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Review Article

Storage and stability of organic matter and fossil carbon in a Luvisol and Phaeozem with continuous maize cropping: A synthesis§

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Abstract

Quantitative information about the amount and stability of organic carbon (OC) in different soil organic-matter (OM) fractions and in specific organic compounds and compound-classes is needed to improve our understanding of organic-matter sequestration in soils. In the present paper, we summarize and integrate results performed on two different arable soils with continuous maize cropping (a) Stagnic Luvisol with maize cropping for 24 y, b) Luvic Phaeozem with maize cropping for 39 y) to identify (1) the storage of OC in different soil organic-matter fractions, (2) the function of these fractions with respect to soil-OC stabilization, (3) the importance and partitioning of fossil-C deposits, and (4) the rates of soil-OC stabilization as assessed by compound-specific isotope analyses. The fractionation procedures included particle-size fractionation, density fractionation, aggregate fractionation, acid hydrolysis, different oxidation procedures, isolation of extractable lipids and phospholipid fatty acids, pyrolysis, and the determination of black C. Stability of OC was determined by ^{13}C and ^{14}C analyses. The main inputs of OC were plant litter (both sites) and deposition of fossil C likely from coal combustion and lignite dust (only Phaeozem).

Total soil OC stocks down to a depth of 65 cm (7.83 kg m^{-2} in the Luvisol and 9.66 kg m^{-2} in the Phaeozem) consisted mainly of mineral-bound OC (87% of total SOC in the Luvisol and 69% in the Phaeozem). In the Luvisol, free light particulate OM, OM associated with sand and coarse silt, and particulate OM occluded in macro-aggregates represented SOM fractions with mean turnover times shorter than that of the bulk soil OC (54 y). Additionally, the turnover of all individual compounds or compound classes (except for black carbon) was faster than that of bulk soil OC. These OM fractions that were less stable than the bulk soil OM made up 13% to 20% of the total OC. Organic matter in fine and medium silt and clay fractions, particulate OM occluded in micro-aggregates (53–250 μm) and OM resistant to acid hydrolysis had intermediate turnover times of about 50–100 y. These fractions with intermediate turnover times contributed 70%–80% to total soil OC. Passive OM with turnover times >200 y was isolated from the mineral-bound OM by different oxidation procedures (H_2O_2, $Na_2S_2O_8$) and made up ≤10% of the total OC. The isotopic signature of PLFAs suggests an efficient recycling of OC derived from C3 substrate.

In the Phaeozem, partitioning of maize-derived C exhibited a pattern similar to the Luvisol, but turnover rates of vegetation-derived soil OC were lower, probably because of the considerably smaller input of plant residues. Fossil C contributed approx. 50% to the total OC and accumulated preferentially in the particulate OM occluded in aggregates and in the fine-sand and

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coarse-silt fractions. It formed a large stock of passive soil OM but a minor part also entered the microbial C cycle. The results show that the partitioning of OC derived from vegetation and deposition of fossil compounds among soil fractions differed mainly because of their different bioavailability and recalcitrance. There was no evidence for a high recalcitrance of individual plant compounds. Mineral-bound OM resistant to oxidation by H_2O_2 and $Na_2S_2O_8$ represented highly stable OC pools in both soils.

Key words: soil organic matter / ^{13}C natural abundance / maize cropping / radiocarbon / fossil carbon / organic-matter fractions / organic-carbon turnover / lipids / lignin / black carbon / pyrolysis

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1 Introduction

The storage of organic carbon (OC) in agricultural soils depends on the quantity and quality of organic-matter (OM) inputs (plant residues, organic fertilizers), and on its microbial turnover. Not all constituents of soil organic matter (SOM) are rapidly converted to CO_2, and they may be then stabilized in soil for a limited period of time. Several mechanisms have been described that contribute to SOM stabilization: (1) selective preservation resulting from recalcitrance of SOM, (2) spatial inaccessibility of soil OM to decomposer organisms due to occlusion, intercalation, hydrophobicity, and encapsulation, and (3) interaction with mineral surfaces and metal ions (*e.g.*, *Christensen*, 1996; *Sollins* et al., 1996; *Krull* et al., 2003; *von Lützow* et al., 2006). The contribution of these different mechanisms to OM preservation in different soils and soil horizons is not well understood. Several physical procedures have been proposed to isolate physically stabilized SOM fractions with different composition and stability and to characterize and quantify mechanisms of SOM stabilization in soils. These methods include aggregate-size fractionations (*e.g., Oades* and *Waters*, 1991; *Jastrow* et al., 1996; *Puget* et al., 2000), particle-size fractionations (*e.g.*, *Tiessen* et al., 1981; *Christensen*, 2001; *Jolivet* et al., 2003), density fractionations (*e.g.*, *Balesdent* et al., 1998; *Baisden* et al., 2002; *Yamashita* et al., 2006), and their combinations (*e.g.*, *Cambardella* and *Elliott*, 1993; *Rodionov* et al., 2000; *Six* et al., 2002; *John* et al., 2005). To account for chemical stabilization processes, different extraction procedures (*Balesdent*, 1996; *Ludwig* et al., 2003), wet oxidation (*Eusterhus* et al., 2005; *Mikutta* et al., 2005), acid hydrolyses (*Paul* et al., 2001; *Poirier* et al., 2003; *Plante* et al., 2006), and various combinations of these procedures (*Helfrich* et al., 2007) have been used, frequently on physically isolated soil fractions (*cf.*, *e.g., von Lützow* et al., 2007 for a recent review). In addition, analysis of the quantity and recalcitrance of individual organic compounds and groups of compounds provides information about their stability and their significance for sequestration and stabilization of soil OC. This approach has recently been successfully applied to soil lipids (*Wiesenberg* et al., 2004a, b), lignin (*Dignac* et al., 2005; *Heim* and *Schmidt*, 2007), carbohydrates (*Derrien* et al., 2006), amino acid enantiomers (*Glaser* and *Amelung*, 2002), phospholipids fatty acids (*Kramer* and *Gleixner*, 2006), and pyrolysis products (*Gleixner* et al., 2002). Much of this research has been performed in the framework of the Priority Program 1090 ("Soils as sinks and sources of CO_2") of the German Science Foundation (*cf.*, *Kögel-Knabner* et al., 2008, this issue, pp. 5–13).

In this paper, we summarize and integrate results of several studies from this program, performed on two arable soils with different texture and input of OC under long-term continuous maize cropping to identify: (1) the storage of OC in differently isolated SOM fractions, (2) the function of these fractions with respect to soil OC stabilization, (3) the importance of fossil-C deposits for OC storage in different soil fractions and influence on calculated OC turnover times, (4) the rates of soil-OC stabilization assessed by compound-specific isotope analyses, and (5) the importance of specific mechanisms of OC stabilization.

2 Description of the long-term–maize cropping sites

The results are from two field experiments with continuous maize cropping in Germany (*cf., Kögel-Knabner* et al., 2008, this issue, pp. 5–13). The continuous maize-cropping experiment in Rotthalmünster (48°21′47″ N, 13°11′46″ E, elevation: 360 m asl) was established in 1979 on a Stagnic Luvisol derived from loess. The soil texture was a silty loam consisting of 11% sand, 73% silt, and 16% clay. The dominant minerals of the clay fraction (A horizon) were illite > kaolinite > vermiculite. The mean annual precipitation and temperature were 886 mm and 8.7°C, respectively. Fertilization was achieved solely with mineral fertilizers, and only the grain was harvested. The mean amount of maize C input by aboveground residues (total aboveground biomass except grains) and roots that was ploughed in was estimated to 0.63 kg m^{-2} y^{-1} (*John* et al., 2005). An adjacent soil with continuous wheat cropping (since 1969) was used as reference site for the determination of the amount of young, maize-derived C and older C from C3 vegetation in different fractions of soil OC. The depth of the ploughed horizon was 30 cm for both fields (maize and wheat).

The continuous maize-cropping experiment at Halle (51°30.8′ N, 11°59.9′ E, elevation: 110 m asl) was established in 1961 on a Luvic Phaeozem derived from sandy loess. The texture of the soil was a loamy sand consisting of 70% sand, 20% silt, and 10% clay. The dominant minerals of the clay fraction (A horizon) were illite and smectite. The mean annual precipitation was 465 mm, and the mean air temperature was 9.2°C. Maize was produced for silage-making with mineral NPK fertilization (NPK treatment) and without fertilization

(0-fertilization treatment). The mean quantity of maize C input (approx. 0.08 kg m^{-2} y^{-1} for the NPK treatment) was much lower than that of the Luvisol at Rotthalmünster because only short maize stubbles and roots were ploughed in. An adjacent field with continuous rye cropping (since 1878) was used as reference site for the ^{13}C natural abundance approach. The depth of the ploughed horizon was 25–30 cm. The experiment at Halle is located in an industrial area where inputs to the soil of coal dust and coal-combustion products (*e.g.*, soot from the nearby industry, former steam engines, and thermal-power plants) took place. This resulted in high amounts of fossil C in this soil as indicated by low ^{14}C concentrations (Tab. 1).

