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ORIGINAL PAPER

Soil organic carbon stocks, distribution, and composition affected by historic land use changes on adjacent sites

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Abstract Historic alterations in land use from forest to grassland and cropland to forest were used to determine impacts on carbon (C) stocks and distribution and soil organic matter (SOM) characteristics on adjacent Cambisols in Eastern Germany. We investigated a continuous Norway spruce forest (F-F), a former cropland afforested in 1930 (C-F), and a grassland deforested in 1953 (F-G). For C and N stocks, we sampled the A and B horizons of nine soil pits per site. Additionally, we separated SOM fractions of A and B horizons by physical means from one central soil pit per pedon. To unravel differences of SOM composition, we analyzed SOM fractions by ^{13}C-CPMAS NMR spectroscopy and radiocarbon analysis. For the mineral soils, differences in total C stocks between the sites were low (F-F=8.3 kg m^{-2}; C-F=7.3 kg m^{-2}; F-G=8.2 kg m^{-2}). Larger total C stocks (+25%) were found under continuous forest compared with grassland, due to the C stored within the organic horizons. Due to a faster turnover, the contents of free particulate organic matter (POM) were lower under grassland. High alkyl C/O/N-alkyl C ratios of free POM fractions indicated higher decomposition stages under forest (1.16) in relation to former cropland (0.48) and grassland (0.33). Historic management, such as burning of tree residues, was still identifiable in the subsoils by the composition and ^{14}C activity of occluded POM fractions. The high potential of longer lasting C sequestration within fractions of slower turnover was indicated by the larger amounts of claybound C per square meter found under continuous forest in contrast to grassland.

Keywords ^{13}C-CPMAS NMR · Radiocarbon · Density fractionation · Particulate organic matter · Black carbon

Introduction

There is considerable concern about land use changes inducing alterations of the soil carbon (C) cycle and, thus, having a marked influence on global carbon fluxes (UN 1998; IPCC 2007). Against the background of the global change scenario, the management of terrestrial C resources has to conserve existing C stocks and to sequester additional C from the atmosphere (Malhi et al. 1999). The equilibrium between C input and mineralization is altered by land use change until a new potential equilibrium is reached (Guo and Gifford 2002). Losses of soil C are reported due to deforestation, whereas regenerating forests may sequester C in both biomass and soils (Thuille et al. 2000). After afforestation of croplands, a fast accumulation of C takes place (Richter et al. 1999; Wall and Hytonen 2005). Nevertheless, the major part of the C in newly growing forests is allocated to tree biomass and organic layers as opposed to the mineral soil. Also, decades after afforestation, C stocks differed from continuously forested sites (Langley-Turnbaugh and Keirstead 2005; Wall and Hytonen 2005). Carbon stocks are closely related to the decay rates within the C cycle and, therefore, to the quantity and quality of the C input (Tate et al. 2000). Land use, therefore, has an impact on the composition of soil organic matter (SOM). For example, Guggenberger et al. (1994) showed that the soil of a long-term spruce forest had

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lower carbohydrate contents in relation to a permanent grassland site. The authors also showed a higher decomposition of SOM in forested soils than in agricultural soils. Larger C storage in particulate organic matter (POM) than for mineral associated C were found by John et al. (2005) at a forested site in relation to a grassland site.

Nevertheless, studies about properties of certain SOM fractions often lack statistically significant background information on soil properties. It is difficult to transfer observed differences of SOM fractions from one single soil pit into site predictions. In a study about SOM composition under different land use in Costa Rica, Guggenberger and Zech (1999) circumvent this problem by sampling five randomly chosen spots on an area of 500 m^2 in order to get significant data for soil properties. But, on such large areas, the heterogeneity in soil properties increases, whereas additional sampling spots on a smaller area can provide significant information unbiased by large-scale heterogeneities. To obtain datasets of statistical significance describing a single pedon, we sampled eight soil pits, additionally to a main pit, on a small circle of approximately 78.5 m^2 (r=5 m). Therefore, we show specific changes of the chemical composition of SOM fractions due to historic land use alterations between the studied pedons (r=5 m) on a site background. To eliminate effects of differing pedology, we studied adjacent Cambisols on the same bedrock with similar textures. Besides Podzols (14%), Cambisols (12%) are one of the most abundant soil types in Europe and are, therefore, very important for studying alterations in land use systems (European Soil Bureau Network 2005). We sampled a continuous Norway spruce stand (F-F), a former cropland afforested with Norway spruce (C-F), and a former Norway spruce forest converted into grassland (F-G).

It is not well understood how changes in management and vegetation may influence subsoil C stocks and SOM properties (Cole et al. 1993). Due to the additional sampling of organic horizons and subsoils, a better prediction of alterations in C stocks and distributions induced by differing land use was possible. Therefore, the main objective of our study was to elucidate whether and how historic land use alterations are reflected by C stocks, C distribution, C allocated to soil fractions, and chemical composition of the SOM on sites differing only in management.

Materials and methods

Study area

The study area is located in eastern Germany in the Saxon Ore Mountains 25 km south of the city of Dresden near Luchau (50°50′53″ N; 13°44′48″ E). The area is situated 480 m a.s.l. and has a mean annual rainfall of about 800 mm and a mean annual temperature of about 6.5°C. Beginning with the German settlement and deforestation in the early thirteenth century, the former old growth temperate forests were altered into a characteristic mosaic of different land use systems (Blaschke 1966). Burning of tree residues after felling and charcoal production for the local mining industry was widespread but not historically documented for the studied sites. Before the first settlement, the vegetation was dominated by Beech forests (*Fagus sylvatica* L.). Starting in the nineteenth century, a conversion to Norway spruce (*Picea abies* L. Karst) monocultures took place on a large scale. Two adjacent forested and one grassland site on a 200-m transect were investigated on a plateau. The two forested sites were (1) an even aged Norway spruce (*P. abies* L. Karst) forest established in 1927 on a F-F and (2) a C-F afforested in 1930 with even aged Norway spruce. The (3) F-G was cleared of Norway spruce forest in 1953 and ploughed once. Remaining roots and branches were burnt at the site after the clear cut. During its existence, the grassland was mainly used for hay production, and, therefore fertilized and limed regularly. The soils are Leptic Cambisols (dystric) at the forested sites and Leptic Cambisol (eutric) under grassland (WRB 2006). The soils are rich in coarse material and evolved from gneiss, the dominant parent material in the Saxon Ore Mountains. An abrupt boundary between A and B horizons at the former cropland and the grassland indicated former tillage. At the forested sites, the organic horizons Oe and Oa were composed of acidic needle litter with abrupt boundaries between the horizons. The organic horizons (sum of Oe and Oa) had a thickness of 6.3±1.0 cm at the continuous forest and 5.2±1.5 cm at the former cropland (Table 1). Soil mineralogy was very similar among all three sites; the clay separates were composed of: 70% chlorite, 20% illite, and 10% kaolinite. The clay content changed slightly from continuous forest to former cropland and grassland (Table 2). Soil pH in all soils ranged from 3.5 in the forest soils to 5.7 in the grassland soils, indicating the absence of carbonates; pH, cation exchange capacity (CEC), and BS were significantly different between the sites, with high pH and BS under grassland concomitant with low CEC values (Table 2).

