figure 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 were similar 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

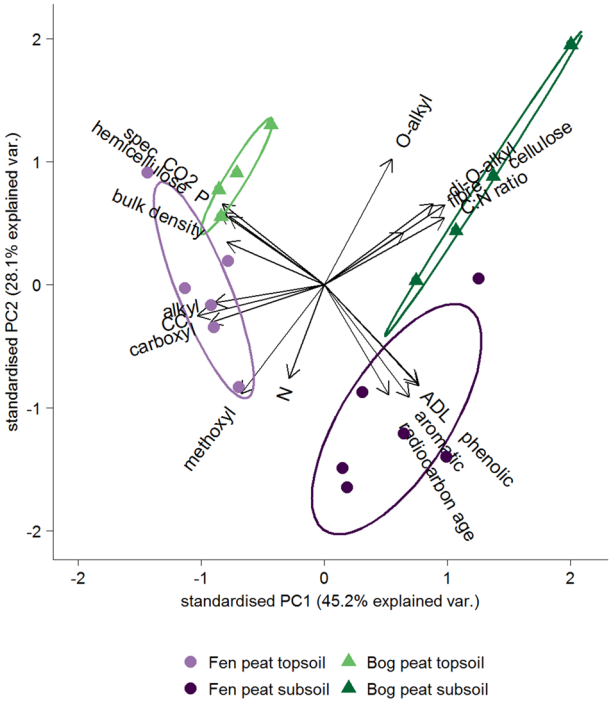

FIGURE 2 PCA biplot based on NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl), fibre analyses products [hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC), fibre], nitrogen (N) content, C:N ratio, bulk density, phosphorus (P) content, radiocarbon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

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 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 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 (49–56%) of the NMR products together, followed by aromatics (Figure 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) (Figure 3B).

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 (Figure 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 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 (Figure 3D).

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).

3.2 | Peat quality and mineralisation rates

Topsoil samples had nine times higher specific CO_2 fluxes on average than subsoil samples (Table 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 (Figure 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 significant 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.

3.3 | Radiocarbon analysis

Radiocarbon dating showed that topsoil samples were always younger than subsoil samples (Figure 5A). The age range of topsoils (100–2800 years) was smaller than in the subsoil samples (850–