The two experimental sites, field management, vegetation history, and soils were described in more detail by *Flessa* et al. (2000), *John* et al. (2005), *Ludwig* et al. (2005), and *Kögel-Knabner* et al. (2008, this issue, pp. 5–13). General soil properties of the maize fields in Rotthalmünster and Halle are summarized in Tab. 1.

3 Total and fossil organic C in soils

The two experimental sites differ with respect to several key factors that influence storage and stabilization of soil OC. The most important differences are: (1) the annual input of plant residues, (2) the input of fossil C by atmospheric deposition, (3) soil texture and genesis, and (4) annual precipitation.

Despite a lower input of maize residues and a considerably higher sand content, total soil OC stocks down to a depth of 65 cm were larger in the Phaeozem (9.66 kg m^{-2}) than in the Luvisol (7.83 kg m^{-2}), this difference being largely attributed to subsoil SOM (Tab. 1). The larger soil OC stocks in the Phaeozem were based on the larger quantities of old C derived from C3 vegetation (including deposition of fossil C), since the amount of young maize-derived soil OC was 2.4 times higher in the Luvisol (2.24 kg m^{-2}) than in the Phaeozem (0.92 kg m^{-2}, calculated from Tab. 1).

The ratio (maize-derived soil OC stocks) to (total maize C input) indicated that turnover of a mass unit maize residues was approx. 2 times more rapid in the Luvisol (total maize-derived soil OC 2.24 kg m^{-2}, total maize C input 15.12 kg m^{-2}) than in the Phaeozem (total maize-derived soil OC 0.92 kg m^{-2}, total maize C input 3.12 kg m^{-2}). The portion of maize-derived C retained in the soil profile was about 15% (Rotthalmünster) and 30% (Halle) of the estimated cumulative maize C input (calculated from data of *Flessa* et al., 2000; *Ludwig* et al., 2003, 2005; *John* et al., 2005). This difference might be explained by litter quality: maize residues in Rotthalmünster (Luvisol) consisted mainly of aboveground biomass, whereas in Halle (Phaeozem) mainly maize roots were incorporated. A slower decay of maize roots compared with aboveground litter has been attributed to a higher lignin-to-N ratio in root material and to the more direct introduction of root-derived products into the soil clay matrix, which may protect them from microbial degradation (*Balesdent* and *Balabane*, 1996). In addition, the drier conditions at the Halle site (precipitation of 465 mm compared to 886 mm at Rotthalmünster) may have contributed to the slower decomposition of plant litter.

The apparent turnover time of soil OC was calculated from the change of the C3- and C4-derived soil OC according to the following formula:

$$T = 1 / k = -(t - t_0) / \ln(C_t / C_{t0}), \quad (1)$$

where k stands for the rate constant of the first-order decay, t for the year of sampling, t_0 for the year of vegetation change, C_t for the remaining proportion of C3-C at the time of sampling (%), and C_{t0} for the proportion of C3-C at t_0 (100%).

Table 1: Soil pH (0.01M $CaCl_2$), C : N ratio, soil organic C (SOC, concentration and stock), percentage of maize-derived soil organic carbon, mean apparent turnover time of SOC (calculated from ^{13}C natural abundance) and mean ^{14}C concentration of the humic and humic acid fraction at different depths of the soils with continuous maize cropping at Rotthalmünster (Stagnic Luvisol) and Halle (Luvic Phaeozem, NPK treatment).

Site	Depth	pH*	C : N*	SOC*		Maize-derived SOC*	SOC turnover time	^{14}C concentration#	
								Humic	Humic acid
	[cm]			[g kg^{-1}]	[kg m^{-2}]	[% of total SOC]	[y]	[pMC]	
Rotthalmünster	0–30	6.9	9.6	12.9	5.35	35.6	54	103	110
Rotthalmünster	30–45	6.5	8.7	6.7	1.55	14.9	144	82	101
Rotthalmünster	45–65	6.6	7.4	4.1	0.93	10.3	223	73	100
Halle	0–25	5.7	16.0	12.8	4.79	14.8	244	32	50
Halle	25–35	6.4	10.3	7.3	1.28	5.5	696	42	61
Halle	35–45	6.7	9.7	7.2	1.27	5.6	684	nd**	nd**
Halle	45–55	7.0	10.1	7.3	1.28	2.7	1393	nd**	nd**
Halle	55–65	7.2	10.2	5.9	1.04	3.4	nd**	54	65

* Data from *Flessa* et al. (2000), *Ludwig* et al. (2003 and 2005)

\# Data from *Rethemeyer* et al. (2004); ^{14}C data of the site "Halle" are from the continuous-rye field; sampling depth for some of the ^{14}C analysis slightly differed from the values given in the table.

** not detected

C_t was calculated as 100% – (f × 100%). This approach (Eq. 1) is based on the assumptions that the fractions are homogeneous and can be described with a single-pool model.

The mean apparent soil-C turnover was 54 y in the Luvisol and 244 y in the Phaeozem (Tab. 1, data from *John* et al., 2005 and calculated from data of *Ludwig* et al., 2003). Radiocarbon concentrations in bulk soil of the Phaeozem (54.4 pMC) revealed that the high C-turnover time calculated for this soil was influenced by the accumulation of fossil OC (*Rethemeyer* et al., 2004a). As a consequence of these fossil-C stocks with a C3 isotopic signature, the calculated C turnover did not adequately reflect the stability of SOC derived from plant residues (*Rethemeyer*, 2004).

The contribution of fossil C that contains no ^{14}C to total SOC can be estimated from a simple mass-balance calculation if the ^{14}C concentration of SOC derived from vegetation (SOC free of fossil C) is known:

$$X = [1 - (^{14}C_{measured} / {}^{14}C_{(SOC\ free\ of\ fossil\ C)})] \times 100, \quad (2)$$

where X is the amount of fossil C (% of total SOC), $^{14}C_{measured}$ is the ^{14}C concentration (pMC) of bulk soil SOC, and $^{14}C_{(SOC\ free\ of\ fossil\ C)}$ is the ^{14}C concentration (pMC) of SOC derived from vegetation (SOC free of fossil C).

Assuming a modern ^{14}C age of soil OC derived from vegetation in the Ap horizon such as that found in Rotthalmünster (107.6 pMC), it was estimated that the deposition of fossil C contributed 50% to the total soil OC in the Ap horizon of the Phaeozem at Halle, whereas the increasing radiocarbon concentration with soil depth reflected primarily the decreasing contamination with fossil C (*Rethemeyer*, 2004; *Rethemeyer* et al., 2004a). There was no evidence of fossil-C contamination of the Luvisol. Subtracting the 50% fossil C from the C stocks in the Ap horizon of the Halle soil results in an average C stock derived from vegetation of 2.4 kg m^{-2}, which is about half that of the SOC found in the Luvisol Ap. *Rethemeyer* (2004) proposed to model the ^{14}C concentration of soil OC that originates from vegetation using the Rothamsted Carbon Model (RothC) taking into account atmospheric ^{14}C variations and the decay of plant residues. For the Phaeozem at Halle, this approach resulted in a ^{14}C concentration of soil OC derived from vegetation of 114 pMC (*Rethemeyer*, 2004). Using this modeled ^{14}C value in Eq. 2 results in a similar amount of fossil C (52% of total soil OC) as the estimate that was based on the ^{14}C concentration of soil OC in the Ap horizon of the Luvisol (50% of total soil OC).

The results show that deposition of fossil-C compounds with high recalcitrance can be an important factor determining the quantity and turnover of OC in soils of industrialized areas, where energy production and heating is or was mainly based on coal burning. In addition to the deposition of fossil C, features of the Phaeozem genesis such as extensive bioturbation and stabilization of OM in deeper soil horizons have to be taken into consideration as a factor determining current soil OC stocks, particularly in the subsoil. To further understand the mechanisms of OM stabilization at the sites, additional information is required on the localization of SOM within operationally defined C pools and on its compound-specific properties.