Soil sampling

Soil samples were taken in July 2006 from the A and B horizons at the three sites, additionally the litter (Oi) at all sites and the organic horizons (Oe, Oa) at the two forested sites were sampled. We also sampled eight pits on a circle (r=5 m) around the main soil pit in the centre (Fig. 1), in order to obtain bulk density, pH values, CEC, as well as C

Table 1 Thickness of horizon, bulk density, texture (*n*=3), pH values in H_2O and 0.01 M $CaCl_2$, effective cation exchange capacity, potential cation exchange capacity, and base saturation of continuous forest, former cropland, and grassland

Site	Horizon	Thickness (cm)	Bulk density ($g\ cm^{-3}$)	Sand ($g\ kg^{-1}$)	Silt ($g\ kg^{-1}$)	Clay ($g\ kg^{-1}$)	pH/ H_2O	pH/ $CaCl_2$	ECEC ($\mu mol_c\ g^{-1}$)	PCEC ($\mu mol_c\ g^{-1}$)	BS %
F-F	Ah	5±1	0.86±0.08	397±10	357±9	246±15	3.6±0.1	2.9±0.1	156.3±5.8	344.3±23.1	9.4±2.9
	Bw	28±2	1.27±0.13	402±18	391±38	207±20	3.9±0.1	3.4±0.3	110.2±9.4	238.7±34.2	9.7±5.0
C-F	Ap	12±2	1.05±0.15	441±9	349±9	209±5	3.8±0.1	3.2±0.1	127.4±5.4	276.8±31.6	9.8±2.1
	Bw	27±3	1.32±0.14	461±40	347±26	192±13	4.2±0.1	3.7±0.1	68.6±9.8	199.5±17.2	13.3±2.5
F-G	Ap	15±1	0.91±0.07	449±3	350±10	202±13	5.2±0.2	4.6±0.2	124.3±19.1	244.3±18.4	94.2±3.8
	Bw	20±3	1.51±0.11	556±42	283±10	161±31	5.4±0.3	4.6±0.3	56.2±5.4	161.8±14.6	63.3±16.8

Data are given as mean.

ECEC effective cation exchange capacity, *PCEC* potential cation exchange capacity, *BS* base saturation, *F-F* continuous forest, *C-F* former cropland, *F-G* grassland

and N contents. Due to the chosen circular sampling scheme, we obtained highly significant datasets describing a single pedon for every site.

Undisturbed soil cores (100 cm^3) were taken in triplicate from A and B horizons for bulk density determination at all nine pits per site. The samples were dried at 105°C for 24 h, and the amount of coarse material was subtracted. The organic horizons were sampled for C and N balance in triplicate with a wooden frame (10×10 cm). For all further analyses, the soil samples were air-dried and sieved with a sieve of 2 mm mesh size.

Soil texture and mineralogy

To evaluate pedogenic similarities between the sites, we analyzed soil texture and the mineralogy of the adjacent Cambisols. For soil texture analysis, organic matter was oxidized (H_2O_2 30%). For particle dispersion, we used 0.025 M $Na_4P_2O_7$ solution. The fractions >63 µm were determined via wet sieving and weighing. The fractions <63 µm were determined using the X-ray attenuation method (Micromeritics, Sedigraph 5100). The mineralogy of soils was determined on clay separates from the Bw horizons (after OC removal by H_2O_2) by X-ray diffractometry using K-α-radiation (Philips, PW 1830).

Table 2 Carbon recovery after treatment with 10% hydrofluoric acid of bulk soils and clay fractions from continuous forest, former cropland, and grassland

Site	Horizon	C recovery after HF treatment (%)	
		Bulk soil	Clay
F-F	Ah	80.5	79.3
	Bw	41.7	53.2
C-F	Ap	81.3	72.8
	Bw	45.9	49.0
F-G	Ap	49.7	75.1
	Bw	68.9	55.0

HF hydrofluoric acid, *F-F* continuous forest, *C-F* former cropland, *F-G* grassland

Physical fractionation

A combined density and particle-size fractionation was applied. Air-dried soil material (30 g<2 mm) from the main soil pit (Fig. 1) were capillary-saturated with sodium polytungstate solution (1.8 g cm^{-3}) and allowed to settle overnight. The floating free POM (fPOM) was extracted by sucking via a water jet pump. The remaining slurry was dispersed ultrasonically (Bandelin, Sonopuls HD 2200) with an energy input of 440 J ml^{-1} in order to break down soil aggregates. The energy input was tested in advance to avoid disruption of coarse POM along with aggregate disruption. Centrifugation (30 min at 3,074×*g*) was used to separate the occluded POM (oPOM) from the mineral residue. To remove the Na-polytungstate from the POM fractions, the samples were washed several times with deionized water over a sieve

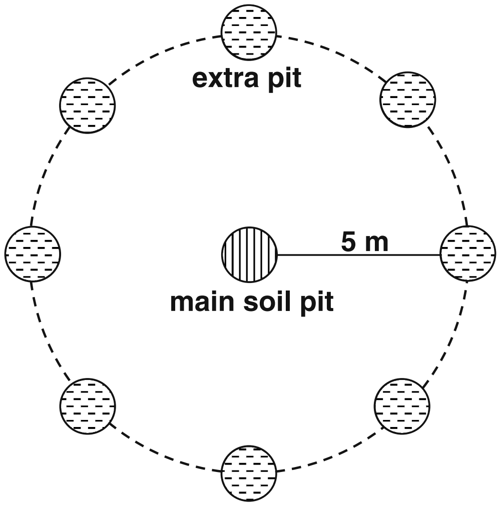


Fig. 1 Sampling design; main soil pit in the center and eight additional pits on a circle of 5 m radius

of 20 μm mesh size. The obtained fraction (oPOM<20 μm) from the washing of the oPOM was washed via pressure filtration until the electric conductivity dropped below 5 μS cm^{-1}. Sand (>63 μm) and coarse silt (>20 to 63 μm) were separated by wet sieving. Medium silt (6.3 to 20 μm), fine silt (2 to 6.3 μm), and clay (<2 μm) were obtained by sedimentation. All fractions were freeze-dried, weighed, and subjected to C N elemental analysis; 92.2±4.3% of the original C of the bulk soil sample were recovered after the fractionation. For analyses of chemical composition of mineral bound SOM, only the clay fractions were used. The sum of C stored in POM and clay fractions accounted for between 68% (F-G, Ap horizon) and up to 87% (F-F, Ah horizon) of the total C of the bulk soils (Fig. 2).

