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Organic matter stocks in temperate forest soils: Composition, radiocarbon age and spatial variability

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Summary

In temperate forests, more than 60% of the total carbon reserves are located in forest floor and mineral soil. The main objectives of this study were (1) to investigate the composition and radiocarbon age of organic matter (OM) pools of different stability in mineral soils, (2) to identify associations between iron oxides and specific carbon species, and (3) to analyse the small scale spatial variability of soil organic carbon (SOC) stocks. Composition, radiocarbon age and associations between iron oxides and SOC were studied in various soil profiles under managed beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L.) forest sites along a European North-South transect. Soils comprised Cambisols, Leptosols, Luvisols and a Phaeozem. Specific methods used were particle size fractionation in combination with accelerator mass spectroscopy (AMS), solid state ^{13}C nuclear magnetic resonance (^{13}C CPMAS NMR) spectroscopy and lignin analysis (CuO-oxidation). Spatial variability of organic carbon (OC) stocks was studied in a stone free Luvisol under a 10,000 m² managed beech (*Fagus sylvatica* L.) forest site located at Leinefelde, Germany. Starting from 9 randomly chosen primary stations, substations in distances of 0.2, 0.6, 1.8, 5.4 and 16.2 m were sampled, resulting in a total of 54 sampling points. At all sampling points, OC stocks in the litter and the complete solum were determined. Variability of OC stocks was analysed by descriptive statistics and variogram analysis.

Due to the high enrichment of OC and the high contribution of clay to the mineral soil, OC in mineral soils was preferentially associated with clay fractions (<2 μm fractions). In all horizons clay fractions contained more than 27% of the total C stock. Throughout Cambisol and Luvisol profiles the contribution of OC in the clay fraction to the total OC increased from 27-53% in the A horizons to 44-86% in B and E horizons. This suggests that with increasing depth the magnitude of leaf and root litter incorporated into coarse particle size fractions decreased. The OC in the 200-2000 μm fractions from all sites and all depths had a percentage of modern carbon (pmC) of >100. They were enriched in ^{14}C owing to high inputs of recent material from leaves and roots. Clearly less active material was associated with <2 μm and 2-20 μm fractions. This showed that the particle size fractionation was capable to separate young and old OC fractions. The pmC values were strongly decreasing with depth but the decrease was much more pronounced in the fine fractions. <2 μm and 2-20 μm fractions of B and E horizons

from two Luvisols and one Cambisol revealed radiocarbon ages between 512 and 4745 years before present which indicated that the soil organic matter (SOM) in those horizons was only little affected by the recent vegetation.

The structure of both, labile and stable SOM pools was dominated by alkyl C (14-48%) and O/N-alkyl C (28-53%). Strongest resonances in ^{13}C CPMAS NMR spectra of the bulk soil samples and the particle size fractions appeared in the O/N-alkyl C region at 72 ppm and 105 ppm and were most probably assigned to C2, C3, C5 and C1 in cellulose and non-crystalline polysaccharides. Further strong resonances occurred in the alkyl C region at 30 ppm, typical for methylene in long chain aliphatic compounds. The spectra of the coarse fractions had strong features of lignin and tannins with resonances around 56, 130 and 150 ppm. The signals attributed to lignin and tannins decreased with decreasing particle size, indicative of a complete decomposition and/or transformation with a loss of the phenolic and aromatic structures. Although lignin is believed to be highly recalcitrant, only low amounts of lignin were found in clay fractions. These results pointed to stabilisation processes operating specifically on polysaccharides (O/N-alkyl C) and alkyl C, but not on aryl C. Positive site specific relations were obtained between the O-aryl C intensity and the pmC values at all sites. Fractions containing the youngest C were enriched in O-aryl C, whereas the fractions with the oldest C were depleted in O-aryl C. However, a correlation between pmC values and O/N-alkyl C, alkyl C, aryl C or carbonyl C intensities in particle size fractions throughout soil profiles could not be observed. This indicated that the long term stabilisation of SOM was mainly controlled by the existence of various mechanisms of protection offered by the soil matrix and soil minerals but not by the chemical structure of the SOM itself.