4 Physical-fractionation procedures

4.1 Organic matter in particle-size fractions

The major part of soil OC (84% in the Phaeozem and 88% in the Luvisol, Ap horizon) was associated with the silt and clay fraction in both soils, despite the difference in yield of the fraction <63 μm in these soils (Tab. 2). This shows, that storage and stabilization of organic compounds was controlled mainly by the formation of organo-mineral associations. Since the input of root debris decreased and the degree of OM decomposition increased with soil depth, the contribution of silt- and especially clay-associated OM to total soil OC even increased in deeper horizons (*Ludwig* et al., 2005), as reported for other soils with similar genesis (*Rodionov* et al., 1998). Various mechanisms such as ligand exchange, polyvalent cation bridges, and hydrophobic interactions contribute to the binding of organic compounds to mineral surfaces (*von Lützow* et al., 2006). The specific loading of mineral particles <63 μm with organic compounds (expressed as mg C [kg particle-size fraction]$^{-1}$) was higher in the Phaeozem than in the Luvisol, as commonly found for sites with higher sand content (*Christensen*, 1996), and ^{14}C data revealed the binding of fossil C to mineral surfaces in the Phaeozem (Tab. 2).

The C : N ratio decreased with particle size since (Tab. 2). Interlayer NH_4^+ and especially microbial products that accumulate in the fine-mineral fractions (*Guggenberger* et al., 1994; *Kandeler* et al., 2000) probably contributed to this general phenomenon. The apparent turnover time of C3-derived C (calculated from Eq. 1) in the Ap horizon of the Luvisol increased with decreasing particle size (from 28 y in the coarse-silt fraction to 77 y in the clay fraction, Tab. 2). A similar order of OC stability was found in the subsoil horizons, but the turnover times in the subsoils were considerably higher (*Ludwig* et al., 2005). *Von Lützow* et al. (2007) concluded that lower C-turnover rates in clay fractions when compared to coarser-particle fractions are due to a combination of different mechanisms of SOM stabilization: the chemical change in OM composition, an increase in spatial inaccessibility and the adsorption of OM on mineral surfaces.

The fossil-C deposits at Halle contributed to higher C : N ratios in all particle-size fractions (Tab. 2). Assuming a constant modern ^{14}C age of the soil OC derived from plant residues in all particle-size fractions of 114 pMC (*Rethemeyer*, 2004, see section 3), it was calculated (Eq. 2) that 41% to 83% of the soil OC in these fractions originated from fossil C (*Rethemeyer*, 2004). The relative accumulation of fossil C was highest in the fractions medium and fine sand and coarse silt. Even if this approach to estimate the proportion of fossil C is a simplification since C turnover and thus ^{14}C activity of soil OC originating from vegetation is not the same in different particle-size fractions (see results from Rotthalmünster), it provides quite reliable estimates of fossil C since the variation of the ^{14}C age in soil OC fractions originating from

plant residues in biologically active Ap horizons is small compared to the ^{14}C shift induced by the admixture of fossil C. The accumulation of fossil C resulted in high bulk soil OC-turnover times, as calculated from $\delta^{13}C$ data, of 216 to 378 y in clay and silt fractions (Tab. 2). Carbon-turnover times were considerably shorter and decreased from sand (43 y) to clay (159 y) when the amount of fossil C was deducted from the total soil OC content and changes of C4-derived soil OC stocks were related to the fossil C–free soil (*Rethemeyer*, 2004). These corrected turnover times provided a more realistic picture of the stability of plant-derived C in different particle-size fractions.

The results show that particle-sizes fractionation was able to isolate SOM pools with different composition and stability. The higher C concentrations in bulk soil and particle-size fractions at Halle can in part be explained by the higher recalcitrance of fossil-C inputs that were detected in all size fractions.

4.2 Organic matter in density fractions

Soil density fractionation was used to determine the quantity, composition, and stability of free particulate OM (fPOM, density < 1.6 g cm^{-3}), particulate OM occluded in aggregates (oPOM with the density < 1.6 g cm^{-3} [$oPOM_{<1.6}$] and 1.6 to 2.0 g cm^{-3} [$oPOM_{1.6–2.0}$]), and mineral-bound OM (density > 2 g cm^{-3}) (*John*, 2003; *John* et al., 2005; *Yamashita* et al., 2006). The particulate OM (fPOM + oPOM) contributed 13% (Luvisol) and 31% (Phaeozem) to the total soil OC stored in the Ap horizons (Fig. 1). Larger stocks of POM C in the Phaeozem than in the Luvisol have to be attributed mainly to the accumulation of fossil C in free and occluded POM. The ^{14}C concentration of OC in the Phaeozem Ap horizon (data from the maize field without fertilization) was considerably lower in the oPOM fraction (10 to 26 pMC) than in fPOM and in the mineral-bound OM (57 to 59 pMC) (*Rethemeyer* et al., 2005). In contrast, OC in all density fractions of the Luvisol had a modern ^{14}C age of 103 pMC except OC in the $oPOM_{<1.6}$ fraction that had a lower ^{14}C content (98 pMC). Based on Eq. 2 and on the assumption that OC in soil density fractions that originate from vegetation had a modern ^{14}C age of 114 pMC (*Rethemeyer*, 2004; *cf.*, section 3.), it was estimated that fossil C contributed 50% and 92% to the total OC in fPOM and $oPOM_{<1.6}$, respectively. The results agree with the observation of preferential accumulation of charcoal in POM fractions of soils with repeated burning (*Skjemstad* et al., 1990). The amount of POM occluded in aggregates (oPOM in Fig. 2) was more than two times higher in the Phaeozem than in the Luvisol even if obvious macro-aggregation occurred only in the finer-textured Luvisol. This suggested that extensive micro-aggregation occurred in the Phaeozem, and the high proportion of fossil C in oPOM (up to 90%) raised the question about the influence of fossil C on aggregate formation (*Brodowski* et al., 2006).

Carbon-13 nuclear–magnetic resonance analyses of OM in soil density fractions of the Luvisol confirmed previous findings in other soils (*e.g., Golchin* et al., 1994) that OM in the isolated density fractions represented different stages of SOM decomposition: the contributions of O-alkyl-C to total signal intensity decreased and those of alkyl-C, carbonyl-C, and aryl-C increased in the order maize litter, fPOM, oPOM (*Helfrich* et al., 2006). Aromaticity was highest in mineral-associated OM. The apparent turnover time of C3-derived C (calculated from Eq. 1) in the Luvisol Ap horizon increased in the order: fPOM (22 y) < $oPOM_{1.6–2.0}$ (49 y) < mineral-bound OM (63 y) (Fig. 1), which is again in line with previous findings for other soils (*von Lützow* et al., 2007). Yet the apparent C-turnover time of oPOM increased with decreasing aggregate size from 20 to 30 y in aggregates >1000 μm to 166 y in aggregates <53 μm (*Yamashita* et al., 2006). These findings support the hypothesis that macro-aggregates (>250 μm), micro-aggregates (53 to 250 μm), and the smallest micro-aggregate stuctures (<53 μm) have different roles in the protection of SOM (*Besnard* et al., 1996; *Jastrow* et al., 1996). It

Table 2: Yield (as percentage of soil dry weight), C : N ratio, soil organic-carbon (SOC) content, contribution of maize-derived SOC to total SOC, ^{14}C concentration of SOC and apparent turnover time of total SOC (calculated from ^{13}C natural abundance), and vegetation-derived SOC (lignite-free SOC, calculated after estimating the amount of fossil C from the ^{14}C concentration of SOC, see Eq. 2 and section 4.1) of fine-particle-size fractions in the Ap horizon of the soils with continuous maize cropping at Rotthalmünster (Stagnic Luvisol) and Halle (Luvic Phaeozem, NPK treatment).

Site	Particle size	Yield*	C : N*	SOC*		Maize-derived SOC*	^{14}C concentration#	SOC turnover time	
								Total SOC*	lignite-free SOC#
	[μm]	[%]		[% of total SOC]	[g (kg fraction)$^{-1}$]	[%]	[pMC]	[y]	
Rotthalmünster	20–63	40.5	11.6	11.9	3.5	57.2	nd**	28	nd**
Rotthalmünster	2–20	30.4	9.6	28.1	11.1	30.7	nd**	65	nd**
Rotthalmünster	<2	17.4	8.5	48.1	33.1	26.9	nd**	77	nd**
Halle	20–63	13.7	28.8	19.7	17.4	11.9	33	308	108
Halle	2–20	10.9	16.9	32.5	35.2	9.8	50	378	169
Halle	<2	8.6	10.4	31.6	42.5	16.5	67	216	159

* Data taken or calculated from *John* (2003) and *Ludwig* et al. (2005)

\# Data from *Rethemeyer* (2004): The mean apparent turnover time of lignite C–free SOC was calculated for the adjacent unfertilized maize plot (0-fertilization treatment).