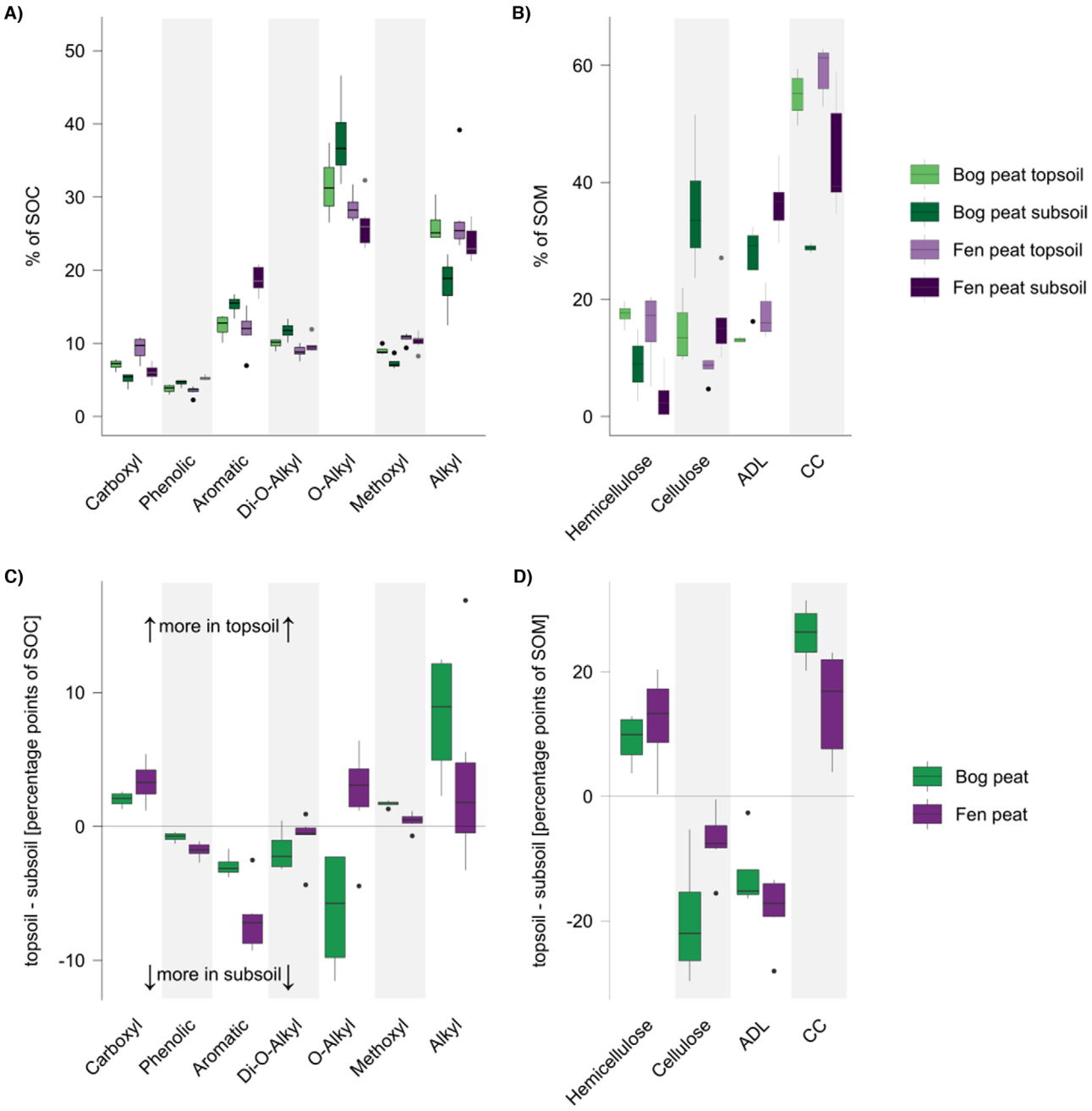

FIGURE 3 (A) NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl) and (B) fibre analysis products [hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC)] of the grouped samples. (C) Respective differences between topsoil and subsoil of fen and bog peat 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

10,700 years). 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 (Figure 5B).

Significant correlations between chemical compounds and carbon age were detected for aromatics, phenolics, hemicellulose and ADL (Figure 4). The strongest correlation was found for aromatics (Figure 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 if the differences were only induced by aging, that is, anoxic

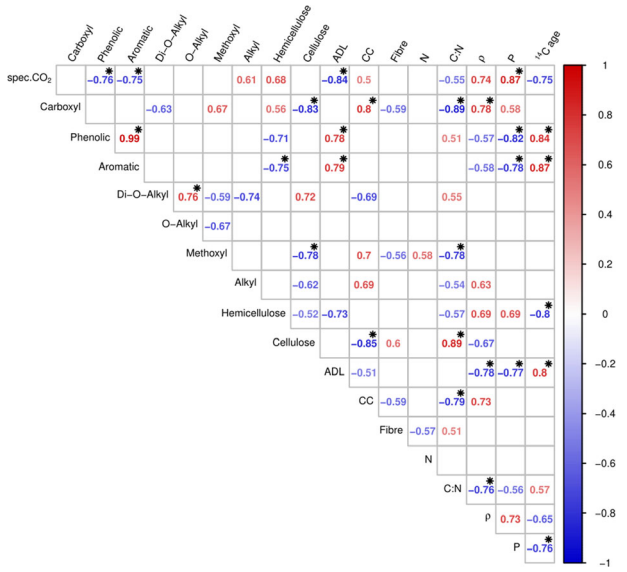

FIGURE 4 Correlation coefficients after Spearman ($r \geq 0.5$) for specific CO_2 fluxes, NMR products (carboxyl, phenolic, aromatic, di-O-alkyl, O-alkyl, methoxyl, alkyl), fibre analyses products [hemicellulose, cellulose, acid detergent lignin (ADL), cell components (CC), fibre], nitrogen (N) content, C:N ratio, bulk density (ρ), phosphorus (P) content and radiocarbon (^{14}C) age. Significant correlations ($p < 0.05$) are marked with asterisks

decomposition (Figure 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 topsoils was lower than expected from differences in age alone.

4 | DISCUSSION

4.1 | Chemical composition of peat substrate

4.1.1 | 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 & Zeitz, 2002), 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) (Figure 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 and underwent stronger microbial transformation than the drained peat at the 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. The 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 1). Furthermore, the samples from the fen peat subsoil came from greater depths 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 & Liefveld, 1997) that are identified as O-alkyls. This might also explain the high share of these compounds (Figure 3A).

Given that SOC contents in the subsoils are always higher than in the topsoils (Table 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 4.2). 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 & Schmidt, 2007). Due to access to oxygen in the topsoil peat layer, numerous enzymes, for example 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; Figure 1) and the decrease in phenolics in the topsoil compared with the subsoil samples (Figure 3).