In many ^{13}C CPMAS NMR spectra of untreated clay fractions the signal intensities of O/N-alkyl C (45-110 ppm) were diminished. After removal of Fe oxides by demineralisation with hydrofluoric acid (HF), ^{13}C CPMAS NMR spectra of clay fractions from A horizons of Leptosols and Luvisols showed increases of O/N-alkyl C intensities between 3% to 20%. The difference in O/N-alkyl C intensity before and after demineralisation was strongly correlated with the ratio of the concentration of dithionite-extractable iron oxides and the OC concentration. A variable contact time experiment with an untreated clay fraction from a Luvisol revealed that protons in the

vicinity of O/N-alkyl C relaxed faster than in the vicinity of other functional groups since paramagnetic iron shortened the relaxation of O/N-alkyl C. This demonstrated an intimate association between iron oxides and O/N-alkyl C, which most probably contributed to the stabilisation of O/N-alkyl C in clay fractions.

The spatial analysis of OC stocks in mineral soils at a beech forest stand in Leinefelde showed that the range of OC stocks was higher than its average value. Subsoils contained more than 50% of OC and should, therefore, be considered if estimating OC stocks. Variogram analysis failed to demonstrate a spatial pattern in the litter layer, whereas semivariograms of OC stocks in the solum 0-0.12 m and the solum >0.12 m showed a spatial continuity of less than 5.4 m. The nugget variance accounted for 30% of the sill in the solum 0-0.12 m and for more than 50% of the sill in the solum >0.12 m. These results emphasised the high small scale variability at the stand scale, which should be considered in quantitative analyses of OC stocks. Spatial correlations indicated that the OC stocks were strongly affected by the thickness of the solum, whereas a relation between the distance to the next tree and the magnitude of OC stocks was not found. Considering statistical independence and the variability of the study area, the minimum detectable difference of OC stocks ranged between 0.2 kg m⁻² in the litter layer and 4.5 kg m⁻² in the complete soil profile. At this site more than 300 samples would be required to detect a relative OC stock change of 10% in the solum.

Based on above results, the following conclusions can be drawn: A major proportion of OC in temperate forest soils is stored in the subsoil, reveals high radiocarbon ages and consists of O/N-alkyl C and alkyl C. The chemical composition of OC stocks falls short of explaining the variation of radiocarbon age of SOC. In fact, the interaction with soil minerals such as the adsorption to iron oxides most probably controls long term stabilisation of SOC. Due to the high small scale variability of soil OC stocks an extensive soil sampling is required to detect small changes of OC stocks in mineral soils.

Zusammenfassung

In Wäldern der gemäßigten Breiten sind mehr als 60% der Kohlenstoffvorräte in der organischen Auflage und im Mineralboden gespeichert. Hauptziel dieser Arbeit war es, (1) die chemische Zusammensetzung und das Radiokohlenstoffalter von Kohlenstoffpools unterschiedlicher Stabilität in Mineralböden zu untersuchen, (2) Assoziationen zwischen Eisenoxiden und Bestandteilen der organischen Substanz zu identifizieren und (3) die kleinräumige Variabilität von Kohlenstoffvorräten zu analysieren. Zusammensetzung, Radiokohlenstoffalter und Assoziationen zwischen Eisenoxiden und organischer Bodensubstanz wurden an Bodenprofilen unter bewirtschafteten Rotbuchen- (*Fagus sylvatica* L.) und Fichten- (*Picea abies* L.) Beständen entlang einer europäischen Nord-Süd Transekte untersucht. Die Böden wurden als Cambisole, Leptosole, Luvisole und Phaeozem klassifiziert. Als Hauptmethoden wurden die Korngrößenfraktionierung in Kombination mit der ^{14}C Radiokohlenstoffdatierung, der Festkörper ^{13}C -Kernresonanzspektroskopie (^{13}C CPMAS NMR Spektroskopie) sowie der Ligninanalyse (CuO-Oxidations Methode) angewendet. Die räumliche Variabilität der Kohlenstoffvorräte wurde in einem steinfreien Luvisol unter einem 10.000 m² Rotbuchenbestand (*Fagus sylvatica* L.) untersucht. Ausgehend von 9 zufällig ausgewählten Startpunkten, wurden jeweils Proben in Abständen von 16.2 m, 5.4 m, 1.8 m, 0.6 m and 0.2 m entnommen, so dass sich eine Gesamtzahl von 54 Entnahmestellen ergab. An allen Entnahmestellen wurden die organischen Kohlenstoffvorräte in der Streu und im gesamten Solum bestimmt. Die Variabilität der organischen Kohlenstoffvorräte wurde mit Methoden der deskriptiven Statistik und der Variogrammanalyse analysiert.