** not detected

is probable that more rapid turnover of macro-aggregates contributed to a more rapid cycling of its oPOM (*Oades* and *Waters*, 1991).

In the Phaeozem, accumulation of fossil C in all POM fractions resulted in very long mean apparent turnover times calculated from $\delta^{13}C$ values between 148 y (fPOM) and >1000 y ($oPOM_{<1.6}$) (Fig. 1). Correcting for the amount of fossil C as described in section 4.1 (considering only SOC pools free of fossil C in Eq. 1; *Rethemeyer*, 2004) resulted in considerably shorter turnover times of plant-derived C (52 to 165 y, Fig. 1), and the same sequence of OC stability in soil density fractions as in the Luvisol (fPOM < mineral-bound < $oPOM_{1.6–2.0}$ < $oPOM_{1.6}$) was obtained (Fig. 1). The results show that C partitioning derived from the two different substrates (plant residues, lignite-derived compounds) among soil density fractions differed: The more recalcitrant fossil compounds accumulated preferentially in POM fractions in particular in oPOM, wheras C from plant residues was more rapidly introduced into the heavy, mineral-associated SOM pool. The results of ^{13}C-NMR analyses revealed that the stability of POM fractions derived from plant litter depended largely on their chemical structure and recalcitrance (*Helfrich* et al., 2006). However, current results do not allow a clear differentiation between C stabilization by physical protection within aggregates and recalcitrance.

5 Chemical-fractionation procedures

To elucidate the chemical recalcitrance of SOM at soil interfaces, five chemical-fractionation methods (acid hydrolysis, treatment with H_2O_2, $Na_2S_2O_8$, NaOCl, and demineralization of the NaOCl-resistant fraction [NaOCl+HF]) were applied to the Ap horizon of the Luvisol and Phaeozem and to the E horizon (30–45 cm) of the Luvisol (*Helfrich* et al., 2007). Fresh plant debris was removed by density fractionation before chemical fractionation, because acid hydrolysis and oxidation by H_2O_2 may leave fresh aliphatic plant materials unaffected (*von Lützow* et al., 2007). Across all procedures, 15%–35% (Phaeozem, Ap horizon) and 9%–22% (Luvisol, Ap) of the mineral-bound soil OC survived these chemical attacks, and the proportions of residual soil OC increased with soil depth (11%– 38% in the Luvisol E horizon). Similar results were reported also for forest soils, suggesting that such formations of tight organic loadings on minerals develop during SOM genesis (*Eusterhues* et al., 2003, 2005). The lower proportion of resistant soil OC (as percentage of initial, mineral-bound soil OC) in the A horizon most likely resulted from higher C loads compared to deeper soil horizons. High OC loads are probably associated with a weaker association of recently deposited SOC to mineral surfaces due to the occupation of high-affinity sites by pre-existing OM. These weaker bonds probably offered less protection to chemical treatments. The natural abundance of ^{13}C and ^{14}C confirmed that the residual OM was old and that especially the $Na_2S_2O_8$ and H_2O_2 treatments successfully removed young and maize-derived SOC (Fig. 2). The mean ^{14}C age of SOC calculated from the pMC values shown in Fig. 2 was 1,000 to 10,000 y higher after chemical fractionation than in the mineral-bound SOC and increased in the order: NaOCl < NaOCl+HF stepwise hydrolysis << H_2O_2 $Na_2S_2O_8$ (Fig. 2). Lower ^{14}C concentrations and correspondingly higher ^{14}C ages of residual SOC fractions were found for the Phaeozem, suggesting that fossil-C contaminants contributed to these refractory SOM pools.

The results show that all tested chemical-fractionation procedures were able to isolate an older, hence more stable C pool, but treatment with H_2O_2 and $Na_2S_2O_8$ were the most effective methods. However, none of the residual C pools adequately

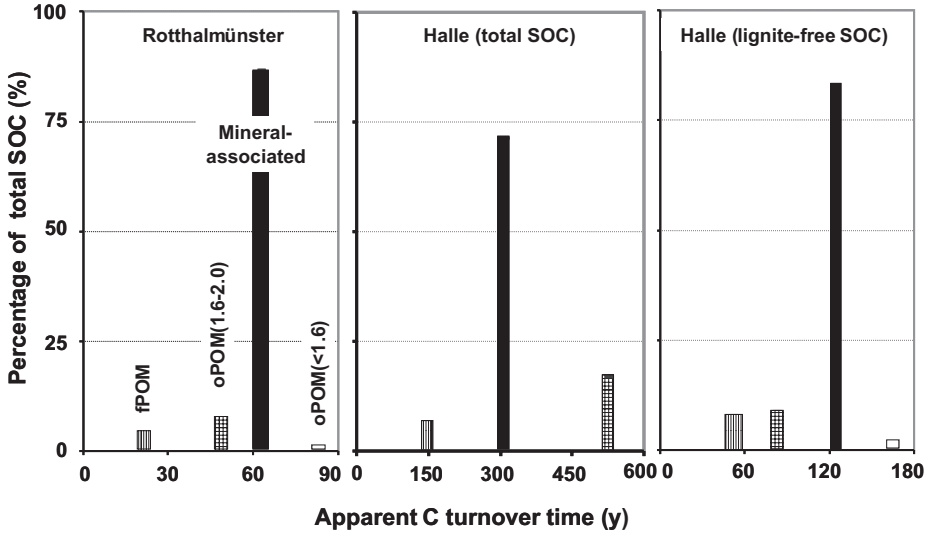

Figure 1: Storage and apparent turnover time of organic carbon (OC) in soil density fractions (free particulate OM (fPOM), light particulate OM occluded in aggregates ($oPOM_{<1.6}$), dense particulate OM occluded in aggregates ($oPOM_{1.6-2.0}$), mineral-associated OM) of the Ap horizons of the continuous maize fields at Rotthalmünster (Stagnic Luvisol) and Halle (Luvic Phaeozem, 0-fertilization treatment). Turnover times were calculated from ^{13}C values of fractions separated from soils with C3- and C4-crops (Eq. 1, section 3). For the soil at Halle, OC turnover was calculated for total soil OC including fossil C and for vegetation-derived soil OC (lignite-free SOC). The amount of fossil C was estimated from the ^{14}C concentration of soil OC (Eq. 2, section 3). The proportion of maize C in the fraction $oPOM_{<1.6}$ of the Halle soil was too low to calculate a reliable turnover time for total SOC. (Data from *John*, 2003; *John* et al., 2005; *Rethemeyer*, 2004; *Rethemeyer* et al., 2005).

reflected the size of the inert–organic matter pool (IOM) as estimated by the Rothamsted Carbon Model for these sites (*Ludwig* et al., 2003, 2005). For the Phaeozem, the model IOM pool was 3 to 5 times larger than the amount of residual OC after chemical fractionation, and for the Luvisol the H_2O_2- and $Na_2S_2O_8$-resistant C fractions were about twice as large as the calculated IOM pool of the Rothamsted Carbon Model.

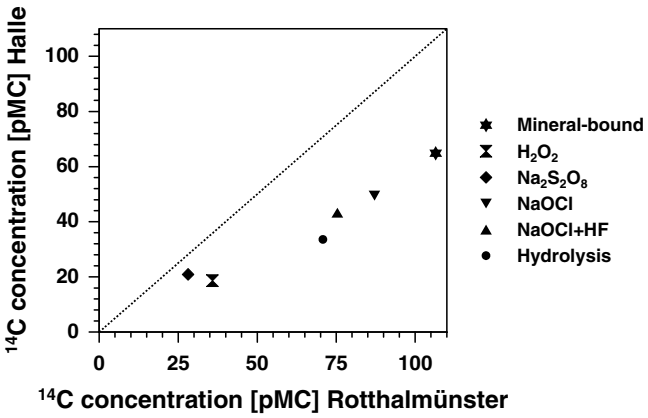

Figure 2: Mean ^{14}C concentration (expressed as pMC) of soil organic carbon (SOC) in the Ap horizon of the Luvic Phaeozem at Halle (NPK treatment) and the Stagnic Luvisol at Rotthalmünster after removal of light particulate organic matter (= mineral-bound SOC) and after subsequent chemical-fractionation procedures as described by *Helfrich* et al. (2007) (SOC resistant to hydrolysis, to oxidation by H_2O_2, $Na_2S_2O_8$, NaOCl, and to oxidation by NaOCl with subsequent HF treatment [NaOCl+HF]) (modified after *Helfrich* et al., 2007).