Chemical analyses

The pH values of the bulk soils were measured in deionized H_2O and 0.01 M $CaCl_2$ at a soil to solution ratio of 1 to 2.5 with a glass electrode. The C and N contents were measured in duplicate by dry combustion (Elementar, vario MAX CNS Analyzer for bulk soils; vario EL CN Analyzer for SOM fractions). Since all samples were free of carbonates, the measured C concentrations equal the organic C concentrations. For the calculation of C and N stocks, the bulk density values were corrected for the content of coarse material. To obtain comparable C stock values for the different thickness of horizons at the three sites, the C stocks were normalized on 1-cm thickness of

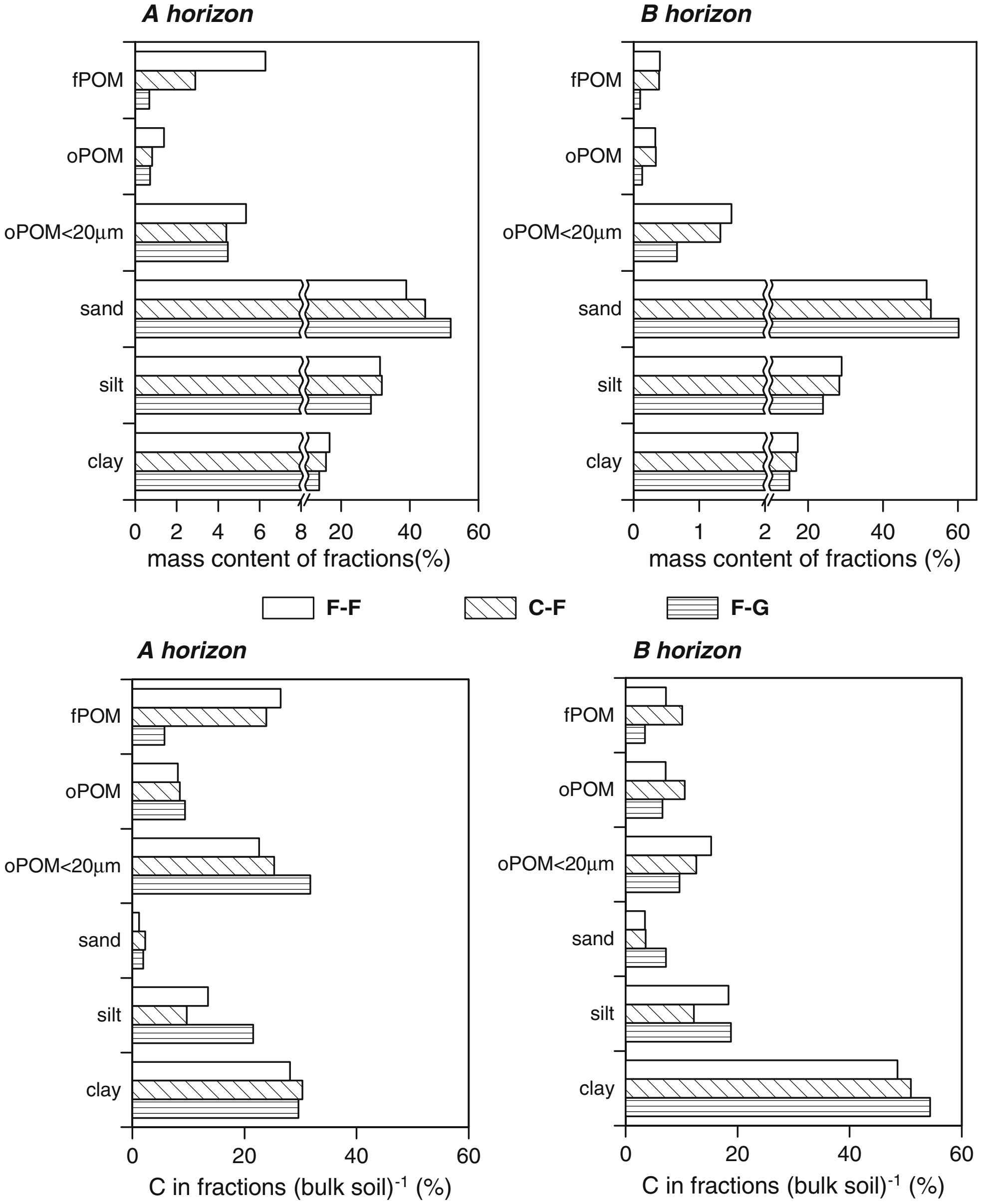


Fig. 2 Mass contents of fractions and distribution of organic C within soil fractions of bulk soil <2 mm originated from continuous forest (*F-F*), former cropland (*C-F*), and grassland (*F-G*)

horizon (Table 3). For the analysis of exchangeable base cations, we used 1 M ammonium acetate and 1 M KCl for the reexchange (Van Reeuwijk 2002). The percolates were measured for K, Mg, Ca,and Na with an ICP-OES (Varian, Vista Pro). The NH_4^+ concentrations from the reexchange were measured with a Segmented Flow Analyzer and accounted for the potential cation exchange capacity. For the determination of exchangeable Al, Fe, Mn, and acidity, 1 M KCl was used. The percolates were measured also with ICP-OES (Varian, Vista Pro). The exchangeable acidity was calculated from the difference in the pH values of the 1 M KCl solution and the percolates. From the obtained data, the effective CEC (ECEC) and the base saturation (BS) were calculated.

Prior to ^{13}C-CPMAS NMR spectroscopy, bulk soils and clay fractions were treated with 10% hydrofluoric acid (HF) to remove mineral material, including paramagnetic compounds such as iron, and to concentrate the SOM (Schmidt et al. 1997; Schöning et al. 2005b). Carbon recovery after HF treatment is shown in Table 2. To evaluate possible preferential dissolution of certain SOM components due to HF treatment, measurements with a higher number of scans (up to 300,000) were conducted for the clay fractions before HF treatment. ^{13}C-CPMAS NMR spectroscopy was accomplished with a Bruker DSX 200 spectrometer (Bruker BioSpin GmbH, Karlsruhe, Germany). Samples were filled into zirconium dioxide rotors and spun in a magic angle spinning probe at a rotation speed of 6.8 kHz to minimize chemical anisotropy. A ramped ^{1}H pulse was used during a contact time of 1 ms to prevent Hartmann–Hahn mismatches. The delay times ranged from 300 ms for bulk soil samples to 1,000 ms for litter and POM samples. Chemical shifts are referenced to tetramethylsilane (TMS=0 ppm). For integration, chemical shift regions were used as given: alkyl C (−10 to 45 ppm), O/N-alkyl C (45 to 110 ppm), aryl/olefine C (110 to 160 ppm), and carbonyl/carboxyl/amide C (160 to 220 ppm).

The ^{14}C values were obtained at the KECK Carbon Cycle AMS Facility at the Earth System Science Department at the University of California Irvine. For the ^{14}C measurements, ^{14}C-free acetanilide was used as sample background. All ^{14}C results have been corrected for isotopic fractionation according to the convention of Stuiver and Polach (1977). Organic material with Δ^{14}C values>0‰ indicate the presence of bomb C, reflecting higher ^{14}C activities than the 1950 atmosphere. Negative Δ^{14}C values indicate that the main part of the C has resided long enough in the soil for a significant radioactive decay (Trumbore 2000).