Aufgrund der hohen Anreicherung von organischem Kohlenstoff in der Tonfraktion und des hohen Beitrags von Ton zu der Gesamtbodenmasse, war der größte Anteil des organischen Kohlenstoffes in den Tonfraktionen (<2 µm Fraktionen) zu finden. Alle Tonfraktionen enthielten mehr als 27% des jeweiligen Gesamtvorrats an organischem Kohlenstoff. Innerhalb der Cambisol und Luvisol Profile nahm der Anteil des in der Tonfraktion gespeicherten organischen Kohlenstoffs von den A Horizonten (27-53%) zu den B und E Horizonten (44-86%) zu. Dies deutete darauf hin, dass mit zunehmender Bodentiefe weniger Blatt- und Wurzelstreu in die gröberen Fraktionen eingetragen wurde. Der organische Kohlenstoff in der 200-2000 µm Fraktion aller

Untersuchungsflächen und -tiefen zeigte pmC Werte >100 (pmC = Prozentanteil von modernem Kohlenstoff). Dies lässt sich durch die dieser Fraktion zugeführte frische Pflanzenstreu mit ihren hohen ^{14}C Gehalten erklären. Die $<2\ \mu\text{m}$ und $2\text{-}20\ \mu\text{m}$ Fraktionen waren dagegen durch deutliche niedrigere ^{14}C Gehalte gekennzeichnet. Dies zeigte sehr deutlich, dass die hier verwendete Korngrößenfraktionierung geeignet war, junge und alte Kohlenstofffraktionen voneinander zu trennen. Mit zunehmender Tiefe nahmen die pmC Werte stark ab, wobei die Abnahme in den feinen Fraktionen am deutlichsten ausgeprägt war. Die $<2\ \mu\text{m}$ und $2\text{-}20\ \mu\text{m}$ Fraktionen der B und E Horizonte von zwei Luvisolen und einem Cambisol wiesen ein Radiokohlenstoffalter zwischen 512 und 4745 Jahren „vor heute“ auf, was darauf hindeutet, dass die organische Substanz in diesen Horizonten nur wenig durch die derzeitige Vegetation beeinflusst war.

Die Struktur sowohl der labilen als auch der stabilen Pools der organischen Substanz war dominiert durch Alkyl C (14-48%) und O/N-Alkyl C (28-53%). Die stärksten Signale in ^{13}C CPMAS NMR Spektren waren sowohl in Gesamtböden als auch in den spezifischen Korngrößenfraktionen in dem Bereich von O/N-Alkyl C bei 72 ppm und 105 ppm vorzufinden und sind höchstwahrscheinlich den C2, C3, C5 und C1 Kohlenstoffatomen in Cellulose und nicht kristallinen Polysacchariden zuzuordnen. Weitere deutliche Signale traten im Alkyl C Bereich bei 30 ppm auf und sind typisch für Methylen in langkettigen aliphatischen Verbindungen. Die ^{13}C CPMAS NMR Spektren der groben Fraktionen enthalten zusätzlich Signale, die bei 56, 130 und 150 ppm vorzufinden sind. Diese auf Lignin und Tannin zurückzuführenden Signale wurden kleiner mit abnehmender Korngröße, was auf den Abbau bzw. die chemische Umwandlung von Lignin und Tannin und den Verlust phenolischer und aromatischer Strukturen hindeutete. Obwohl Lignin als schwer abbaubare Substanz angesehen wird, wurden nur geringe Ligninmengen in den Tonfraktionen vorgefunden. Dies deutet auf Prozesse hin, die spezifisch Polysaccharid und Alkyl C Verbindungen stabilisieren, jedoch nicht für Aryl C relevant sind. Positive standortspezifische Beziehungen wurden zwischen den O-Aryl C Intensitäten und den pmC Gehalten in A Horizonten nachgewiesen. Während in Fraktionen mit „jungem“ Kohlenstoff O-Aryl C angereichert war, enthielten Fraktionen mit „älterem“ Kohlenstoff deutlich geringe Mengen O-Aryl C. Eine Korrelation zwischen den pmC Gehalten und den O/N-Alkyl C, Alkyl C, Aryl C und Carbonyl C Intensitäten in den Korngrößenfraktionen der