6 Analysis of specific compounds and compound classes

The SOM pools isolated by physical and chemical-fractionation procedures still comprised a vast range of different organic molecules which also have different residence time in soil and thus differently contribute to mean ^{14}C ages and turnover times of these pools. To get more detailed information on the turnover of individual compounds or compound classes in the soils under consideration, particular emphasis has been paid to extractable lipids, including phospholipid fatty acids, pyrolysis products, and black C.

6.1 Extractable lipids

Lipids constitute a major part of the organic components of fresh plant materials and soil OC (*Gregorich* et al., 1996). However, extractable lipids only comprised 3%–4% of soil OC in the Phaeozem and 2%–3% of SOC in the Luvisol, respectively (*Wiesenberg*, 2004; *Wiesenberg* et al., 2006), which was similar in magnitude to that reported by *Amblès* et al. (1994) and *Lichtfouse* et al. (1995). The high-molecular lipids (including mainly wax esters) as well as the fraction of low-polar compounds (including, *e.g.*, alkanes and ketones) each amounted to approx. 30% of the total lipids (*Wiesenberg* et al., 2004a). The remaining fractions were acids, alcohols, and sterols. Less than 5% of total extractable lipids were included in the basic fraction and the high-polarity fraction.

Parts of the acid fraction in soils can be related to microbial sources, whereas especially the long-chain *n*-carboxylic acids with 20–30 carbons are exclusively derived from plant-biomass input. They have a faster turnover in arable soils than the long-chain *n*-alkanes, which are also mainly plant-derived (Fig. 3; *Wiesenberg* et al., 2004b). The calculation of turnover times using $\delta^{13}C$ analyses of the weighted averages of the most abundant carboxylic acid homologues was consistent with estimates based on compositional changes between C3 and C4 plants (*e.g.*, *Wiesenberg* and *Schwark*, 2006). This suggests that a reliable estimate of a residence time for long-chain acids can be given for both soils. It corresponded to 33 y in the Luvisol Ap horizon but to 300 y in the Ap horizon of the Phaeozem (*Wiesenberg*, 2004). Such a difference in turnover time is hardly due to different stabilization mechanisms but probably reflects the additional input of lipid C from fossil sources and probably even the transformation of fossil C into microbial-derived lipid sources (*Rethemeyer* et al., 2004b; *Brodowski* et al., 2007). Hence, the apparent slow turnover rate of lipid C in the Phaeozem was mirrored by fossil-C contaminations, and, if the latter are likely to be ubiquitous, turnover times of lipid compound classes in general may be underestimated. Nevertheless, and in agreement with other findings on individual C constituents (*Dignac* et al., 2005; *Derrien* et al., 2006), the turnover of the lipids was faster than that of bulk soil OC (Fig. 3). It was concluded that in both agricultural soils, the lipids do not contribute to the stable soil OC pool (*Wiesenberg* et al., 2004b). Similar results were reported from lipid acids in grassland soils (*Wiesenberg* et al., 2007). Contrastingly, n-alkanes turned over more slowly than bulk soil OC in grassland soils. But thus far, very old *n*-alkanes have only been detected in the acidic, waterlogged Gleysols of the British uplands (*e.g.*, *Bol* et al., 1996). According to *Moucawi* et al. (1981), *Marseille* et al. (1999), and *Bull* et al. (2000), soil lipid degradation can be significantly retarded at higher soil acidity especially in forest or waterlogged soils.

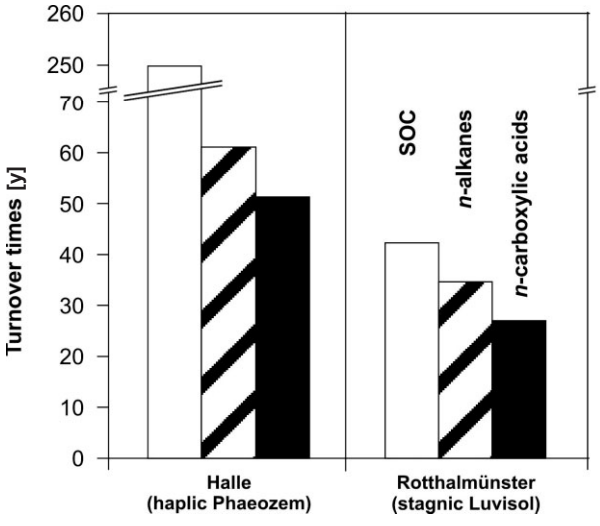

Figure 3: Apparent turnover time calculated from ^{13}C data of total soil organic carbon (SOC) and of nalkanes and n-carboxylic acids in the Ap horizon of the soil with continuous maize cropping at Rotthalmünster (Stagnic Luvisol) and Halle (Luvic Phaeozem, NPK treatment) (modified after *Wiesenberg* et al., 2004b).

6.2 Phospholipid fatty acids

Phospholipids are membrane lipids that are only present in living biomass and are rapidly degraded after cell death. When plant remains are removed from soil samples, extracted microbial phospholipids are valuable biomarkers for microbial biomass (*Zelles*, 1999). After extraction of phospholipids (*Zelles* and *Bai*, 1993), these molecules were hydrolyzed, and released phospholipid fatty acids (PLFAs) were derivatized to obtain phospholipid fatty acid–methyl esters (PLFA-ME). After further purification, they were separated by gas chromatography and analyzed by online coupled gas chromatography / mass spectrometry–isotope-ratio mass spectrometry (GC/MS-IRMS) to identify individual PLFAs and determine their $\delta^{13}C$ value (*Zelles* et al., 1995; *Kramer*, 2004).

The isotopic signature of PLFAs with 14 to 20 C atoms chain length isolated from the Ap horizons of the two maize sites ranged from –11.0‰ to –25.7‰ and thus between the $\delta^{13}C$ value of bulk soil OC and fresh maize litter (Fig. 4). This demonstrates that variable substrates were used for microbial growth (*Kramer* and *Gleixner*, 2006). Generally, PLFAs with $\delta^{13}C$ values close to that of soil OC indicated that soil OC was the major C source of the respective microorganisms, whereas an isotopic signature close to that of maize litter showed that recent plant litter served as major substrate. Distinct microbial C sources used for the synthesis of PLFAs that are characteristic for Gram-positive and Gram-negative bacteria could not be identified. However, some mono-unsaturated PLFAs, that are characteristic for Gram-negative bacteria (*Zelles*, 1999), appeared to indicate a preferred substrate usage of plant material, whereas saturated PLFAs (iso, anteiso, and branched chain), typical components of Gram-positives (*Haack* et al., 1994), seem to suggest a preference of these bacteria for SOM C. This would be in line with results from *Waldrop* and *Firestone* (2004), but further research is needed on that topic.

The $\delta^{13}C$ value of the PLFA indicative for fungi (18:2ω6) could only be analyzed in the Rotthalmünster soil because of the very small C yield. Its isotopic signature (–21.6‰) suggests that recent plant litter was a major C source for fungi (Fig. 4). The $\delta^{13}C$ in the respective PLFA was about 10‰ lower than in maize litter, which may result from isotopic fractionation during the formation of this PLFA and/or selective usage of ^{13}C-depleted compounds such as lignin. The phenomenon of ^{13}C depletion during PLFA formation was reflected by the general lower $\delta^{13}C$ values of PLFAs from the Rotthalmünster soil compared with the substrate mixture at this site (Fig. 4). No comparable depletion in isotopic signature of PLFAs was found in the Halle soil, where fossil-C inputs resulted in a lower $\delta^{13}C$ of soil OC.

