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Clay fraction properties and grassland management imprint on soil organic matter composition and stability at molecular level

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Abstract

The dynamics of soil carbon in grassland are partly determined by soil organic matter (SOM) composition. However, it remains unclear which role grassland management plays in the interplay between SOM composition and carbon dynamics. Using pyrolysis-field ionization mass spectrometry (Py-FIMS), we studied the effect of meadow, mown pasture and pasture on the molecular SOM composition in German topsoils. In sandy soils of the Schorfheide-Chorin region, SOM composition and stability were strongly affected by clay contents and concentrations of crystalline Fe-oxides. Here, the grassland management type influenced lipid proportions, which accounted for a maximum of 11.1% of the total ion intensity (TII) under mown pasture. In the Hainich-Dün region, SOM composition was mainly related to the SOM decomposition stage (abundance of potentially recalcitrant compounds) but not to minerals. Compound classes of carbohydrates (4.3% TII), phenols and lignin monomers (8.5% TII), N-containing compounds (2.2% TII) and peptides (4.6% TII) were highest under meadow, while compound classes of lignin dimers (3.4% TII) and lipids (8.1% TII) were highest under pasture. In the Schwäbische Alb region, the proportion of free fatty acids (1.6 to 2.3% TII) was positively related to the C/N ratio ($r = 0.86$); SOM stability was positively affected by poorly crystalline Fe-oxide content ($r = 0.85$). The results suggest that grassland management is affecting SOM composition and stability and thus influence SOM dynamics in grasslands. However, the proportion and composition (Fe-oxide content) of the soil clay fraction overrode grassland management effects if soil clay/OC ratios were <10.

KEYWORDS
clay, decomposability, grassland, grassland management, Py-FIMS, soil organic matter

1 | INTRODUCTION

Covering about 40% of the total land area and storing 579 Pg carbon (C) in their soils, grasslands play a significant role in the global biogeochemical C cycle (White et al., 2000). The dynamics of soil organic matter (SOM) in grassland soils is a key factor in the network of above- and belowground parameters, eventually determining biodiversity, food security and climate change (Huguenin-Elie et al., 2018; Lal, 2004; Rumpel et al., 2015). SOM dynamics includes accumulation and decomposition of organic matter (OM) in soil, whereby not only the recalcitrance of the OM but also mainly physicochemical and biological properties from the surrounding environment such as organo-mineral associations, and the prevailing microbial community was recognized to affect SOM (Baldock & Skjemstad, 2000; Schmidt et al., 2011). Also, human interventions can influence SOM dynamics in grassland soils by plant species choice, management system (mowing vs. grazing) and type of fertilization (Rumpel et al., 2015). In experimental soils that received no organic amendments but the residues of mown grass, the composition and stability of SOM were determined largely by the reactive surfaces of size fractions such as clay and silt (Leinweber & Schulten, 1993). So far, however, the effects of different clay contents and composition of the clay fraction along with grassland management types on SOM composition and stability in soilscapes differing in the geological background and soil textures have not been investigated and the importance of the different mechanisms in interplay is unknown.

The content of the clay fraction in the bulk soil, and its composition, which includes layer silicates, sesquioxides and small pieces of primary minerals (Sarkar et al., 2018), can influence SOM decomposition and, thus, the SOM dynamics (Singh et al., 2019). The formation of organo-mineral complexes which may protect SOM from decomposition thereby depends on the mineralogical composition of the soil and the molecular structure of the organic matter that enters the soil (Schulten & Leinweber, 2000). This could lead to preferential accumulation of certain compound classes, which in turn characterize the composition and stability of bulk SOM. For instance, Schulten et al. (1996) reported that highly aliphatic SOM was associated with external and interlayer surfaces of a swelling clay from New Zealand. Furthermore, selective extractions followed by mass-spectrometric analyses indicated preferences in the binding of certain compound classes by pedogenic oxides in soil (Schulten & Leinweber, 1995). Along this line of evidence, Chen et al. (2018) suggested that in clay-associated SOM, the stability of potentially recalcitrant compounds (e.g. lignins) was strongly determined by their high affinity for oxides and aluminosilicates while the abundance of potentially labile compounds (e.g. carbohydrates) was more strongly affected by changes in environmental conditions such as soil pH. From this, it may be expected that not only characteristics of the clay fraction of a region but also the land use or management practices will imprint on SOM composition and stability and thus on SOM dynamics.

Grassland management can affect SOM dynamics by mowing, grazing intensity and the use of fertilizers (Rumpel et al., 2015). For example, Sanaullah et al. (2010) reported that mowing or grazing affected the chemical composition of SOM not only by different proportions of fresh and senescent litter returned to the soil but also by differences in litter composition. While fresh green litter (predominantly accruing at mowing) was characterized by, e.g. a high nitrogen (N) content, senescent litter (predominantly accruing at grazing) had a high lignin content, which resulted in a higher degradation rate of fresh compared with senescent litter (Sanaullah et al., 2010). Grazing removes mainly fresh litter and results in a higher and more diverse OM input (due to senescent plant and grazing animal deposition input) compared with mowing when no additional organic manure is applied (only plant input) (Gilmullina et al., 2020). The effect of grazing intensity on soil organic C storage was shown to be climate-dependent (Abdallah et al., 2018), but differences in SOM composition due to grazing intensity were not detected using ^{13}C nuclear magnetic resonance (NMR) spectroscopy in a fencing experiment, which regulated grazing intensity (Steffens et al., 2011). Fertilizer application, particularly N, could improve the quantity and quality of grassland production by altering the C/N/P ratio of plants and affecting plant communities (Li et al., 2014; Vargová et al., 2020). This could lead to altered above- and belowground OM inputs into the soil and can affect decomposer communities, which could influence SOM composition and stability and thus SOM dynamics (Malhi et al., 2005; Rumpel et al., 2015). However, the effects of typical grassland management on SOM composition and stability within restricted study areas of diverse geological backgrounds have not yet been investigated.

To study the effect of clay content and management type on grassland SOM composition and stability, pyrolysis-field ionization mass spectrometry (Py-FIMS) may be used (Schulten et al., 1996; Schulten & Leinweber, 1999). This method is a powerful technique to simultaneously determine different molecular compound classes and to identify their stability (Leinweber et al., 2009). It fingerprints the ion intensities of molecules thermally released from complex biomaterials and reveals the stability (thermal resistance) of chemical bonds within molecules or between organic molecules and reactive mineral surfaces, thus elucidating microbial decomposability of the

OM (Leinweber et al., 2008; Schulten & Leinweber, 1999; Wiedow et al., 2007). The method has been used before to analyze the molecular structure of grassland soils and was thereby also successful in detecting differences in SOM depending on soil depth and slope position (Chen et al., 2018; Leinweber et al., 2009).

In Germany, differently managed grassland plots (meadow, mown pasture, pasture) located within three geologically different regions are part of the 'German Biodiversity Exploratories' (Fischer et al., 2010). By analyzing soil samples of those grassland plots using Py-FIMS we aimed to disclose the effects of reactive soil surface properties and management type on SOM composition and stability at the molecular level.

We hypothesized (i) an effect of the reactive soil surfaces (clay, (non)crystalline Fe-oxide, inorganic carbon (IC) content), which stabilize SOM or fractions of it. With increasing reactive soil surfaces, we expected an increase in the soil organic carbon (OC) content and an increase in the proportion of degraded plant material (decrease in hexoses/pentoses ratio, increase in potentially recalcitrant compounds/OC ratio). Also, we expected an increase in compound thermostability due to an increased interaction of the compounds with mineral surfaces.