Mathematical analyses

To exclude the influence of the differing thickness of horizon on the total C and N stocks, we normalized the values on 1 cm thickness of horizon (Eq. 1):

$$\begin{aligned} &\mathit{normalized}\ C; N\ \mathit{stocks}\ \left(g\, m^{-2} cm^{-1}\right) \\ &\quad = C; N\ \mathit{stock}\left(g\, m^{-2}\right) \big/ \mathit{thickness\ of\ horizon}\ (cm) \end{aligned} \tag{1}$$

For statistical analysis of the datasets, SPSS 14.0 for Windows (SPSS Inc., Chicago, IL, USA) was used. Significant differences of soil parameters between the studied pedons were tested by the nonparametric Mann–Whitney *U* test.

Table 3 Carbon, N contents, and stocks as mean values (*n*=9) with standard deviations from continuous forest, former cropland, and grassland

Site	Horizon	C mg g^{-1}	N mg g^{-1}	C/N	C-stock kg m^{-2}	C-stock kg m^{2} normalized on 1 cm thickness	N-stock g m^{-2}	N-stock g m^{-2} normalized on 1 cm thickness
F-F	Oe	440.9±38.5	17.8±0.8	24.8±1.2	0.83±0.29	0.45±0.08	33.5±11.5	18.3±3.4
	Oa	357.5±42.1	17.2±1.0	20.7±1.0	1.95±0.54	0.43±0.08	93.9±26.1	20.7±3.7
	Ah	90.6±6.9	4.7±0.5	20.0±0.6	2.9±0.4	0.58±0.09	144.2±21.8	28.9±4.4
	Bw	22.6±3.3	2.4±0.5	17.8±0.8	5.4±0.5	0.19±0.02	304.0±21.7	10.9±0.8
	Σ				11.1±0.7		575.6±20.8	
C-F	Oe	465.8±40.1	21.5±1.6	21.7±1.2	0.80±0.15	0.46±0.14	37.0±6.9	21.1±6.3
	Oa	443.3±39.5	22.7±1.1	19.5±1.1	1.46±0.47	0.48±0.13	75.0±23.9	24.6±6.6
	Ap	43.5±9.4	4.5±0.7	18.1±1.1	3.7±0.7	0.31±0.06	205.6±30.8	17.1±2.6
	Bw	15.2±1.9	1.3±0.2	15.3±0.9	3.6±0.9	0.13±0.03	232.3±53.4	8.6±2.0
	Σ				9.6±1.7		549.9±75.4	
F-G	Ap	52.5±8.5	1.1±0.2	11.6±0.2	6.3±1.2	0.42±0.08	544.0±100.2	36.3±6.7
	Bw	9.2±1.0	0.8±0.1	12.3±0.6	1.9±0.3	0.10±0.01	157.2±23.5	7.9±1.2
	Σ				8.2±1.2		701.2±21.7	

F-F continuous forest, *C-F* former cropland, *F-G* grassland

Results

C and N stocks

A large amount of C was present in the organic horizons under forest (Table 3). No significant differences were found for the total C stocks of the mineral soils between continuous forest (8.3 kg m^{-2}) and grassland (8.2 kg m^{-2}). The C stocks normalized on 1 cm (Table 3) were significantly different ($p<0.01$) between all three sites and between A and B horizons. The lowest normalized C stocks for the A horizons were detected at the former cropland (Table 3). The normalized C stocks of the B horizons showed a clear trend towards lower values under former cropland and grassland (F-F>C-F>F-G). Under grassland, the decrease of the normalized C stocks was less pronounced in the Ap horizon (−28%) than in the Bw horizon (−48%) compared with continuous forest.

The organic horizons at the former cropland contained less N (112.0±15 g N m^{-2}) than under continuous forest (127.4±16 g N m^{-2}). The highest N stocks of the A horizons could be detected under grassland and the lowest at the former cropland (Table 3). A clear trend towards lower N stocks was shown for the Bw horizons in the order of continuous forest to former cropland and grassland. In contrast to the C stocks, the largest total N stocks of the mineral horizons were found under grassland (F-F=448.2 g N m^{-2}, C-F=437.9 g N m^{-2}, F-G=701.2 g N m^{-2}).

SOM fractions

Clear differences in the mass content of the three POM fractions could be found between the sites (Fig. 2), with most distinctive differences in the fPOM fractions. The highest fPOM contents were obtained for soils of the forested sites. For the A horizons, the oPOM and oPOM< 20 µm contents were similar under grassland and former cropland ($\Sigma_{[\mathrm{oPOM,\ oPOM<20\mu m}]}=52.0$ mg g^{-1}). Contents of both oPOM fractions decreased in the order of continuous forest to former cropland and grassland in the Bw horizons. The content of clay-sized fractions decreased in the same order in both horizons.

To obtain more detailed and mechanistic information about the C distribution, the C concentrations of the SOM fractions are given in relation to their total mass content (Fig. 2). At the continuously forested site, the largest portion of POM related C was found in the fPOM fraction, whereas for the grassland, the oPOM<20 µm showed the largest C content in relation to the bulk soil of the A horizons. The values of the POM fractions from the former cropland were on an intermediate level between the two other sites. For C situated in the clay fraction, slightly larger values were observed for the former cropland and the grassland. Most of the C within the Bw horizons was present in the clay fractions. The total C present in sand and silt ranged between 12% (C-F, Ap horizon) and 26% (F-G, Bw horizon) in relation to the bulk soils (Fig. 2).

The total C stocks of the single SOM fractions normalized on 1 cm thickness of horizon are given in Fig. 3. The lowest C stocks of the occluded SOM, silt, and sand in the A horizons were found at the former cropland. The largest C stocks of the POM fractions within the Bw horizons were found under forest, whereas a clear decrease of mineral-bound C stocks was observed in the order of continuous forest to former cropland and grassland.

Chemical composition

Major resonances of the measured bulk soils and fractions showed differing intensities in the NMR spectra, with peaks centered around 27 to 30, 55 to 57, 70 to 73, 100 to 105, 115, 125 to 129, 148 to 151, 170 to 175, and 201 to

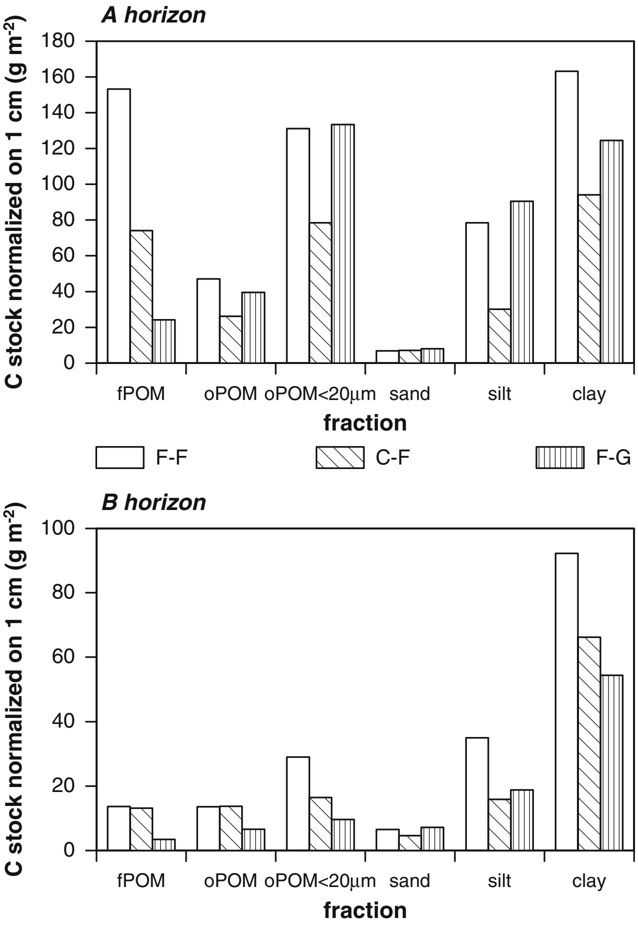


Fig. 3 Total OC stocks within soil fractions normalized on 1 cm thickness of horizon for the continuous forest (*F-F*), former cropland (*C-F*), and grassland (*F-G*)