The results at both sites showed that soil microbial biomass contained considerable quantities of C3-derived OC even after several decades of maize cropping. The reason of this phenomenon is not completely understood. It might be due to an efficient microbial recycling of C3-derived soil OC, but it

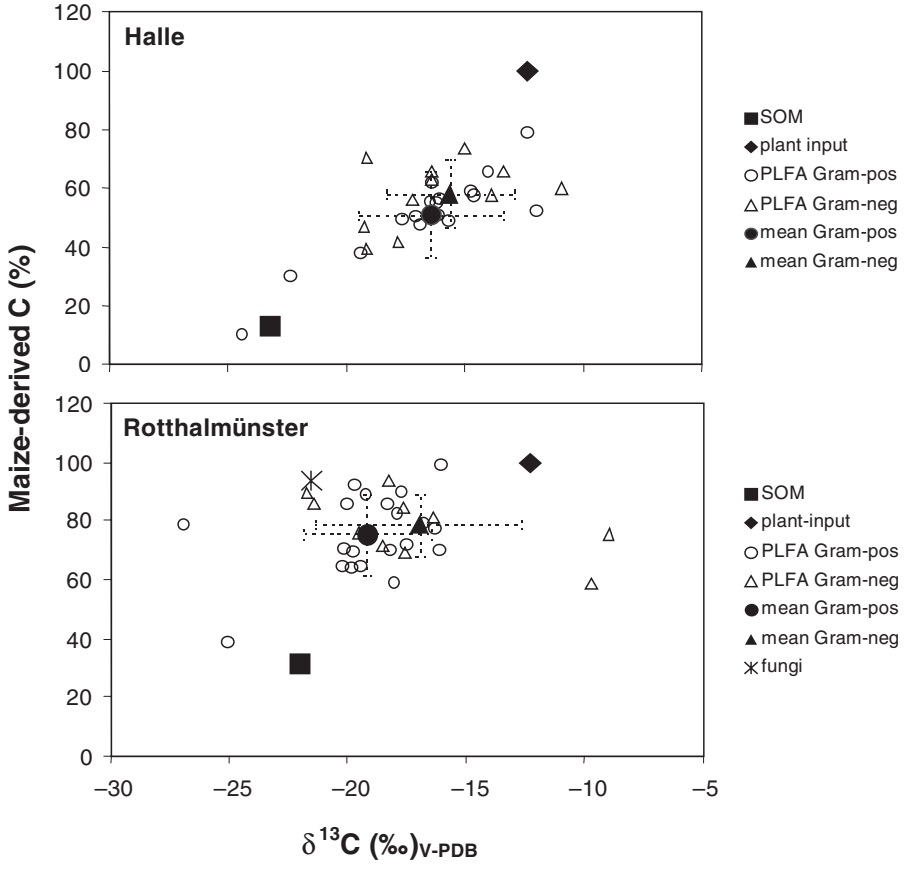

Figure 4: $\delta^{13}C$ value and maize-derived C in soil organic matter (SOM), current input of maize residues and phospholipid fatty acids (for Gram-positive bacteria, Gram-negative bacteria, and fungi) in the Ap horizon of the Luvic Phaeozem at Halle (NPK treatment) and the Stagnic Luvisol at Rotthalmünster. Data from *Kramer* and *Gleixner* (2006).

could also be influenced by the introduction of another C source with high ^{13}C content, such as atmospheric CO_2 into the microbial C cycle (*Miltner* et al., 2004).

6.3 Pyrolysis products

A broad screening of the turnover times of a range of different organic molecules has been achieved by pyrolysis–gas chromatography–combustion IRMS analyses (*Gleixner* et al., 1999, 2002). Lack of chromatographic separation currently still limits the isotopic tracing of an even broader range of organic substances (*Glaser*, 2005), and mass fragmentation and low pyrolysis yields do produce further uncertainties compared with other sophisticated ionization techniques, such as Py-FIMS (field-ionization mass spectrometry, not yet combined with IRMS; *e.g.*, *Schulten* and *Leinweber*, 1996). To overcome such problems, the Pyrolysis-GC/MS-IRMS method was applied to both C3 and C4 vegetation sites, *i.e.*, where isotopic differences between individual peaks may be reliably interpreted. The soil samples were obtained from the Ap horizons (maize and wheat) of the Rotthalmünster Luvisol. Nineteen major pyrolysis products were selected for isotopic analysis. They originated from carbohydrates, proteins/chitin, lipids, humic substances or were of unspecific origin (Fig. 5). Generally, about 5% of the pyrolysis products were derived from lipids and 42% from unspecific sources. Pyrolysis products of carbohydrates and proteins/chitin were most abundant, each accounting for 21%–26% of pyrolysis yields. The pyrolysis products of carbohydrates comprised 3-furancarbox-aldehyde, 2-furancarbox-aldehyde, 5-methyl-2-furaldehyde, and 2,4-pentadienal (*Gleixner* et al., 2002; *Nierop* et al., 2005; *van Smeerdijk* and *Boon*, 1987). Pyrolysis products reflecting protein and chitin were pyridine, indole, C1-pyrrole, 1H-pyrrole, n-methylpyrrole (*Nierop* et al., 2001; *Subbalakshmi* et al., 2000; *White* et al., 2004). Naphthalene, a polycyclic compound, is mainly detected in pyrolysis products of humic substances (*Tinoco* et al., 2002). The alken was the only compound assigned to lipids. There was also an unspecific group of pyrolysates comprising substituted aromatic compounds, phenol, and benzofuran. In particular, aromatic compounds and phenol have multiple origins. Lignin- and protein-derived products could contribute to the peaks of benzene, C2-benzene, toluene, styrene, and phenol (*Chiavari* et al., 1994; *Li* et al., 2004; *Nierop* et al., 2001; *Stankiewicz* et al., 1997a, b; 1997b; *Stout* et al., 1988), but, including C3-benzene, most of these compounds may as well originate from carbohydrates (*Faure* et al., 2004; *Park* et al., 2002). The source of benzofuran and o-xylene is not clear.

The dominant feature of this Luvisol and its pyrolysis products is the small abundance of lignin-derived pyrolysis products, only few unspecific pyrolysis products could be related to lignin (see above). Apparently there was a minor contribution of fresh plant material to this SOM (*Nierop* et al., 2005). And indeed, it has also been reported for similar soil types that lignin rapidly decomposes and does not contribute as much to SOM as other, potentially more labile compounds may (*Dignac* et al., 2005; *Rasse* et al., 2006; *Heim* and *Schmidt*, 2007). The differences in natural ^{13}C abundances allowed for the calculation of turnover times for the pyrolysis products. The average mean turnover time of 52.8 y for all compounds was similar to the average mean turnover time of the bulk soil OC, 54 y (see section 3). The unspecific (mean turnover time of 60.5 y) and carbohydrate-derived compounds (mean turnover time of 55 y) also had a mean turnover time close to that of bulk SOC. The pyrolysis products of proteins had an average turnover time of 43 y. These low turnover times for proteins and carbohydrates do not reflect the stability of their precursors (*Azam* et al., 1985). However, both compound classes, carbohydrates and proteins, are to a large extent of microbial origin. On the one hand, microbial products may be well-stabilized within soil micro-aggregates and at oxide surfaces (*e.g.*, *Ladd* et al., 1993), and turnover times of several decades to centuries have also been suggested for other soils (*e.g.*, *Amelung* et al., 2006). On the other hand, frequent microbial resynthesis may have contributed to the apparent high residence time of these compounds in soil (*Gleixner* et al., 2001).

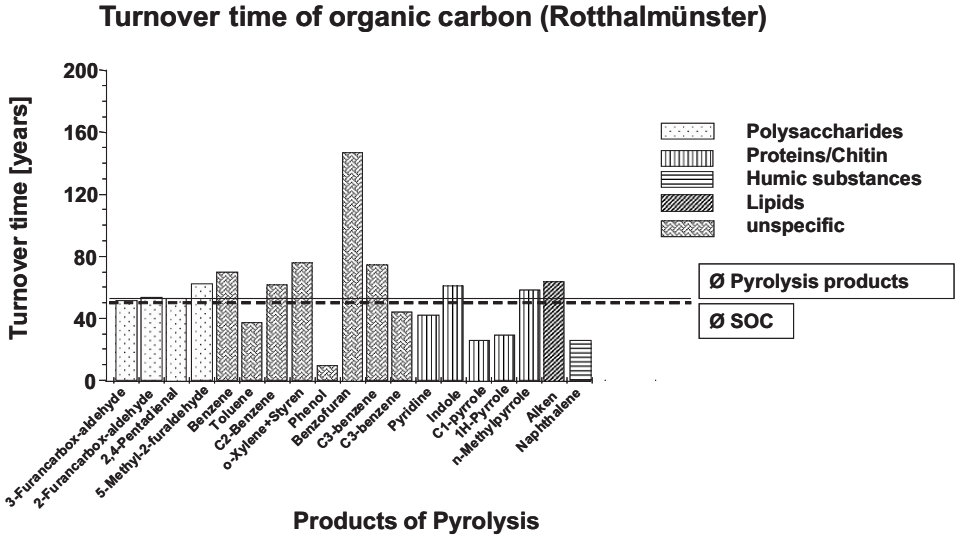

Figure 5: Apparent C-turnover time determined *via* natural ^{13}C labeling of different pyrolysis products as indicated by compound-specific $\delta^{13}C$ analyses (Ap horipzon of the Stagnic Luvisol at Rotthalmünster).

The individual residence time of the pyrolysates showed a range of 9 to 147 y. Phenol and toluene exhibited the most rapid turnover time of 9 and 31 y, respectively. The low turnover time of phenol can be reconciled with above mentioned discussion of rapid lignin decay. Benzofuran had the highest turnover time, but the reason for this remains unclear as the precursors for this pyrolysis product are not known.