Further, we hypothesized that (ii) grassland management type (meadow, mown pasture, pasture) affects SOM composition and stability by providing different precursor compounds to the SOM originating from fresh litter, senescent litter, animal deposition and organic fertilizer, respectively. In detail, we expected the highest proportion of easily degradable compounds (from fresh litter; e.g. carbohydrates) to decrease in the order meadow > mown pasture > pasture while potentially recalcitrant compounds (from more senescent litter, animal excrements and organic fertilizer; e.g. phenols, lignins) were expected to increase in that order. The total thermostability of a sample was expected to increase in the order meadow < mown pasture < pasture.

2 | MATERIALS AND METHODS

2.1 | Study areas, grassland management types and sample collection

The three study areas Schorfheide-Chorin (North-East Germany), Hainich-Dün (mid Germany) and Schwäbische Alb (South-West Germany) are part of the German Biodiversity Exploratories (Fischer et al., 2010). In the following, they are referred to as Schorfheide, Hainich and Alb, respectively. The regions are characterized by mean annual temperatures of 8 to 8.5°C and mean annual precipitations of 500 to 600 mm (Schorfheide), 6.5 to 7.5°C and 750 to 800 mm (Hainich) and 6 to 7°C and 700 to 1000 mm (Alb; Fischer et al., 2010). Combinations of geology and major soil units are glacial sand and till with Luvisols (Schorfheide), limestone with Stagnosols and Cambisols in Hainich, and calcareous bedrock with Leptosols in Alb. The mineralogical composition of soil clay fractions in Germany is dominated by 2:1 layer silicates (mainly illite and illitic mixed-layer minerals), contains only a small proportion of 1:1 minerals (mainly kaolinite) and variable contents of pedogenic oxides (Ito & Wagai, 2017; Six et al., 2002; Wäldchen et al., 2012). The grassland plots from which soil samples were taken had been managed as grasslands for at least 15 years and differed in management type (Fischer et al., 2010; Vogt et al., 2019). They were either mown for hay or silage production, grazed by livestock or both and were either unfertilized or fertilized to varying degrees as stated by the land owners (Vogt et al., 2019; Table 1). Based on this information for the years 2006 to 2010, the predominant grassland management type was either meadow (M), mown pasture (MP) or pasture (P). In Schorfheide, MP plots were fertilized, while M and P plots remained mainly unfertilized. In Hainich and Alb, M plots received most fertilizer and P plots remained mainly unfertilized. Plant species richness depended on region and grassland management type (Socher et al., 2012, 2013).

Mineral topsoil samples used for detailed chemical analyses were collected during the coordinated soil sampling campaign of the Biodiversity Exploratories in May 2011. In each of the plots, 14 soil samples were taken from the upper 10 cm of the soil using a 4.8 cm (diameter) auger sampler. Mineral soil was then mixed, sieved to <2 mm and air-dried to obtain one composite soil sample per plot. For total element content and Py-FIMS analyses, the soil was finely ground using a ball mill. Analyses of the present study were performed on mineral soil samples from nine grassland plots of the exploratories Schorfheide and Alb, and 15 grassland plots of Hainich.

2.2 | Basic soil properties

Soil texture was determined by sieving and sedimentation and the soil pH was measured in 0.01 M $CaCl_2$ (1:2.5 w:v) after Blume et al. (2010).

Pedogenic oxides were extracted by oxalate after Schwertmann (1964) and by dithionite-citrate-bicarbonate (DCB) after Mehra and Jackson (1960) before the concentration of Fe was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 3300 DV, Perkin-Elmer, Norwalk, CT, USA). Since these chemical methods could not be expected to perfectly distinguish

TABLE 1 Management of grassland plots in the regions Schorfheide, Hainich and Alb (means and standard deviations integrating the years 2006 to 2010); LSU= livestock unit; '–' = no grazing animals, M = meadow, MP = mown pasture, P = pasture; based on Vogt et al. (2019)

Region	Plot ID	Location		Mowing (times year^{-1})	Grazing animals	Grazing intensity (LSU d^{-1} ha^{-1} year^{-1})	Total N fertilization (kg N ha^{-1} year^{-1})	Predominant management type 2006–2010
		lat (N)	long (E)					
Schorfheide	SEG18	53°8′	13°52′	1.8 ± 0.4	–	0 ± 0	0 ± 0	M
	SEG31	53°8′	13°50′	1.6 ± 0.5	–	0 ± 0	0 ± 0	M
	SEG32	53°9′	13°49′	1.6 ± 0.5	–	0 ± 0	0 ± 0	M
	SEG33	52°59′	13°50′	0.6 ± 0.5	Cattle	247 ± 88	26 ± 37	MP
	SEG34	52°58′	13°50′	0.8 ± 0.4	Cattle	125 ± 39	71 ± 49	MP
	SEG35	52°58′	13°50′	1.0 ± 0.0	Cattle	97 ± 47	71 ± 49	MP
	SEG42	52°52′	13°58′	0.0 ± 0.0	Cattle	788 ± 185	8 ± 18	P
	SEG47	52°59′	13°49′	0.2 ± 0.4	Cattle	257 ± 193	0 ± 0	P
	SEG48	52°5′	13°36′	0.2 ± 0.4	Cattle	324 ± 209	0 ± 0	P
Hainich	HEG1	50°58′	10°24′	2.4 ± 0.5	Sheep	19 ± 26	160 ± 57	M
	HEG2	51°0′	10°24′	3.0 ± 0.0	Sheep	13 ± 18	122 ± 42	M
	HEG3	50°59′	10°25′	3.0 ± 0.0	Sheep	13 ± 18	122 ± 42	M
	HEG4	51°6′	10°26′	1.2 ± 0.4	Cattle	145 ± 30	54 ± 38	MP
	HEG5	51°12′	10°19′	2.2 ± 0.4	Cattle	97 ± 40	86 ± 22	MP
	HEG6	51°12′	10°23′	1.0 ± 0.0	Cattle	46 ± 40	108 ± 20	MP
	HEG7	51°16′	10°24′	0.0 ± 0.0	Cattle	304 ± 162	17 ± 38	P
	HEG8	51°16′	10°25′	0.0 ± 0.0	Cattle	282 ± 171	17 ± 38	P
	HEG9	51°13′	10°22′	0.0 ± 0.0	Cattle	69 ± 8	0 ± 0	P
	HEG13	51°15′	10°22′	2.6 ± 0.5	Cattle	56 ± 21	0 ± 0	MP
	HEG26	51°16′	10°22′	1.2 ± 0.4	–	0 ± 0	17 ± 38	M
	HEG27	51°5′	10°35′	1.0 ± 0.0	–	0 ± 0	60 ± 1	M
	HEG30	51°12′	10°21′	2.8 ± 0.4	Cattle	9 ± 21	76 ± 21	M
	HEG39	51°7′	10°20′	0.0 ± 0.0	Cattle	200 ± 119	0 ± 0	P
	HEG43	51°18′	10°26′	0.2 ± 0.4	Sheep	75 ± 37	0 ± 0	P

(Continues)

TABLE 1 (Continued)

Region	Plot ID	Location		Mowing (times year^{-1})	Grazing animals	Grazing intensity (LSU d^{-1} ha^{-1} year^{-1})	Total N fertilization (kg N ha^{-1} year^{-1})	Predominant management type 2006–2010
		lat (N)	long (E)					
Alb	AEG1	48°23′	9°20′	2.0 ±0.0	–	0 ±0	73 ±75	M
	AEG2	48°22′	9°28′	3.0 ±0.0	–	0 ±0	244 ±54	M
	AEG3	48°24′	9°31′	2.4 ±0.5	–	0 ±0	77 ±0	M
	AEG4	48°22′	9°25′	1.0 ±0.0	Cattle	86 ±31	38 ±7	MP
	AEG5	48°23′	9°26′	1.0 ±0.0	Cattle, horse	92 ±40	46 ±7	MP
	AEG6	48°24′	9°26′	1.0 ±0.0	Cattle, horse	421 ±266	46 ±7	MP
	AEG7	48°23′	9°22′	0.0 ±0.0	Sheep	36 ±8	0 ±0	P
	AEG8	48°25′	9°29′	0.8 ±0.4	Sheep	122 ±20	0 ±0	P
	AEG9	48°23′	9°30′	0.0 ±0.0	Sheep	46 ±23	0 ±0	P

degrees of crystallinity (Rennert, 2019), DCB-extractable Fe (Fe_{DCB}) was taken as the 'pseudo-total' content of the pedogenic oxides and oxalate-extractable Fe (Fe_{ox}) was taken as a proxy for poorly crystalline species. The difference ($_{DCB-ox}$) was then used as a proxy for the content of crystalline species.