205 ppm (Fig. 4). The signal between 27 and 30 ppm is typical for methylene C from lipids and aliphatic biopolymers such as suberin and cutin (Kögel-Knabner 2002). Signals around 72 and 103 ppm and the shoulders around 65 and 80 to 90 ppm arise mainly from cellulose and hemicellulose (Kögel-Knabner 1997; Preston et al. 1998). The resonances around 56, 130, and 150 ppm are attributed to methoxyl, H-/C-substituted and phenolic C in lignin and tannins. The high relative intensity around 130 ppm for C-substituted aromatic C can mark not only highly altered lignin structures but also material which is derived from black C or soot (Kögel-Knabner 1997). Figure 4 shows the ^{13}C-CPMAS NMR spectra obtained from the bulk A and B horizons and soil fractions, and Table 5 lists the integrated areas; in Fig. 5, the spectra of material from the organic horizons and roots are shown.

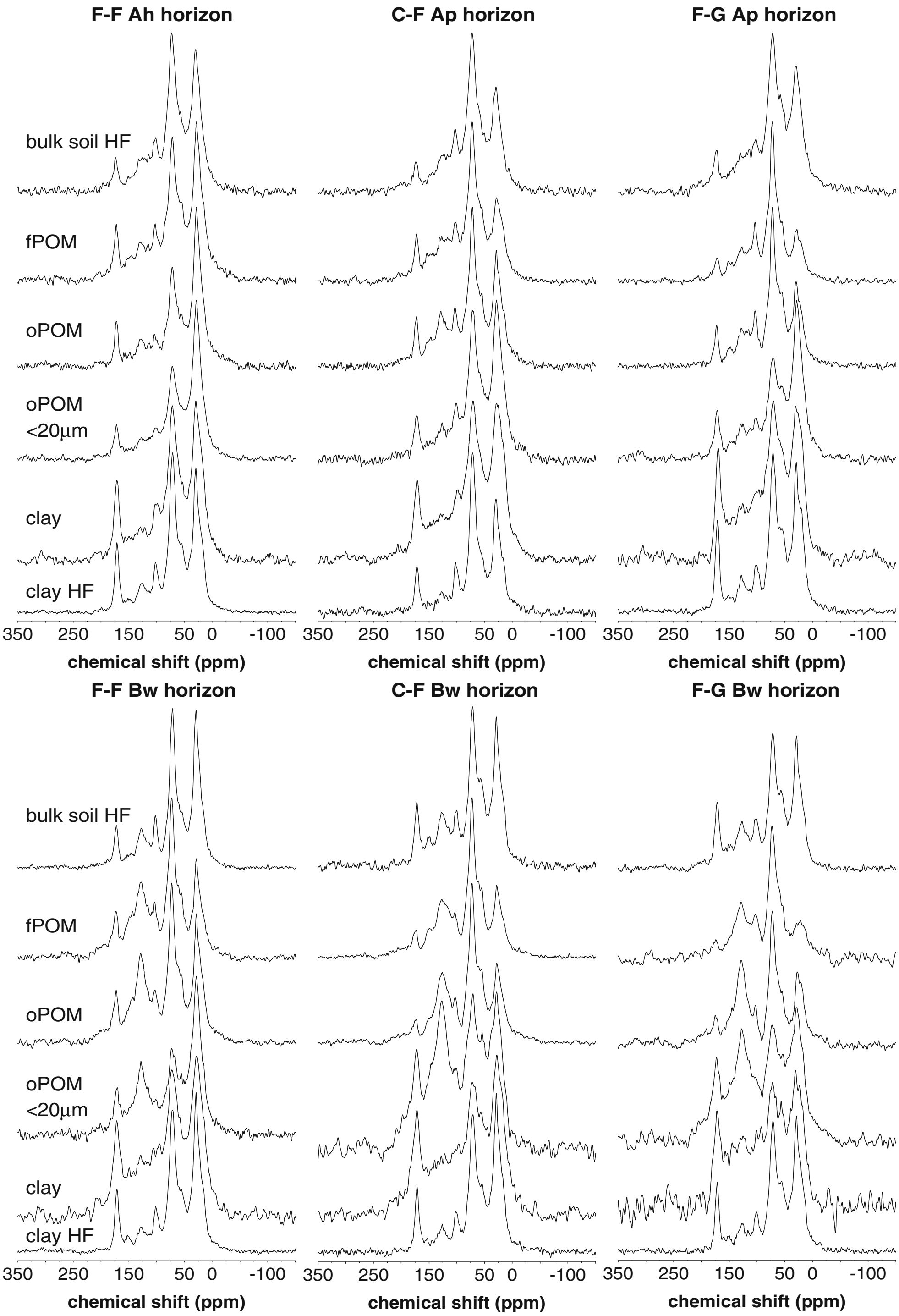


Fig. 4 ^{13}C-CPMAS-NMR spectra of the bulk soils and SOM fractions from the A and B horizons of continuous forest (*F-F*), former cropland (*C-F*), and grassland (*F-G*)

The spectra of the Oi from all three sites showed a major peak in the O/N-alkyl C region (Fig. 5). Spruce litter (forested sites) showed higher values in the alkyl C and aromatic C region in contrast to the grass litter (grassland).

Very similar NMR spectra were obtained for the more decomposed Oe and Oa horizons of both forested sites. A distinctive increase in the alkyl C and carbonyl C signals was detected for the Oe and Oa horizons compared with the Oi layer.

The spectra of the bulk soil material from the A and B horizons were similar for all sites, except slightly higher signal intensities in the alkyl C region of the samples from the continuous forest (Table 5).

A clear trend of decreasing intensities in the alkyl C region and increasing resonances in the O/N-alkyl C region was found for the fPOM in the sequence from continuous forest to former cropland and grassland (Fig. 4 and Table 5). Therefore, the spectra of the fPOM from the A horizons were similar to the Oi material under grassland and former cropland. Clear differences between the sites could be detected for the alkyl C and O/N-alkyl C of the fPOM and oPOM from the A horizons. This is well reflected in the decrease of the alkyl C/O/N-alkyl C ratios in the order of continuous forest to former cropland and grassland (Table 5). The lowest O/N-alkyl C contents were found for both horizons in the oPOM$<$20 μm.