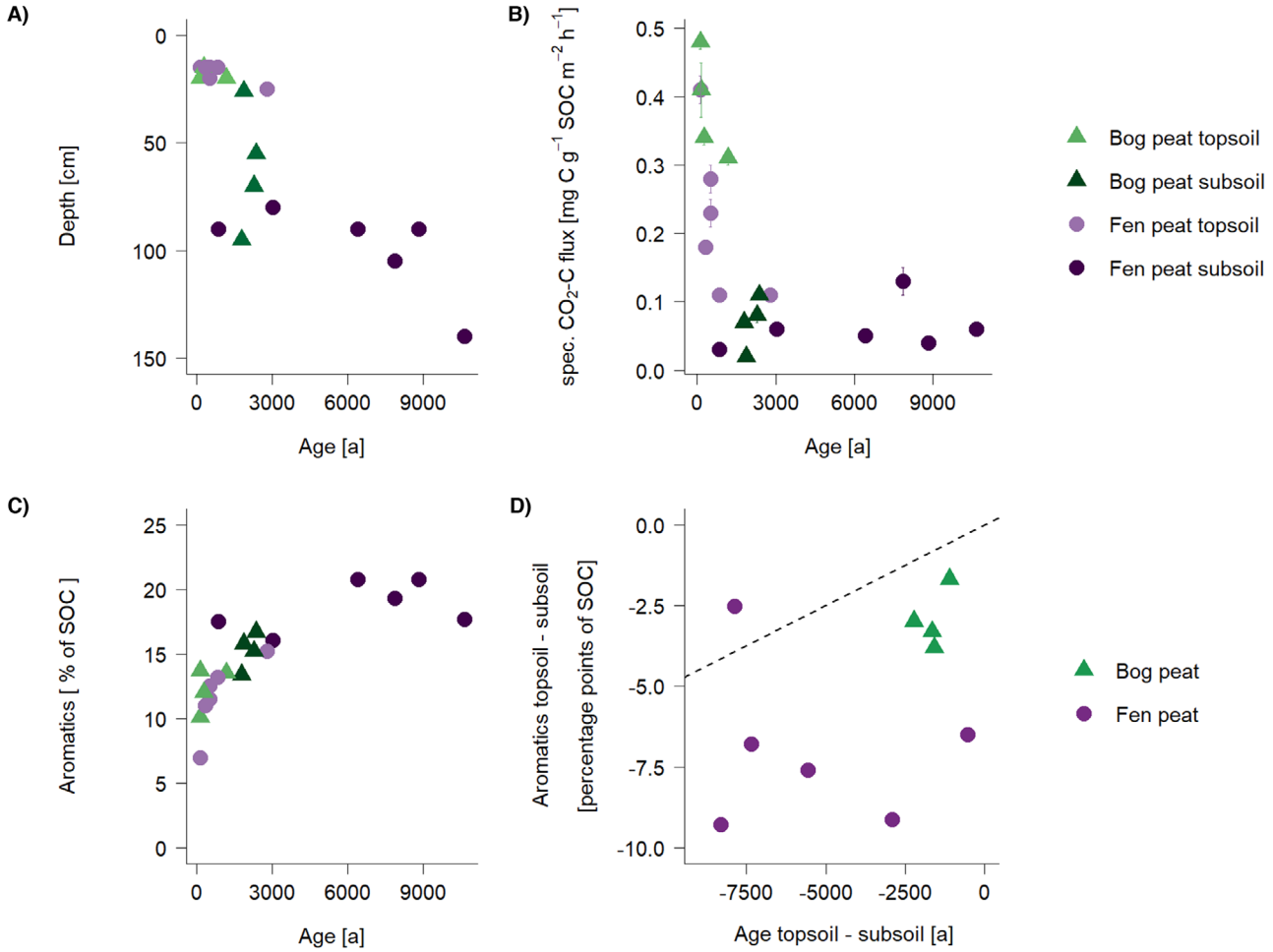

FIGURE 5 Radiocarbon age versus (A) depth of the soil samples, (B) specific CO_2 fluxes including standard errors and (C) content of aromatics identified by NMR. Standard deviations of ^{14}C dating are too small to be visible on this scale. (D) Differences between radiocarbon age and aromatic content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

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 (Figures 2 and 3) since hemicellulose mainly consists of carbohydrates (Figure 1). Furthermore, the decomposition rates of these compounds should follow the order cellulose > hemicellulose > ADL (Reddy & DeLaune, 2008). Thus, this divergence was probably caused by uncertainties in this analytical method (see Section 4.4).

4.1.2 | 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 (Figure 3). Due to drainage and agricultural use, the microbial community and biogeochemical conditions of fens and bogs converge (Urbanová & Bárta, 2016), hence, the similar chemical composition of the topsoils (Figure 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 (Figure 3). Phenolic compounds are inhibitors of hydrolase enzymes, which are major agents in the decomposition of organic matter (Dunn & 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 & 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.

4.2 | 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 (Figure 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. Assuming a subsidence rate of 1 cm y^{-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 & 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 northwest Germany during the Subatlantic about 2600 BP (Rydin & 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 (Figure 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 Figure 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 for age determination in soil science (Krüger et al., 2015; Bader et al., 2017; 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 Figure 5.

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 (Figure 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 & Bárta, 2016). 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, Tiemeyer, Don et al., 2019). 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 | Measurement methods for peat quality

As proposed in Figure 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) (Figures 2 and 4). Even though the results of ADL and shares of aromatics and phenolics fit well here, the method after Goering & van 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 (Figure 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.

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 and transformation than the reason behind increased mineralisation rates.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in OSF Home at https://doi.org/10.17605/OSF.IO/CAERD.

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SUPPORTING INFORMATION

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

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