Total C (TC) and N (TN) were analyzed by dry combustion (Vario Max, Elementar Analysensysteme GmbH, Hanau, Germany). Inorganic C (IC) was determined with the same elemental analyzer after ignition of organic C (OC) at 450°C for 16 h. Organic C concentrations were calculated as the difference between TC and IC.

2.3 | Pyrolysis-field ionization mass spectrometry (Py-FIMS)

Soil samples were analyzed in triplicate (about 2 mg each) by pyrolysis-field ionization mass spectrometry (Py-FIMS). Pyrolysis took place in the ion source (emitter: 4.7 kV, counter electrode −5.5 kV) of a double-focussing Finnigan MAT 95 mass spectrometer (Finnigan, MAT, Bremen, Germany). Within 15 min, samples were heated in a vacuum (10^{-4} Pa) from 50°C to 650°C. A magnetic scan took place at each 10 K temperature step and a mass range of 15 to 900 m/z was recorded before the emitter was flash heated to avoid residues of pyrolysis products. Volatile matter (VM) of the sample was expressed as loss of sample weight. Total ion intensity (TII) was normalized to 1 kg of the sample and was expressed in counts per kg.

Ion intensities of indicator signals (m/z) were assigned to nine classes of chemical compounds as outlined in Table 2. The relative abundance of these compound classes in the samples was expressed as % TII. The hexoses/pentoses ratio, a measure of microbial- compared with plant-derived sugars (Oades, 1984), was calculated using the m/z characteristic for hexoses (m/z 162, 163, 144, 145, 126, 127) and pentoses (m/z 132, 133, 114, 115). Total thermostability of a sample and the thermostability of each compound class were calculated by dividing the mass loss of OM at high temperature (sum of all ion intensities from 400 to 650°C) by mass loss over the whole temperature range (the sum of all ion intensities from 50 to 650°C).

2.4 | Statistical analyses

Partially least-square discriminant analysis (PLS-DA) was performed on relative ion intensities and on thermostabilities of all compound classes to identify the probability of a sample belonging to a certain exploratory (class). Note that unlike in principal component analysis (PCA),

TABLE 2 Py-FIMS compound classes with assigned biomolecules (based on Hempfling et al., 1988; Schnitzer & Schulten, 1992; Schulten & Leinweber, 1996; Leinweber et al., 2009, 2013)

Py-FIMS compound class	Assigned biomolecules
CHYDR	Carbohydrates
PHLM	Phenols, lignin monomers
LDIM	Lignin dimers
LIPIDS	Lipids, alkanes, alkenes, alkyl monoesters, sterols
ALKYL	Alkylaromatics
NCOMP	Mainly heterocyclic N-containing compounds
PEPTI	Peptides
SUBER	Suberin
FATTY	Free fatty acids C_{16}-C_{34}

PLS-DA maximizes the separation between predefined classes, rather than explaining the variations within a data set (Wong et al., 2013). Heteroscedastic t-test was used to detect significant differences within parameters between grassland management types. Spearman's rank correlation coefficient was used to identify significant relationships between parameters derived from Py-FIMS and soil variables. All statistical analyses were performed using R software (version 3.6.1, R Development Core Team, 2019). Significant differences refer to $p \leq .05$.

3 | RESULTS

3.1 | Basic soil parameters

Soil properties varied between regions. Of all three regions, Schorfheide had the highest proportion of sand (626 g kg^{-1}), Hainich had the highest proportion of silt (494 g kg^{-1}) and Alb had the highest proportion of clay (542 g kg^{-1}) (Table 3). Clay and Fe$_{DCB\text{-}ox}$, OC and TN content significantly increased in the order Schorfheide < Hainich < Alb. Also, all further soil parameters differed between regions except for the C/N ratio. The mean clay/OC ratio was 7.0 and 7.9 in Schorfheide and Alb, while it was 10.7 in the Hainich region. Although soil properties differed between regions, soil abiotic parameters were consistent within each region (Figure S1).

Because soil parameters differed between regions, management effects were analyzed for each region separately (Table 3). In Schorfheide, none of the soil parameters was affected by grassland management. In Hainich, IC ranged between 1.80 and 4.73 g kg^{-1} and was significantly higher for meadows (M) compared with pastures (P). In Alb, oxalate-extractable Fe was higher in mown pastures (MP; 4.3 g kg^{-1}) compared with the other management types.

3.2 | Organic matter composition

Generally, SOM consisted of high proportions of ALKYL (9.04% to 11.42%TII), LIPIDS (7.53 to 10.13%TII) and PHLM compounds (6.01% to 8.48%TII; Table 4).

Organic matter composition and stability differed between regions. Comparing all regions, the hexoses/pentoses ratio was lowest in Schorfheide. The LDIM/OC ratio decreased in the order Schorfheide > Hainich > Alb (LDIM was used as a marker for less degraded lignin-derived compounds (compared with PHLM)). The thermostability was higher for SOM compounds in Hainich compared with that in the other two regions.

Also, the partial least-square discriminant analysis (PLS-DA) separated the samples by region, particularly the Hainich SOM composition, based on all relative ion intensities (Figure 1a) and thermostabilities (Figure 1c) with only a small overlap between Schorfheide and Alb samples. Compound classes (relative ion intensities) that were most influential in the separation of the different regions were PHLM and ALKYL, which were highest in Hainich, and LIPIDS and FATTY, which were high in Schorfheide and Alb samples (1c). Mainly the thermostability of SUBER and LIPIDS compounds, which were highest in Hainich samples, were most influential for separation in terms of thermostability (1D).

Because organic matter composition and thermostability were region-specific, management effects were analyzed for each region separately. In the Schorfheide region, the relative ion intensity of the compound class LIPIDS was significantly higher at MP (11.09% of TII) compared with M (8.72% of TII) (Table 4). The thermostability of LIPIDS (0.403) was significantly lower at MP compared with M and the hexoses/pentoses ratio (2.12) was lowest at MP compared with the other two management types (Table 4, Figure 2).

In Hainich, the relative ion intensity of the compound classes CHYDR, PHLM, NCOMP and PEPTI (4.25, 8.48, 2.22 and 4.58% of TII, respectively) were significantly higher at M compared with P, while the hexoses/pentoses ratio (2.63) was higher at P compared with the other two management types.

In Alb, the thermostability of the compound class FATTY was significantly higher at M compared with P (Table 4, Figure 2).