In comparison to the A horizons, very high aromatic C signals (21–29%) were detected in the POM fractions of the B horizons. The highest signal intensities of aromatic C were found in the oPOM of the former cropland and the oPOM$<$20 μm of the grassland.

The spectra of the clay fractions after HF treatment were very similar for all sites in both horizons (Fig. 4 and Table 5) dominated by alkyl C (44–52%) and O/N-alkyl C (34–38%). Aromatic C (8–10%) and carbonyl C (7–11%) signals were considerably lower. The alkyl C/O/N-alkyl C ratios (0.7 to 0.8) were the same before and after HF treatment, whereas the aromatic C/alkyl C ratios decreased from values of around 0.5 to values of around 0.3 due to HF treatment (Table 5). The signals of the O/N-alkyl C region were larger for all samples after HF treatment.

Radiocarbon data

We analyzed samples from the unaltered continuous forest and the most altered grassland in order to obtain distinctive differences of the radiocarbon data related to different land use, as given in Table 4. The radiocarbon data showed clear differences between the continuous forest and grassland. The values for bulk soil material of the A horizons at both sites (Δ^{14}C F-F=−15.4‰, F-G=92.0‰) were higher than in the B horizons (Δ^{14}C F-F=−31.1‰, F-G=−0.4‰), whereas the grassland soils showed a higher content of bomb C. A high incorporation of bomb C was especially observed for the samples of the A horizon from the grassland. In contrast to the continuous forest, the lowest ^{14}C activity under grassland could be observed for the oPOM fraction in both horizons (Δ^{14}C F-G, Ap=55.6‰, Bw=−92.9‰), whereas the lowest Δ^{14}C values of the material from continuous forest were observed in the oPOM$<$20 μm fraction (Δ^{14}C F-F, Ah=−30.7‰, Bw=−68.6‰). In all cases, the clay fractions showed higher radiocarbon activities than the oldest POM fractions. A trend towards increasing Δ^{14}C values was observed in the order of oPOM$<$oPOM$<$20 μm$<$clay for both horizons under grassland.

Discussion

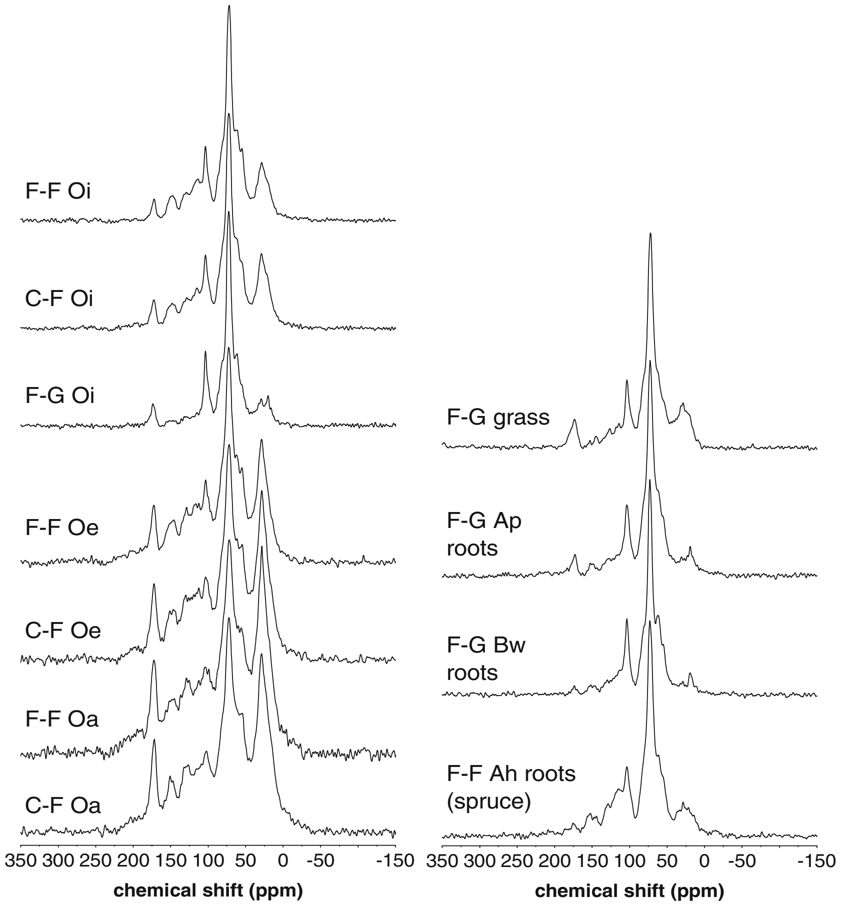
C stocks and distribution

We found no clear difference of total C stocks between continuous forest and grassland in the mineral soil (Table 3). This contradicts the findings of John et al. (2005) who observed distinctively lower total C stocks in the mineral soil in an 80-year-old Norway spruce forest compared with a grassland established in 1961. Guo and Gifford (2002) also showed an increase in soil C by 8% in a global meta-analysis due to conversion from forest to pasture but primarily in tropical and subtropical ecosystems. The observed difference of the total C stocks (Table 3) between continuous forest and grassland accounted for 2.9 kg m^{-2}, representing approximately the amount of C situated in the organic horizons at the forested sites. This finding highlights the important contribution of organic horizons to the amount of C sequestered in acidic forest soils. Although the study was conducted in central Europe, we assume a similar influence of the removal or rebuilding of organic horizons on the C balance on a global scale. We assume that the effects found are applicable to a wide range of forest ecosystems with naturally occurring organic horizons, e.g., a wide range of evergreen forests.

The main reason for the high N stocks under grassland was their periodic fertilization. The concomitant decrease of the C/N ratios (Table 3) together with higher pH and BS values led to more favorable conditions for decomposition under grassland.

The low normalized C stocks (Table 3) at the former cropland, 77 years after afforestation, did not achieve the specific C stocks of the continuous forest. Defining the continuous forest as the climax stage of the C accumulation under the given conditions, we assume that the former cropland has still not reached a new equilibrium of C input and output. The lower normalized C stocks of the Ap horizon at the former cropland can also be explained by the

Fig. 5 ^{13}C-CPMAS-NMR spectra of the organic layers or horizons as well as grass and root samples from the grassland (*F-G*) and Norway spruce roots from the Ah horizon under continuous forest (*F-F*)



delayed OM input resulting from the still ongoing C accumulation in the organic horizons after afforestation of the arable land. This is supported by the lower thickness of the organic horizons on the former cropland compared to the continuous forest. Other studies also found higher C stocks on permanent woodlands 60 to 120 years after afforestation of cultivated land, mainly due to lower C stocks of the organic horizons (Compton and Boone 2000; Wall and Hytonen 2005). Via the specific normalized C stocks (Table 3), it was possible to unravel land use impacts on C sequestration not only in the topsoil but also in the Bw horizons. In addition to the C stocks, the amount and distribution of SOM fractions entering the mineral soil was also affected by the organic horizons under forest. Using ^{14}C measurements, Baisden et al. (2002) showed that greater than or equal to 90% of fPOM turns over in less than 10 years, indicating fPOM to be a sensitive measure of land use changes. In our study, the C located in the fPOM