The results suggest that most C in this soil, including that of microbial origin, can be assigned to a C pool with "intermediate" turnover time. There was no evidence from pyrolysis for compounds with higher turnover times that contribute to a passive SOM pool.

6.4 Origin and function of black carbon in the soils under study

Black carbon (BC) is produced by the incomplete combustion of both fossil fuels and biomass (*Goldberg*, 1985). It consists of a continuum of mainly aromatic structures; the degree of condensation increases in the order of char > charcoal > soot (*Hedges* et al., 2000; *Goldberg*, 1985; *Schmidt* and *Noack*, 2000). Yet, similar chemical structures may also be found in uncharred coals, such as lignite (*Laskov* et al., 2002).

Radiocarbon dating confirmed that the Haplic Luvisol at Rotthalmünster contained little if any anthropogenic C (*Rethemeyer* et al., 2005), *i.e.*, the BC was mainly derived from vegetation fires and made up 2.7% of topsoil OC. This is small compared to other pasture and agricultural land on the globe (*Schmidt* et al., 1999; *Glaser* and *Amelung*, 2003; *Rodionov* et al., 2006). Here, usually between 5% and 15% of total soil OC can be assigned to BC. In the Phaeozem at Halle, BC explained approx. 12% of OC of the topsoils (*Brodowski* et al., 2007). These BC contents were not influenced by inorganic fertilization. However, as previously indicated, this site has been contaminated with fossil C (*Rethemeyer* et al., 2004a). And indeed, also the isolated BC showed very old radiocarbon ages (Fig. 6), suggesting that it did not solely derive from vegetation fires but that a major part of this BC derived from fossil-fuel combustion. Higher proportions of mellitic acid in the Ap horizon had suggested that most of these fossil BPCA sources were indeed allocated in the surface rather than in the subsurface soil (*Brodowski* et al., 2007). We did not yet date BPCA from the different depths using our revised BPCA method (*Brodowski* et al., 2005a); however, results from older dating using the method of *Glaser* et al. (1998) indeed supported the hypothesis that BPCAs of the surface soils were depleted in ^{14}C compared to those from the subsoil (data biased by artificial charring and therefore not shown here).

Brodowski et al. (2007) determined benzene polycarboxylic acids as molecular markers for BC. Their high radiocarbon ages clearly showed that at least for these contaminated sites, any biological production of the polycarboxylated benzoic acids as claimed by *Glaser* (2005) is insignificant, *i.e.*, we could use the pattern of benzene polycarboxylic acids to identify the sources of BC. It confirmed the presence of highly condensed aromatic structures in the BC found in the topsoil, which are typical for fossil-fuel combustion residues and probably coal dust (*Brodowski* et al., 2007). Such material was indeed recently deposited on the E German topsoils under study during the last few decades, and it was abundant in scanning–electron microscopy pictures (*Brodowski* et al., 2005b). We estimated from the pattern of BC markers isolated from soil that approx. 60% of BC was of fossil origin, corresponding to 10% of total C that may be assigned to such condensed, intact BC structures (*Brodowski* et al., 2007). The estimation is consistent with compound-specific radiocarbon ages of the BPCA (Fig. 6). Yet, 10% fossil C in BC is much less than total fossil-C contents, amounting up to 50% of total OC found in the surface soil (see section 3). Apparently, a major part of this fossil C is not recovered in the

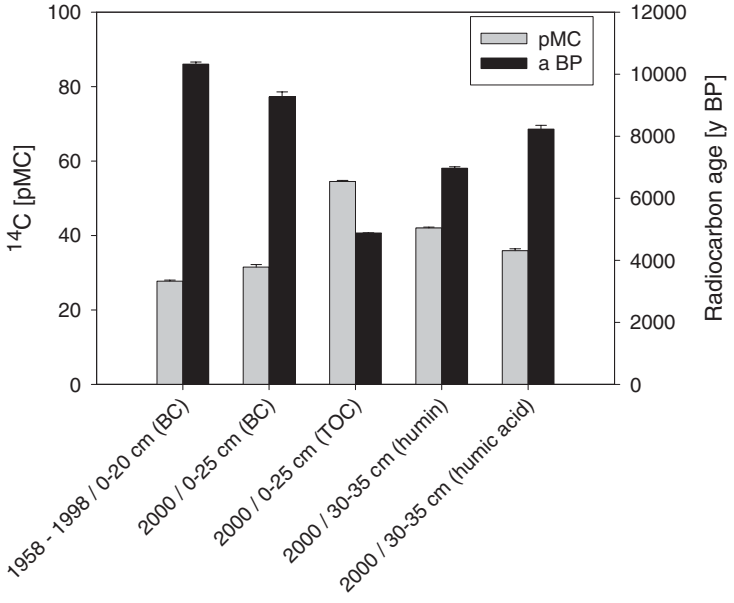

Figure 6: ^{14}C content and radiocarbon age of total organic C (TOC), the humin and humic acid fractions (data from *Rethemeyer* et al., 2004) and of black carbon (BC) in soil at the Halle site sampled during various years (years 1958–1998 represent the mean of ten sampling events within this time span) and at various depths. The error bars represent the standard deviation of the ^{14}C measurement.

BC structures. Three reasons may account for this. Firstly, the BPCA oxidation method fails to quantitatively assess BC because originally BC-inherent C may be lost as CO_2 during oxidation (see *Brodowski* et al., 2005a, for further discussion on the factor used) and some extremely highly condensed pyrogenic C such as soot may partly survive the oxidation (*Hammes* et al., 2007). Secondly, other fossil C entered the soil, such as lignite with large proportions of nonaromatic and only small proportions of highly condensed aromatic and, hence, BPCA-assessable structures (*Laskov* et al., 2002); and thirdly, former BC from fossil sources may already have been converted into other SOM structures.

As soil depth increased, the BC contents (in g (kg soil)$^{-1}$) decreased, and bulk soil OC dropped even more. Hence, the C-normalized BC concentrations increased with depth, reaching 20% of OC at a depth of 83–100 cm at Halle. We conclude that a refractory nature of C added to soil may indeed favor its accumulation, *i.e.*, at least for BC, the hypothesis of selective chemical preservation as one of three major stabilization mechanisms can be supported.

Energy-dispersive X-ray analysis of BC particles from a site at Bad Lauchstädt, located approx. 20 km from Halle, suggested that BC particles undergo surface oxidation (*Brodowski* et al., 2005b). This phenomenon makes the BC particle prone to sorption at mineral surfaces. And indeed, BC was found closely attached to minerals and *vice versa* in Phaeozems (*Brodowski* et al., 2005b, 2007). Moreover, BC was significantly enriched in the small micro-aggregate fraction of the Luvisol in Rotthalmünster (*Brodowski* et al., 2006), *i.e.*, these BC structures were mainly found in close mineral associations. There may have been a preferential inclusion of BC relative to other organic compounds or a selective enrichment of BC during decomposition of stabilized SOM or both. Which of these processes is truly dominating warrants further investigation, however, it seems obvious that the effectiveness of the process of selective preservation of refractory aromatic structures is, at least for BC, inevitably linked with the other two stabilization processes commonly relevant to SOM: chemical protection at and physical inclusion in-between mineral particles.

7 Conclusion

The significance of 24 different SOM fractions with respect to OC storage and stability is summarized in Fig. 7. This integrated evaluation was performed for the Luvisol, because C yields and OC-turnover times were not affected significantly by deposition of fossil C there. The mean apparent turnover time of the isolated soil OC fractions ranged from 10 y for large free particulate OM to >500 y for OC resistant to oxidation by H_2O_2 or $Na_2S_2O_8$ and black carbon. The results allow separation of SOM fractions with turnover times considerably shorter than that of the bulk soil OC (54 y), soil OC with an intermediate turnover time close to that of the bulk soil OC or not higher than 2 to 3 times the bulk soil OC value, and passive soil OC fractions with turnover times of several hundred years.