TABLE 3 Means of soil parameters of samples from the whole regions Schorfheide, Hainich and Alb and according to land use type; M = meadow, MP = mown pasture, P = pasture, ox = oxalate-extractable, DCB = dithionite-citrate-bicarbonate-extractable; different letters indicate significant differences within one soil parameter and different land use types within one region (a–c) or within one soil parameter between different regions (x–z), respectively; passages with significant differences are marked in bold for easy visibility

	Schorfheide				Hainich				Alb			
Soil parameter	**All**	**M**	**MP**	**P**	**All**	**M**	**MP**	**P**	**All**	**M**	**MP**	**P**
Clay (g kg^{-1})	**147x**	146a	152a	144a	**449y**	495a	404a	429a	**542z**	609a	480a	538a
Silt (g kg^{-1})	**227x**	201a	259a	221a	**494z**	453a	536a	510a	**391y**	344a	442a	388a
Sand (g kg^{-1})	**626y**	653a	589a	634a	**57x**	51a	60a	62a	**66x**	47a	78a	74a
pH ($CaCl_2$)	**5.8x**	5.8a	5.8a	6.0a	**7.0y**	7.1a	6.7a	6.9a	**6.3x**	6.5a	5.7a	6.8a
IC (g kg^{-1})	**0.1x**	0.1a	0.0a	0.3a	**3.0y**	**4.7b**	**2.1ab**	**1.8a**	**4.4xy**	1.0a	0.4a	11.6a
OC (g kg^{-1})	**20.7x**	22.5a	19.8a	19.7a	**43.5y**	41.6a	41.1a	47.5a	**71.3z**	71.9a	72.4a	69.7a
TN (g kg^{-1})	**2.0x**	2.0a	1.9a	1.9a	**4.3y**	4.2a	4.1a	4.6a	**6.9z**	7.3a	7.3a	6.1a
C/N ratio	10.7x	11.2a	10.5a	10.2a	10.2x	10.0a	10.1a	10.4a	10.4x	**9.8a**	**9.9a**	**11.5b**
Clay/OC ratio	**7.0x**	6.2a	7.6a	7.3a	**10.7y**	**12.3b**	**10.5ab**	**9.0a**	**7.9x**	8.7a	7.4a	7.7a
$Fe_{DCB\text{-}ox}$ (g kg^{-1})	**3.6x**	4.3a	3.0a	3.5a	**12.0y**	12.6a	10.9a	12.3a	**22.1z**	23.1a	23.0a	20.2a
Fe_{ox} (g kg^{-1})	**1.5x**	1.3a	1.8a	1.4a	**2.2y**	1.9a	2.6a	2.3a	**2.6y**	**2.2a**	**4.3b**	**1.4a**

3.3 | Spearman correlations

Organic matter differences between regions were mainly related to the clay/OC content. Across all regions, the clay/OC ratio was positively correlated with % TII of CHYDR, PHLM, ALKYL, NCOMP and PEPTI compounds and negatively with SUBER and FATTY compounds (Table 5). The thermostability of FATTY compounds was positively correlated with the clay/OC ratio.

Within the Schorfheide region, the relative ion intensities of CHYDR, PHLM, ALKYL, NCOMP and PEPTI compounds were positively correlated with the clay content and with the $Fe_{DCB\text{-}ox}$ content of the soils (except for CHYDR) while those of LDIM and FATTY were negatively correlated with the clay content (Table 5). Further, the relative ion intensities of SUBER and FATTY were negatively correlated with the $Fe_{DCB\text{-}ox}$ content of the soils. The thermostability of FATTY was positively correlated with clay and $Fe_{DCB\text{-}ox}$ content of the soil. The thermostability of PEPTI compounds was positively correlated with the IC content.

In Hainich, relative ion intensities of PHLM and ALKYL compound classes were negatively correlated with OC and TN, while SUBER was positively correlated with both soil parameters (Table 5).

In Alb, relative ion intensity of CHYDR was negatively correlated with OC and TN but positively with clay/OC content and FATTY compounds increased with increasing C/N ratio (Table 5). The total thermostability and the thermostability of PHLM, LDIM and ALKYL were positively correlated with oxalate-extractable Fe content.

4 | DISCUSSION

Grassland SOM composition of all three regions, Schorfheide, Hainich and Alb, was characterized by generally high relative abundances of ALKYL compounds (9% to 11% TII) followed by LIPIDS (8% to 10% TII) and PHLM compounds (6% to 8% TII; Table 4). Similarly, grassland soils from Pennsylvania, analyzed by Py-FIMS, were reported to have high abundances of ALKYL (9% to 10% TII) and PHLM compounds (9% TII), but LIPIDS abundance was low (6% to 7% TII; Chen et al., 2018). High lipid proportions in German soils may not just originate from OM input of different quality but may also be due to lower microbial activity, increased inputs of OM or fertilizer and/or differences in mineralogy compared with the US soils (Leinweber & Schulten, 1993; Sleutel et al., 2008; von Lützow et al., 2006).

The soils of the three geologically different regions varied in their reactive surfaces suggesting differences in potential C sequestration and SOM stabilization (Bailey

TABLE 4 Means of Py-FIMS parameters in mineral soil samples from whole the regions Schorfheide, Hainich and Alb and according to land use type; M = meadow, MP = mown pasture, P = pasture, VM = volatile matter, TII = total ion intensity; for abbreviations of Py-FIMS compound classes, see Table 2; different letters indicate significant differences within one Py-FIMS parameter and different land use types within one region (a–c) or within one Py-FIMS parameter between different regions (x–z), respectively; passages with significant differences are marked in bold for easy visibility

Py-FIMS parameter	**compound class**	**Schorfheide**				**Hainich**				**Alb**			
		all	**M**	**MP**	**P**	**all**	**M**	**MP**	**P**	**all**	**M**	**MP**	**P**
VM (g kg^{-1})		**86.04x**	90.22a	98.33a	69.56a	**180.20y**	195.56a	155.00a	181.93a	**456.50z**	495.89a	495.67a	377.94a
TII (counts kg^{-1})		**238.53x**	205.82a	254.04a	255.73a	**259.28x**	249.96a	256.14a	272.95a	**438.71Y**	482.80a	494.95a	338.37a
Relative ion intensity (% TII)	CHYDR	**3.08x**	3.02a	3.22a	2.98a	**3.96Y**	**4.25b**	**4.17ab**	**3.43a**	**3.20x**	2.74a	3.12a	3.72a
	PHLM	**6.15x**	6.59a	5.90a	5.96a	**8.03Y**	**8.48b**	**8.25ab**	**7.30a**	**5.90x**	5.82a	5.88a	6.01a
	LDIM	**2.65x**	2.62a	2.55a	2.78a	**3.07Y**	**2.99ab**	**2.83a**	**3.35b**	**2.54x**	2.38a	2.80a	2.44a
	LIPIDS	**9.87Y**	**8.72a**	**11.09b**	**9.79ab**	**7.79x**	**7.53a**	**7.81ab**	**8.10b**	**9.87Y**	10.13a	9.73a	9.75a
	ALKYL	**9.48x**	10.05a	9.04a	9.35a	**11.23Y**	11.42a	11.31a	10.94a	**9.88x**	10.33a	9.69a	9.61a
	NCOMP	**1.39x**	1.43a	1.35a	1.39a	**2.06Y**	**2.22b**	**2.14ab**	**1.79a**	**1.47x**	1.44a	1.48a	1.48a
	PEPTI	**3.50x**	3.58a	3.40a	3.51a	**4.37Y**	**4.58b**	**4.51ab**	**4.01a**	**3.52x**	3.39a	3.49a	3.69a
	SUBER	**0.28z**	0.24a	0.32a	0.28a	**0.12x**	0.09a	0.12a	0.14a	**0.18Y**	0.20a	0.20a	0.15a
	FATTY	**2.55z**	2.29a	2.90a	2.46a	**0.66x**	0.56a	0.71a	0.74a	**1.81Y**	1.58a	1.61a	2.25a
Thermostability	total	**0.483x**	0.491a	0.455a	0.501a	**0.669Y**	0.680a	0.654a	0.668a	**0.498x**	0.507a	0.544a	0.444a
	CHYDR	**0.176x**	0.171a	0.167a	0.188a	**0.295Y**	0.316a	0.279a	0.282a	**0.175x**	0.198a	0.190a	0.138a
	PHLM	**0.363x**	0.358a	0.364a	0.366a	**0.557Y**	0.581a	0.543a	0.541a	**0.392x**	0.401a	0.438a	0.336a
	LDIM	**0.769x**	0.769a	0.753a	0.785a	**0.912Y**	0.916a	0.906a	0.913a	**0.769x**	0.766a	0.817a	0.725a
	LIPIDS	**0.447x**	**0.478b**	**0.403a**	**0.460ab**	**0.675Y**	0.688a	0.673a	0.662a	**0.459x**	0.467a	0.499a	0.411a
	ALKYL	**0.524x**	0.520a	0.513a	0.540a	**0.701Y**	0.714a	0.694a	0.691a	**0.557x**	0.559a	0.606a	0.507a
	NCOMP	**0.314x**	0.299a	0.310a	0.332a	**0.476Y**	0.503a	0.462a	0.453a	**0.297x**	0.313a	0.320a	0.258a
	PEPTI	**0.300x**	0.304a	0.281a	0.314a	**0.446Y**	0.456a	0.424a	0.452a	**0.311x**	0.327a	0.348a	0.257a
	SUBER	**0.511x**	0.501a	0.497a	0.537a	**0.707Y**	0.741a	0.681a	0.688a	**0.437x**	0.443a	0.455a	0.414a
	FATTY	**0.005x**	0.006a	0.005a	0.006a	**0.022z**	0.025a	0.020a	0.019a	**0.009Y**	**0.010b**	**0.010ab**	**0.006a**
Hexoses/pentoses ratio		**2.26x**	**2.35b**	**2.12a**	**2.31b**	**2.43Y**	**2.30a**	**2.36a**	**2.63b**	**2.53Y**	**2.72b**	**2.43a**	**2.45ab**
LDIM/OC ratio		**0.13z**	0.13a	0.13a	0.14a	**0.07Y**	0.07a	0.08a	0.07a	**0.04x**	0.03a	0.04a	0.04a