Table 4 Radiocarbon data of bulk soils and SOM fractions from continuous forest and grassland

Site	Horizon		Bulk soil	oPOM	oPOM< 20 μm	Clay
F-F	Ah	Δ^{14}C (‰)	−15.4±1.3	−9.7±1.5	−30.7±1.3	−27.2±1.3
		Age (year BP)	70±15	25±15	195±15	165±15
F-F	Bw	Δ^{14}C (‰)	−31.1±1.7	3.5±1.4	−68.6±1.3	−37.7±1.3
		Age (year BP)	200±15	Modern	515±15	255±15
F-G	Ap	Δ^{14}C (‰)	92.0±1.5	55.6±2.1	67.4±1.4	88.9±1.6
		Age (year BP)	Modern	Modern	Modern	Modern
F-G	Bw	Δ^{14}C (‰)	−0.4±1.4	−92.9±1.2	−46.4±1.3	7.9±1.4
		Age (year BP)	Modern	730±15	325±15	Modern

For the samples with Δ^{14}C values below 0‰, the conventional radiocarbon ages in years before present (1950) are given
F-F continuous forest, *F-G* grassland

Table 5 C/N ratios and relative contents of alkyl C, O/N-alkyl C, aryl C, carbonyl C, alkyl/O/N-alkyl C, and aromatic/alkyl C ratios of the bulk soils and the SOM fractions as revealed by ^{13}C-CPMAS NMR spectroscopy for continuous forest, former cropland, and grassland

Site	Sample	C/N (%)	Alkyl C	O/N-alkyl C	AromaticC	CarbonylC	Alkyl C /O/N-alkyl C	Aromatic C/alkyl C
A horizon								
F-F	Bulk soil		34	48	12	6	0.71	0.35
	fPOM	20.8	35	43	13	8	0.83	0.37
	oPOM	22.5	44	38	11	7	1.16	0.25
	oPOM<20 µm	14.6	44	39	9	7	1.13	0.21
	Clay	14.3	35	43	11	11	0.81	0.31
	Clay HF	15.4	34	47	10	9	0.71	0.30
C-F	Bulk soil		27	52	14	7	0.52	0.50
	fPOM	23.9	24	50	17	8	0.48	0.72
	oPOM	24.9	28	47	18	8	0.60	0.64
	oPOM<20 µm	18.6	37	45	11	7	0.84	0.28
	Clay	14.8	31	41	17	12	0.75	0.55
	Clay HF	15.4	33	52	8	7	0.63	0.24
F-G	Bulk soil		31	48	13	8	0.65	0.42
	fPOM	24.0	19	58	17	6	0.33	0.87
	oPOM	17.3	25	53	16	6	0.49	0.61
	oPOM<20 µm	12.5	41	39	12	8	1.04	0.29
	Clay	10.8	30	44	16	10	0.69	0.52
	Clay HF	11.0	34	45	10	11	0.75	0.30
Bw horizon								
F-F	Bulk soil		37	42	12	9	0.89	0.33
	fPOM	33.5	21	43	25	10	0.49	1.18
	oPOM	30.6	26	40	25	10	0.64	0.96
	oPOM<20 µm	21.5	37	32	21	10	1.15	0.58
	Clay	12.4	32	39	16	13	0.81	0.51
	Clay HF	12.3	37	45	9	9	0.83	0.25
C-F	Bulk soil		30	44	16	9	0.68	0.54
	fPOM	32.9	20	49	23	8	0.42	1.14
	oPOM	31.6	23	47	24	7	0.48	1.07
	oPOM<20 µm	15.1	23	35	27	14	0.66	1.18
	Clay	11.4	31	37	16	16	0.82	0.53
	Clay HF	10.4	38	44	9	9	0.86	0.24
F-G	Bulk soil		30	44	16	10	0.69	0.52
	fPOM	43.8	18	50	24	8	0.37	1.29
	oPOM	35.0	22	40	29	10	0.55	1.31
	oPOM<20 µm	16.3	26	34	25	14	0.77	0.96
	Clay	9.7	28	40	21	12	0.70	0.75
	Clay HF	10.2	36	45	10	9	0.81	0.28

F-F continuous forest, *C-F* former cropland, *F-G* grassland

could be ranked as continuous forest to former cropland and the regularly limed grassland for the A horizons. The favorable conditions for decomposition (low C/N, higher pH and BS) under grassland (Table 1) due to liming and faster decomposing plant species led to higher proportions of occluded C, whereas an accumulation of fPOM was found under forest. Therefore, a clear relationship was observed between soil properties, such as pH, ECEC, and BS, and the distribution and amount of C sequestered in distinctive SOM fractions. Foereid et al. (2006) also showed that a large part of fPOM was decomposed over a short period after liming on acidic grasslands in Scotland. Large amounts of particulate C were situated within the oPOM<20 µm fraction of the Ap horizon under grassland. Gerzabek et al. (2006) also showed large C amounts under grassland and arable land within particle size fractions to be situated in the silt-sized fraction, mainly present as POM or adsorbed to mineral surfaces as revealed by thermogravimetric analysis. The large C amounts stored in the POM fractions found in the A horizons at our sites disagreed with findings of DeGryze et al. (2004) who observed a clear dominance of mineral-bound C also in 0–7 cm soil depth under forests and arable lands. Nevertheless, in the Bw horizons, the total C situated in mineral fractions (clay, sand, and silt in Fig. 2) superimposed that in POM at all three sites. Concomitantly, with the vertical decrease in POM related C, the amount of mineral-associated SOM increased with soil depth at all sites. Guggenberger et al. (1995) also showed that conversion from primary forest to arable land and pasture considerably reduced SOM related to POM but barely affected the mineral bound SOM in silt and clay separates. The normalized C stocks per square meter within soil fractions showed clear differences between the pedons induced by land use alterations. The mathematical combination of normalized C stocks with the masses of SOM fractions led to even more pronounced differences between the pedons. Thus, in the topsoil and subsoil, the largest amounts of clay bound C per square meter were found under continuous forest. These differences found in mineral bound C exceeded the textural differences between the sites. This reflects the high potential of longer lasting C sequestration within fractions of slower turnover under forest in contrast to that under grassland, e.g., SOM bound on clay surfaces.