Free light particulate OM of different sizes, OM associated with sand and coarse silt, and particulate OM occluded in macro-aggregates represented SOM fractions with mean turnover times <35 y. In addition, in all cases, in which the turnover of individual compounds or compound classes has been assessed, it was more rapid than that of bulk SOC, and

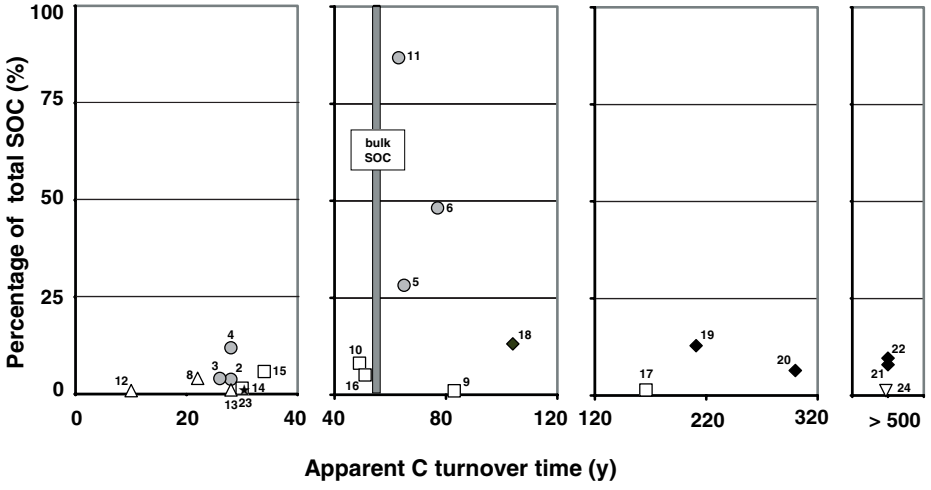

Figure 7: Storage and apparent turnover time of organic C in 24 different OM fractions in the Ap horizon of the continuous maize field at Rotthalmünster (Stagnic Luvisol).The symbols and numbers represent: ● OM in particle-size fractions (2 = medium sand, 3 = fine sand, 4 = coarse silt, 5 = fine + medium silt, 6 = clay, 11 = total mineral-bound); △ free particulate OM (8 = total fPOM, 12 = fPOM > 2000μm, 13 = fPOM 250–1000 μm); □ particulate OM occluded in aggregates (9 = total light oPOM, 10 = total dense oPOM, 14 = oPOM in aggregates > 2000 μm, 15 = oPOM in aggregates 250–1000 μm, 16 = oPOM in aggregates 53–250 μm, 17 = oPOM in aggregates <53 μm); ◆ OM resistant to chemical fractionation (18 = resistant to hydrolysis, 19 = resistant to NaOCl, 20 = resistant to NaOCl + HF, 21 = resistant to H_2O_2, 22 = resistant to $Na_2S_2O_8$), ★ 23 extractable soil lipids, ▽ 24 black carbon (turnover time of black carbon was assumed to be > 500 y according to *Skjemstadt* et al., 1998; *Schmidt* et al., 2002).

there was no evidence that primary recalcitrance of plant litter contributed to the formation of passive SOM pools. The yield of these OM fractions that were less stable than the bulk SOC was between 13% (sum of OM with relatively short turnover times in density fractions) and 20% (sum of OM with relatively short turnover times in particle-size fractions) of the total SOC. Organic matter in fine- and medium-silt and clay fractions, particulate OM occluded in micro-aggregates and OM resistant to acid hydrolysis had intermediate turnover times of about 50 to 100 y. This category made up the predominant fraction (approx. 70%–80%) of the total SOC and consisted mainly of OM bound to clay and fine-silt particles. Passive OM with turnover times >200 y was isolated from the mineral-bound OM by different oxidation procedures (H_2O_2, $Na_2S_2O_8$). These relatively stable OM fractions made up approx. 7%–10% of the total SOC. In addition, black C (approx. 3% of SOC) was assumed to contribute to this slowly decomposing OM pool even if the exact turnover time of this charred material was not determined.

In the Phaeozem at Halle, two sources of OC input with different recalcitrance have to be taken into consideration: the deposition of fossil C and the input of plant residues. The partitioning of these C inputs among SOC fractions differed mainly as a function of their bioavailability. Partitioning of maize-derived C showed a pattern similar to that in the Luvisol but turnover rates of OC that originates from vegetation (calculated after correction for fossil C) were lower probably because of the considerably smaller input of plant residues. Fossil C was found in all soil OC fractions (Fig. 8). It accumulated preferentially in the occluded particulate OM and in OC of coarse-particle-size fractions, but, fossil-C signals were also detected in soil OC resistant to oxidation by H_2O_2 and $Na_2S_2O_8$. Large stocks of passive OM in the Phaeozem were thus formed by fossil C which may be explained by its refractory aromatic structure (*Ludwig* et al., 2003; *Rethemeyer* et al., 2004a) and by close interactions of fossil compounds with mineral surfaces (*Rethemeyer*, 2004; *Brodowski* et al., 2005a). However, it was also shown that some of the fossil C entered the microbial C cycle (*Rethemeyer* et al., 2004b; *Marschner* et al., 2008, this issue, pp. 91–110).

The employed fractionation methods were not specific with respect to stabilization mechanisms (selective preservation due to recalcitrance, spatial inaccessibility, interaction with mineral surfaces) and differences of turnover times are probably due to a combination of two or three of these process groups of OM stabilization. In addition, most fractions were mixtures of different organic compounds and do not represent homogeneous SOM pools with respect to composition and stability. Even isolated organic-compound classes or individual organic compounds in soils are probably not homogeneous with respect to C turnover since stability even of a individual compound strongly depends on its location in the soil matrix.

Despite these restrictions, the combined results of distribution, stability, and composition of OM in different physically and chemically defined soil fractions and in specific classes of organic compounds provide revealing information about dominant mechanisms of soil-OC sequestration in different soils and soil horizons. Measurable OM fractions with differ-

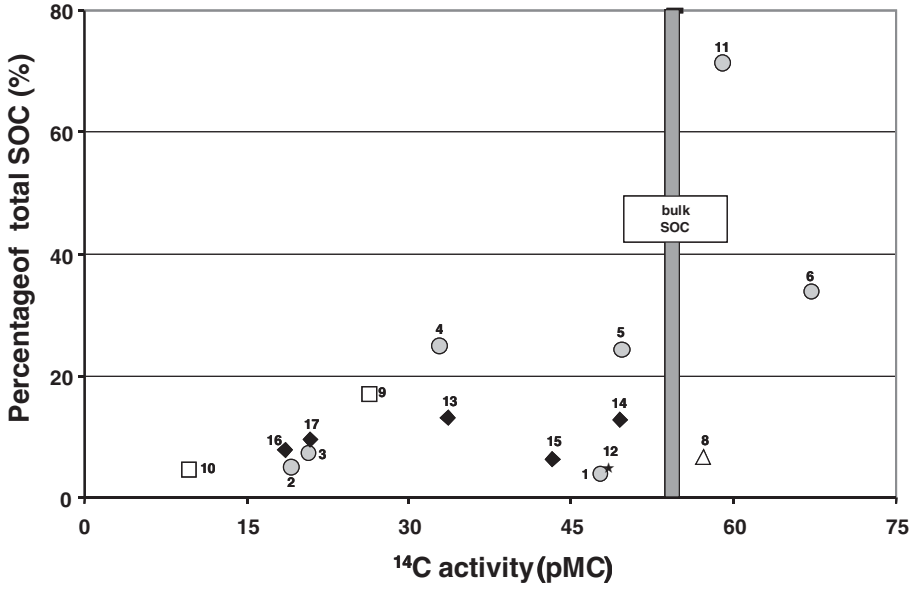

Figure 8: Storage and ^{14}C activity of organic C in 17 different OM fractions in the Ap horizon of the continuous maize fields in Halle (Luvic Phaeozem with contamination by fossil-C deposits). The ^{14}C activity reflects primarily the proportion of fossil C in these OC fractions (increasing contamination by fossil C with decreasing ^{14}C activity). The symbols and numbers represent: ● OM in particle-size fractions (1 = coarse sand, 2 = medium sand, 3 = fine sand, 4 = coarse silt, 5 = fine + medium silt, 6 = clay, 11 = total mineral-bound); Δ 8 free particulate OM; □ particulate OM occluded in aggregates (9 = total light oPOM, 10 = total dense oPOM,); ★12 extractable soil lipids, ◆ OM resistant to chemical fractionation (13 = resistant to hydrolysis, 14 = resistant to NaOCl, 15 = resistant to NaOCl + HF, 16 = resistant to H_2O_2, 17 = resistant to $Na_2S_2O_8$).

ent function for C sequestration are also an important tool for assessing conceptual pools of SOM models by experimental measurements and for evaluating the accuracy of simulation models (*Six* et al., 2002; *Ludwig* et al., 2003, 2005, 2008, this issue, pp. 83–90).

Open questions that arose from the summarized results primarily concern (1) the mechanisms of OM binding to mineral surfaces in different horizons, (2) the microbial recycling of C3-derived OC, and (3) the stability and transformation of fossil C and BC in different soil horizons.

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