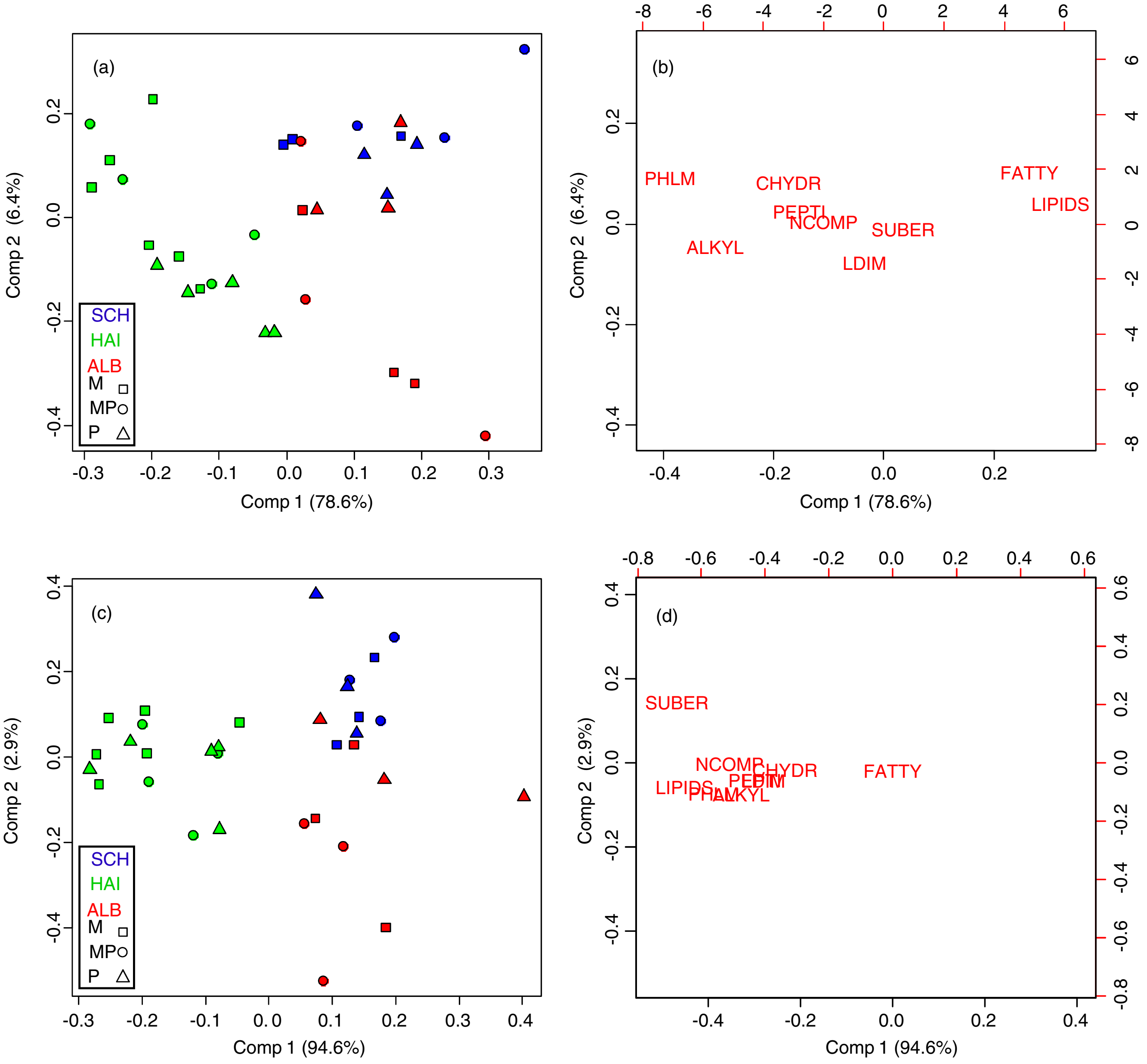

FIGURE 1 PLS-DA score and loading plots for Py-FIMS compound classes of grassland SOM in mineral soil samples from Schorfheide (SCH), Hainich (HAI) and Alb (ALB) differing in management. (a) Score plot of relative ion intensity (% of TII), (b) loading plot of relative ion intensity, (c) score plot of thermostability, (d) loading plot of thermostability. Percentage of variance explained for each PLS-DA axis is given in parentheses; M, meadow; MP, mown pasture; P, pasture

et al., 2018; Six et al., 2002; Wiesmeier et al., 2014). The clay and the crystalline Fe-oxide content increased in the order Schorfheide < Hainich < Alb (Table 3). As expected these increases went along with an increase in the soil OC content, which could be explained by the stabilization of the SOM through clay-sized particles and thus protection from a decomposing microorganism (Baldock, 2002; Roper & Smith, 1991). Further, an increase in the clay fraction could increase soil water retention thus creating favourable conditions for plant (root) growth and microbial activity (Ismail & Ozawa, 2007; Roychand & Marschner, 2013). The increased microbial activity could result in more degraded plant material in clay-rich soils (Wei et al., 2014). Our results confirmed a significantly lower hexoses/pentoses ratio in sandy soils of Schorfheide compared with the other regions and an increasing LDIM/OC ratio in the order Schorfheide < Hainich < Alb pointing to comparably fresh litter in sandy soils of Schorfheide and more degraded plant material in clay-rich soils of Hainich and Alb (Table 4). The highest thermostability for SOM compounds was detected in Hainich suggesting the highest stabilization by mineral association and lowest degradability of SOM in this region. The results are in line with studies by Eusterhues et al. (2003) who observed