SOM—chemical characteristics

Low decomposition degrees and, therefore, good bioavailability of fresh SOM particles were shown by a low alkyl C/O/N-alkyl C ratio of the fPOM from the Ap horizon under grassland (Table 5). The composition of the fPOM was slightly altered and similar to the composition of the Oi layer and grass material. At the forested sites, decomposition processes in the overlying organic horizons altered the SOM entering the mineral soils, whereas a direct litter input took place at the grassland. For this reason, the radiocarbon activities were higher under grassland than under continuous forest. The radiocarbon activity of the bulk soil and SOM fractions of the Ap horizon pointed to a higher incorporation of bomb C under grassland, indicating also a direct litter input together with more favorable decomposition conditions. Schöning and Kögel-Knabner (2006) suggested a direct influence of the type of forest floor on the radiocarbon age of the A horizons, leading to higher ages under spruce due to a delayed litter incorporation in comparison with beech forests without organic horizons. Both Oi and fPOM material of the forested sites showed the relative increase in the alkyl C region accompanied by decreasing intensities of the O/N-alkyl C. The increase of alkyl C/O/N-alkyl C ratios from 0.3 (F-F−Oi) to 0.6 (F-F−Oa) suggested an increased extent of decomposition in deeper organic horizons (Baldock et al. 1997). Therefore, the fPOM of the A horizons, especially under continuous forest, did not show the signature of the initial litter of the Oi layer (Figs. 4 and 5). Forest clearing and subsequent tillage led to the mentioned direct litter input at the grassland, whereas the influence of historic tillage was concealed at the former cropland due to the buildup of new organic horizons. The differences in the chemical composition of the fPOM between our study sites contradict the findings of Golchin et al. (1994), who found no distinctive differences in the fPOM between forested and grassland sites. Macdonald et al. (2007) also found no clear differences, using ^{13}C-CPMAS NMR between the light fractions of an adjacent pasture and bush land. The oPOM <20 μm represented the most decomposed SOM fraction as revealed by the highest alkyl C/O/N-alkyl C ratios over all sites and horizons. These SOM particles were subject to decomposition over a long time and represented a fraction mainly preserved by chemical recalcitrance and spatial inaccessibility. Golchin et al. (1994) considered the oPOM as an SOM pool that has been accreted within aggregates over decades of root growth. Therefore, the oPOM, especially in the Bw horizons, can be seen as a good indicator for historic land use before afforestation (former cropland) and deforestation (grassland) at our sites.

We found a large increase in aromatic structures in the POM fractions of the Bw horizons in relation to the A horizons at all sites. POM fractions of the Bw horizons showed aromatic C contents of over 20%, whereas the oPOM from grassland (28.8%) and the oPOM<20 μm from the former cropland (27.5%) showed the highest values, with large peaks around 125 to 129 ppm. Probably the high intensities at the aromatic C shift region are mainly due to the presence of charred plant material, as supported by the similarity to ^{13}C-CPMAS NMR spectra of mineral soil fractions which were found to be enriched in char obtained by Preston et al. (2002). In accordance with our findings, several authors also showed an enrichment of charred material in oPOM fractions in relation to fPOM fractions (Golchin et al. 1997; Brodowski et al. 2006). Brodowski et al. (2006) also showed higher char contents under grassland than under forest and suggested charred material to be an active contributor to the formation and stabilization of microaggregates.

The ratio between aromatic C and alkyl C provided additional information on the components responsible for the chemical recalcitrance of stabilised SOM (Table 5). Indeed, the lower decomposability of the aliphatic structures dominated the preserved SOM, as shown by the low aromatic C/alkyl C ratios (oPOM=0.96, oPOM<20 μm=0.58) of the Bw horizon under continuous forest, while the higher content of aromatic C in relation to aliphatics (oPOM=1.31, oPOM<20 μm=0.96) played a dominant role in the preserved SOM of the Bw horizon under grassland. This was supported by the concomitant increase in the Δ^{14}C values in the order of oPOM<oPOM<20 μm <clay with increasing aromaticity under grassland. Therefore, the

material from the forested site was dominated by younger but more decomposed SOM rich in aliphatics in contrast to the dominance of older occluded char particles under grassland. The formation and turnover of soil aggregates seemed to be greatly influenced by the amount of charred material under grassland as already suggested by Brodowski et al. (2006), although the Δ^{14}C values were within the range reported for SOM studied on other Cambisols (Schöning and Kögel-Knabner 2006; Eusterhues et al. 2007). A strong influence of historic burning of tree residues since the first settlement (thirteenth century) was still visible by the high age of occluded SOM. The prediction of aggregate turnover solely based on ^{14}C measurements may be biased by accumulated charred material, especially at sites with a high SOM turnover due to favorable decomposition conditions (low C/N, high pH and BS), as were present at our grassland. Nevertheless, the charred SOM particles must have been subject to vertical transport as could be shown by the increased aromaticity of SOM fractions in the Bw horizons.

^{13}C-CPMAS NMR spectra of the clay fractions (Fig. 4 and Table 5) pointed to carbohydrates, aliphatics, and organic acids as the major HF resistant components associated with clay minerals at our sites. No distinctive differences were obtained for the clay fractions after HF treatment between the sites, probably because management alterations did not influence the composition of presumably older mineral bound SOM at our sites. The similar clay mineralogy of the adjacent sites led to the preservation of similar HF resistant SOM compounds. Larger contents of O/N-alkyl C could be shown for the HF resistant SOM in our soils evolved from gneiss, in contrast to the Cambisol studied by Eusterhues et al. (2007) evolved from Triasic sandstone. No clear evidence was found for a preferential dissolution of aromatic compounds by HF as stated by Eusterhues et al. (2007), who found a stronger dissolution of aromatic compounds due to HF. Schöning et al. (2005a) suggested lower alkyl C and O/N-alkyl C intensities, due to signal suppression by high Fe contents, which might explain the increased intensities in both regions after Fe removal by the HF treatment of our samples (Table 5). This finding is also supported by the relative similarities of alkyl C/O/N-alkyl C ratios of the clay fractions before and after HF treatment (Table 5). No distinctive translocation of old aromatic C into the clay separates was assumed due to the similar chemical composition and higher radiocarbon activities of the clay fractions at our sites rich in old highly aromatic POM fractions (Figs. 4 and 5). The positive Δ^{14}C values of the clay fractions from Ap and Bw horizon under grassland indicated a high incorporation of bomb C. Probably at the grassland site, the turnover of mineral bound SOM, mainly driven by adsorption and desorption of DOM and microbial residues, occurred on a shorter timescale than that of charred POM compartments with a very low bioavailability.

Conclusions

The removal of organic horizons after forest clearing led to markedly lower total C stocks. The important contribution of intact organic horizons to the chemical quality and the amounts of SOM reaching the mineral soil might be applicable on a global scale. The ongoing C accumulation within regrowing organic horizons at the former cropland indicate the long-lasting influence of land use alterations, which might also be valid for other secondary forest ecosystems on other soil types. The highly altered C compounds within the fPOM fraction contributed significantly to the C stocks under forest. Larger specific C stocks of the clay fraction indicated a longer ranging ability for C sequestration of the continuously forested pedon. Residual char particles were predominantly situated within soil aggregates, suggesting an important contribution to aggregate buildup. In contrast to the aromatic C structures under grassland, aliphatic C structures dominated the SOM under forest. No relocation of aromatic C situated within the oPOM fraction onto mineral surfaces was found. Combined studies of SOM stocks and composition should be extended to a wide range of land use systems and soil types in order to enable global predictions of C cycling. The study of stabilizing mechanisms and fluxes of C and N cycles simultaneously is crucial for further modeling.

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