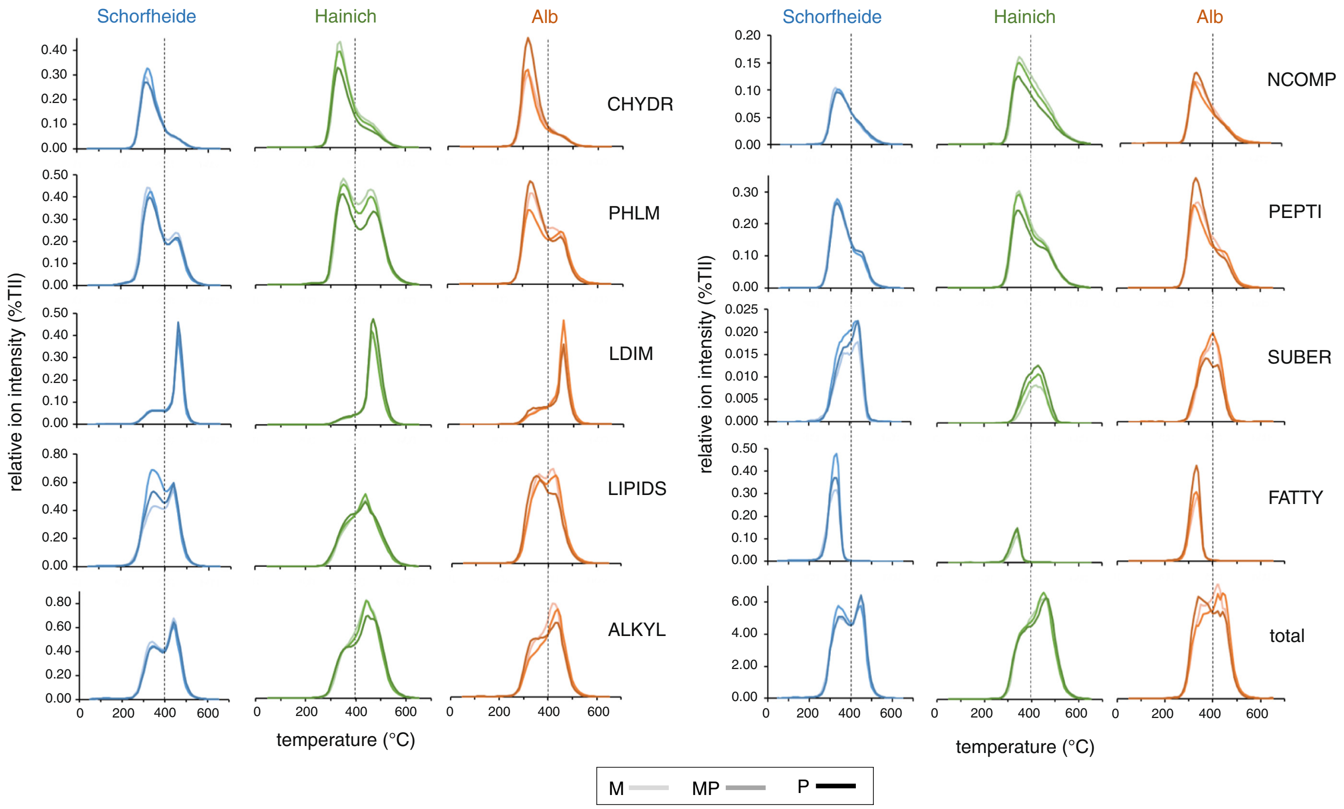

FIGURE 2 Thermograms showing means of relative ion intensity (% of TII) of volatile matter of different compound classes and of total volatile matter during pyrolysis temperature course as detected by Py-FIMS for SOM of Schorfheide, Hainich and Alb samples. TII, total ion intensity; M, meadow; MP, mown pasture; P, pasture; for abbreviations of Py-FIMS compound classes, see Table 2

strong organo-mineral associations of the old and stable carbon fraction with clay minerals and/or Fe-oxides. However, SOM thermostability was lower in Alb although Alb soils were even more clay-rich compared with those in Hainich. The discrepancy may be the result of more plant/microbial available water in the siltier soils of Hainich while the extremely clay-rich soils of Alb contained also more unavailable water.

A strong regional effect on SOM composition and stability was detected by PLS-DA (Figure 1), which mainly resulted from the interplay of the soil clay and SOM content (clay/OC ratio) (Table 5). Given that PLS-DA did not reveal any further separation with regard to grassland management type our results suggest an overriding effect of regional conditions over the grassland management. This is in line with observations on plant species diversity, which differed between these regions but did not show any constant effects related to differences in grassland management (Socher et al., 2012, 2013). Also, soil microbial communities and enzyme activities in these regions were more controlled by differences in soil properties than by grassland management practices (Herold et al., 2014). To eliminate regional effects, further evaluations on grassland management were conducted for the three regions separately.

4.1 | Soil variables and grassland management imprint on SOM composition and stability in Schorfheide

In sandy soils of Schorfheide, the available reactive surface was comparatively low, which underlines its importance for binding of SOM compounds in these soils (Baldock & Skjemstad, 2000; Christensen, 1992; Jones & Edwards, 1998; Schweizer et al., 2021). The clay content was positively correlated with the relative abundance of CHYDR, PHLM, ALKYL, NCOMP and PEPTI compounds while at the same time, it was negatively correlated with LDIM and FATTY compounds (Table 5), thus, confirming our hypothesis that the clay fraction, and its reactive surfaces, influence the SOM composition by preferentially accumulating different SOM compounds. This could be either by direct interaction through binding of SOM constituents onto the reactive surfaces of clay particles or by indirect effects of the clay-sized particles on, e.g. soil moisture, which in turn determines the decomposing microbial communities and, thus, selective decomposition of SOM constituents (Cuadros, 2017; Fomina & Skorochod, 2020; Kögel-Knabner et al., 2008; Wei et al., 2014).

The proportions of CHYDR compounds increased with increasing clay/OC and $Fe_{DCB\text{-}ox}$/OC ratio suggesting that

TABLE 5 Spearman rank correlation coefficient for significant relationships between Py-FIMS parameters and soil variables (correlation coefficients > 0.75 (>−0.75) at $p \leq .05$) for the regions Schorfheide, Hainich and Alb; '–' correlation coefficient < 0.75 (<−0.75) and/or no significant correlation at $p \leq .05$; for abbreviations, see Tables 2 and 3

Region	Py-FIMS parameter	Compound class	Soil variable												
			Clay	Silt	Sand	pH	IC	OC	TN	C/N	Clay/OC	$Fe_{DCB\text{-}ox}$	Fe_{ox}	$Fe_{DCB\text{-}ox}$/OC	Fe_{ox}/OC
All	% TII	CHYDR	–	–	–	–	–	–	–	–	0.81	–	–	–	–
		PHLM	–	–	–	–	–	–	–	–	0.79	–	–	–	–
		ALKYL	–	–	–	–	–	–	–	–	0.77	–	–	–	–
		LDIM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		NCOMP	–	–	–	–	–	–	–	–	0.88	–	–	–	–
		PEPTI	–	–	–	–	–	–	–	–	0.84	–	–	–	–
		SUBER	–	–	–	–	–	–	–	–	−0.76	–	–	–	–
		FATTY	–	−0.75	–	–	–	–	–	–	−0.79	–	–	–	–
	Thermostability	total	–	–	–	–	–	–	–	–	–	–	–	–	–
		CHYDR	–	–	–	–	–	–	–	–	–	–	–	–	–
		PHLM	–	0.78	–	–	–	–	–	–	–	–	–	–	–
		LDIM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	–	0.77	–	–	–	–	–	–	–	–	–	–	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	–	–	–	–	–	–	–	–	–
		SUBER	–	–	–	–	–	–	–	–	–	–	–	–	–
		FATTY	–	–	–	–	–	–	–	–	0.81	–	–	–	–
Schorfheide	% TII	CHYDR	0.90	–	–	–	–	–	–	–	0.82	–	–	0.80	–
		PHLM	0.80	–	–	–	–	0.77	–	–	–	0.90	–	0.82	–
		LDIM	−0.77	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	0.77	–	–	–	–	–	–	–	–	0.88	–	0.83	–
		NCOMP	0.90	–	−0.81	–	–	0.77	–	–	–	0.89	–	0.88	−0.77
		PEPTI	0.83	–	–	–	–	–	–	–	–	0.88	–	0.85	−0.78
		SUBER	–	–	–	–	–	–	–	–	–	−0.88	–	−0.83	–
		FATTY	−0.78	–	0.82	–	–	−0.85	−0.80	–	–	−0.93	–	−0.85	–

TABLE 5 (Continued)

Region	Py-FIMS parameter	Compound class	Soil variable												
			Clay	Silt	Sand	pH	IC	OC	TN	C/N	Clay/OC	Fe_{DCB-ox}	Fe_{ox}	Fe_{DCB-ox}/OC	Fe_{ox}/OC
	Thermostability	total	–	–	–	–	–	–	–	–	–	–	–	–	–
		CHYDR	–	–	–	–	–	–	–	–	–	–	–	–	–
		PHLM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LDIM	–	–	–	–	–	–	–	–	–	–	—	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	–	–	–	–	–	–	–	–	–	–	–	–	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	0.75	–	–	–	–	–	–	–	–
		SUBER	–	–	–	–	–	–	–	–	–	–	–	–	–
		FATTY	0.79	–	−0.86	–	–	0.90	0.85	–	–	0.91	–	0.90	–
Hainich	% TII	CHYDR	–	–	–	–	–	–	–	–	–	–	–	–	–
		PHLM	–	–	–	–	–	−0.76	−0.76	–	–	–	–	0.78	–
		LDIM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	–	–	–	–	–	−0.85	−0.88	–	–	–	–	0.88	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	–	–	–	–	–	–	–	–	–
		SUBER	–	–	–	–	–	0.83	0.85	–	–	–	–	−0.94	–
		FATTY	–	–	–	–	–	–	–	–	–	–	–	−0.82	–
	Thermostability	total	–	–	–	–	–	–	–	–	–	–	–	–	–
		CHYDR	–	–	–	–	–	–	–	–	–	–	–	–	–
		PHLM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LDIM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	–	–	–	–	–	–	–	–	–	–	–	–	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	–	–	–	–	–	–	–	–	–
		SUBER	–	–	–	–	–	–	–	–	–	–	–	–	–
		FATTY	–	–	–	–	–	–	–	–	–	–	–	0.82	–

TABLE 5 (Continued)

Region	Py-FIMS parameter	Compound class	Soil variable												
			Clay	Silt	Sand	pH	IC	OC	TN	C/N	Clay/OC	$Fe_{DCB\text{-}ox}$	Fe_{ox}	$Fe_{DCB\text{-}ox}/OC$	Fe_{ox}/OC
Alb	% TII	CHYDR	–	–	–	–	–	−0.82	−0.86	–	0.83	–	–	–	–
		PHLM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LDIM	–	–	–	–	–	–	–	–	–	–	–	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	0.77	–
		ALKYL	–	–	–	–	–	–	–	–	–	–	–	–	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	–	–	–	–	–	–	–	–	–
		SUBER	–	–	–	–	–	–	–	–	–	–	–	–	–
		FATTY	–	–	–	–	–	–	–	0.86	–	–	–	–	–
	Thermostability	total	–	–	–	–	–	–	–	–	–	–	0.85	–	–
		CHYDR	–	–	–	–	–	–	0.85	–	–	–	–	–	–
		PHLM	–	–	–	–	–	–	–	–	–	–	0.90	–	0.81
		LDIM	–	–	–	−0.77	–	–	–	–	–	–	0.80	–	–
		LIPIDS	–	–	–	–	–	–	–	–	–	–	–	–	–
		ALKYL	–	–	–	–	–	–	–	–	–	–	0.79	–	–
		NCOMP	–	–	–	–	–	–	–	–	–	–	–	–	–
		PEPTI	–	–	–	–	–	–	0.85	–	–	–	–	–	–
		SUBER	–	–	–	–	–	0.88	0.80	–	–	–	–	–	–
		FATTY	–	–	–	–	–	–	–	−0.81	–	–	–	–	–

the presence of clay-sized particles, particularly crystalline Fe-oxides, was the limiting factor for the stabilization of carbohydrates in the sandy soils of Schorfheide. This is in line with a preferential interaction of carbohydrates with Fe-coated sand particles (Gianetta et al., 2019; Schöning et al., 2005) and in turn a retarded decomposition of carbohydrates in the presence of Fe-oxides (Miltner & Zech, 1998).

The relative abundances of PHLM, ALKYL, NCOMP and PEPTI compounds were positively correlated with the amount of crystalline Fe-oxides, at least partially confirming data of preferential findings of alkylaromatics and other compound classes in clay fractions (Schulten & Leinweber, 1995). This may be explained by the occlusion of these compounds in micropores of the pedogenic oxides (Kaiser & Guggenberger, 2003). Given that pedogenic oxide stability is affected by changes in redox conditions (Reddy & DeLaune, 2008), these OM compounds could be prone to drops in redox potentials, which consequently could result in a predominant release of the abovementioned compound classes. A release of NCOMP and PEPTI compounds under reducing conditions could thus contribute to an increased N-availability in Schorfheide soils.

The relative abundance of FATTY compounds was negatively correlated with clay and crystalline Fe-oxide content indicating that in the particular sandy Schorfheide soils with relatively high clay contents, the FATTY compounds were either less abundant in the vegetation residues, more quickly decomposed and/or leached from the topsoil. The latter two explanations partly agree with free fatty acids representing relatively easily decomposable SOM compounds (Dinel et al., 1990; Yang et al., 2020). Also, the thermostability of the FATTY compounds increased with increasing clay and crystalline Fe-oxide content suggesting the association of the remaining FATTY compounds with the abundance of alumino-layer silicates and crystalline pedogenic oxides in the soil clay fraction (Jandl et al., 2004).

The thermostability of PEPTI compounds was positively related to the IC content. Given that in a calcium chelate the binding energy between calcium and PEPTI compound is compound-specific (e.g. Lys > Asp) (Tang & Skibted, 2016) this result implies a soil IC-dependent array of PEPTI compounds, which could have resulted from a different composition of plant and/or microbial biomass and/or decomposition of SOM by different microbial communities and/or uptake by plant and microbial communities (Farzadfar et al., 2021).

The proportion of LIPIDS compounds was unaffected by abiotic soil parameters (Table 5), suggesting that only low amounts of LIPIDS compounds were bound to clay-sized particles in Schorfheide soils. At the same time, LIPIDS was the only compound class, which significantly was affected by the type of grassland management (Table 4). The highest proportions of LIPIDS were detected under mown pasture suggesting accumulation of LIPIDS compounds from the mown vegetation and from excrements of grazing animals and some organic fertilizer. This is in line with Park et al. (2019), who observed about 25% of mass signals in pyrolysis-gas chromatography/mass spectrometry assigned to lipids in commercial cow manure. Also, on pastures, the LIPIDS compound proportion was high, which could be related to cattle excrement deposition and its transformation products. In contrast to pastures, on mown pastures, the additional input of fresh litter by mowing could have resulted in the still high potential decomposability of the LIPIDS compounds as derived from low thermostability (Table 4). Also, a comparably low hexoses/pentoses ratio under mown pasture indicated a high portion of plant-derived sugars (Oades, 1984), which probably resulted from fresh litter input. Under meadow, thermograms showed that the proportion of thermolabile LIPIDS compounds was low indicating that here these LIPIDS compounds originating from fresh litter were quickly degraded by the decomposer community and/or were mainly bound to soil particles (Figure 2). The results confirm our hypothesis that grassland management affects the SOM composition and stability by providing different precursor organic compounds from vegetation residues, remnants of soil biota and excrements of grazing animals. However, the hypothesized order of SOM compound proportions or thermostability (meadow—mown pasture—pasture) was not observed indicating that mainly physicochemical and biological properties from the surrounding environment affect SOM dynamics (Baldock & Skjemstad, 2000; Schmidt et al., 2011).

4.2 | Soil variables and grassland management imprint on SOM composition and stability in Hainich

In Hainich, neither clay nor pedogenic oxide, or IC content nor the clay/OC ratio did affect SOM composition and stability (Table 5) contradicting our hypothesis postulating an influence of reactive surfaces. This on the one hand could be due to sufficient or even a surplus of clay binding sites at a clay/OC ratio >10 (Table 3) and may suggest that the majority of SOM molecules were mineral-bound and/or stabilized against microbial decomposition by occlusion inside aggregates (Six et al., 2002). It implies that in this case, the clay content may not be responsible for changes in SOM composition or stability because clay is not a limiting factor for the binding of SOM constituents or other mechanisms of SOM stabilization. On the other hand, high proportions of SOM may have been occluded as particulate SOM as observed by Schweizer et al. (2021) for soils of high clay content (18% to 37% clay). In this case, much SOM would have been present as a whole not using up many clay binding sites. Also, correlations between SOM content (OC and TN content) and certain SOM compounds suggested that occlusion of particulate SOM could have affected the SOM composition (Table 5): At high SOM content, the proportions of PHLM and ALKYL compounds were low while SUBER compound proportions were high (Table 5) implying that at a high SOM content, compounds to a large extent originated from intact macromolecules of lignin and suberin while their decomposition products were less abundant. Once SOM had been decomposed more strongly resulting in a lower SOM content, the proportion of decomposition products such as PHLM compounds was high.

However, SOM composition was not only a matter of decomposition stage but was also affected by the type of grassland management. A higher PHLM compound proportion was found under meadow compared with that under pasture while SOM content under both types of management was similar (Table 4). This result disagreed with our expectation that the proportion of potentially recalcitrant compounds would increase in the order meadow < mown pasture < pasture confirming that factors in addition to the recalcitrance of compounds affect SOM composition (Baldock & Skjemstad, 2000; Schmidt et al., 2011). Thermograms, for example, indicated that grassland management affected SOM stability and thus decomposability (Figure 2). Under pasture, some PHLM compounds were more strongly bound to minerals compared with those under other management types, which would have lowered the decomposability of these compounds under pasture. Also, the effects of management on SOM composition under meadow and pasture could have been interfered by different soil IC contents (Table 3). The IC, originating from calcium and magnesium carbonate from the parent rock (limestone) in turn could have affected the plant community and/or microbial community and thus the composition of OM input (Socher et al., 2013), the decomposer activity (Herold et al., 2014) or provided calcium as an additional stabilizing agent (Rowley et al., 2018).

As expected, proportions of CHYDR but also NCOMP and PEPTI compounds were highest under meadow and lowest under pasture reflecting the amount of freshly added litter (from mowing) to SOM in the order meadow > mown pasture > pasture. This is also supported by a lower hexoses/pentoses ratio under meadow compared with pasture management. The results confirm our hypothesis that grassland management affects the SOM composition and stability, also in Hainich. This implies that in regions with a clay/OC ratio > 10, management could directly affect SOM storage in soil.

4.3 | Soil variables and grassland management imprint on SOM composition and stability in Alb

Clay-rich soils of Alb accumulated high amounts of OC, which is in line with the report of a positive relationship between soil carbon and clay content (Schimel et al., 1994). In the Alb region, proportions of CHYDR compounds were negatively correlated with SOM content (OC and TN content) but positively related with the clay/OC ratio (Table 5), suggesting accumulation of constantly decomposed SOM over time and preservation of CHYDR compounds by reactive surfaces of C-unsaturated clay particles. Adsorption of carbohydrates on clay minerals is well known (Leinweber et al., 2009; Lynch et al., 1956; Rakhsh & Golchin, 2018; von Lützow et al., 2006) and particle size, specific surface area of the clay and cation exchange capacity were reported to influence the retention of carbohydrates (Leinweber et al., 2009; Rakhsh & Golchin, 2018). In Alb, only CHYDR compounds were related to the clay/OC ratio, which once again supports our hypothesis that clay minerals selectively interact with certain SOM compound classes and, thus, affect the SOM composition. Interestingly, in Alb, similarly to Schorfheide, the clay/OC ratio was < 10 implying that clay content directly affected SOM composition only below a certain threshold ratio.

Also, SOM stability was related to the content of poorly crystalline pedogenic oxides. In the case of the total SOM thermostability and thermostability of PHLM, LDIM and ALKYL compounds, a relationship with oxalate-extractable Fe was positive (Table 5) suggesting stabilization of these compounds by interaction with poorly crystalline Fe-oxides. Although the oxalate-extractable Fe content was (coincidentally) highest under mown pasture the proportions of these compound classes (PHLM, LDIM, ALKYL) were, however, not affected by grassland management. This indicates that management can override the effects of pedogenic oxides probably by the diversity of OM inputs and preferential co-precipitation or adsorption processes by poorly crystalline Fe-oxides depending on the organic or inorganic amendment, respectively (Wen et al., 2019).

In Alb, the proportion of FATTY compounds increased with increasing C/N ratio (Table 5), implying the lowest contribution of free fatty acids from plants and microorganisms under meadow and the highest under pasture (Table 3). A simultaneous decrease in the thermostability of the FATTY compounds in this order (M > P; Table 4) may indicate shorter fatty acid alkyl chains and/or a stronger mineral-bonding of fatty acids under meadow compared with pasture (Yang et al., 2020). Given that particularly the long alkyl chain of fatty acids may enhance hydrophobicity (Ma'shum et al., 1988), an accumulation of FATTY compounds especially in pasture soils may affect water- and thus nutrient transport in the soil.

5 | CONCLUSIONS

The applied Py-FIMS technique was suitable to uncover the effects of soil texture and grassland management on SOM composition and stability at the molecular level. These effects were region-specific indicating that the SOM enrichment or C-storage potential of soil needs to be estimated for each specific geological/pedological region before implementing adapted management. This should be of particular importance if regions also vary in clay mineralogy or show strong climatic differences.

In sandy soils from glacial deposits, particularly the content of clay and crystalline Fe-oxides shaped the SOM composition and stability, highlighting the relative importance of reactive surfaces for binding of SOM constituents and the importance of indirect effects via physical soil properties such as aggregation, occlusion, water holding capacity and thus microbial habitats and activity. In these soils, grassland management was only imprinted on the LIPIDS compound class, which had not been affected by soil parameters.

In clay-rich soils with a clay/OC ratio >10, SOM-binding sites at reactive surfaces were not limited so that only OM input and microbial decomposition determined the SOM composition. Hence, grassland management is strongly imprinted on SOM composition, which may offer opportunities for land users to actively store more C in the soil as an approach to mitigate climate change (e.g. by increasing the C/N ratio as a result of using organic rather than mineral fertilizer).

In clay-rich soils in which the clay/OC ratio was <10, SOM composition and stability were mainly affected by the accumulation of plant and microbial-derived compounds and the additional surface area provided by poorly crystalline Fe-oxides. Here, grassland management imprinted on the decomposability of free fatty acids suggesting consequences for water balance (hydrophobicity) and element transport, which may, however, be managed by a change in grassland management such as through variation in grazing intensity, mowing frequency, or the input of different OM, or amounts of fertilizer.

In summary, we conclude that SOM composition and stability were predominantly driven by the clay/OC ratio, while grassland management only affected SOM if (1) clay binding sites were highly abundant or if (2) no clay-bound compounds were affected or (3) only management unspecific compounds were clay-bound. This implies that SOM dynamics are most importantly ruled by soil properties but that grassland management might be used as a tool to affect SOM composition and stability and, thus, influence SOM storage in grasslands. In the light of climate change mitigation, this means that the potential for storing additional C in soil and eventually earning carbon credits is more site-specific than grassland management-dependent.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in BExIS at https://www.bexis.uni-jena.de/, reference numbers 14446, 14447, 14686, and 19346.

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