Gesamtbodenprofile konnte jedoch nicht nachgewiesen werden. Dies verdeutlicht, dass nicht die chemische Struktur der organischen Substanz, sondern hauptsächlich die Stabilisierung durch Bodenmatrix und Bodenminerale für die Langzeitstabilisierung der organischen Substanz ausschlaggebend ist.

In ^{13}C CPMAS NMR Spektren von unbehandelten Tonfraktionen waren die O/N-Alkyl C Signale vielfach unterdrückt. Nach der Entfernung von Eisenoxiden durch Demineralisierung mittels Flußsäure (HF) Behandlung zeigten die ^{13}C CPMAS NMR Spektren jedoch Zunahmen der relativen O/N-Alkyl C Signalintensitäten, die zwischen 3 und 20% lagen. Der Unterschied in der O/N-Alkyl C Intensität vor und nach der Demineralisierung war eng mit dem Quotienten aus der Konzentration des dithionit-extrahierbaren Eisens und der organischen Kohlenstoffkonzentration korreliert. Ein Kontaktzeitexperiment mit einer unbehandelten Tonfraktion eines Luvisols zeigte, dass Protonen in der Umgebung von O/N-Alkyl C deutlich schneller relaxierten als in der Umgebung von anderen funktionalen Gruppen, da paramagnetisches Eisen die Relaxationszeit von O/N-Alkyl C verkürzte. Ein Teil der O/N-Alkyl C Verbindungen war folglich nicht sichtbar, wenn nicht sehr kurze Kontaktzeiten gewählt wurden. Dies ist ein deutlicher Hinweis darauf, dass enge Assoziationen zwischen Eisenoxiden und O/N-Alkyl C Verbindungen vorlagen, die höchstwahrscheinlich zur Stabilisierung von O/N-Alkyl C in der Tonfraktion beitrugen.

Die räumliche Analyse der organischen Kohlenstoffvorräte zeigte, dass die Spannbreite der Kohlenstoffvorräte höher war als ihr Mittelwert. Unterböden enthielten mehr als 50% des Gesamtkohlenstoffvorrates und sollten deswegen bei Kohlenstoffbilanzen unbedingt berücksichtigt werden. Variogrammanalysen verdeutlichten, dass es nicht möglich war, ein räumliches Muster für die Streuschicht zu identifizieren. Dagegen zeigten Semivariogramme der Kohlenstoffvorräte im Solum von 0-0.12 m und im Solum >0.12 m eine Aussagereichweite (Range) von weniger als 5.4 m. Die Nuggetvarianz betrug ca. 30% des Schwellenwertes (Sill) im Solum von 0-0.12 m and über 50% des Schwellenwertes (Sill) im Solum >0.12 m. Diese Ergebnisse unterstreichen die hohe kleinräumige Variabilität der Kohlenstoffvorräte auf der Skala eines Waldbestandes. Räumliche Korrelationen zeigten, dass die organischen Kohlenstoffvorräte sehr stark von der Mächtigkeit des Solums abhängen, während eine Korrelation zwischen der Höhe des organischen Kohlenstoffvorrates und dem Abstand

zum nächsten Baum nicht vorlag. Unter Berücksichtigung des Kriteriums der räumlichen Unabhängigkeit und der Variabilität der Kohlenstoffvorräte betrug die minimale nachweisbare Differenz der Kohlenstoffvorräte zwischen 0.2 kg m^{-2} in der Streuschicht und 4.5 kg m^{-2} im Gesamtprofil. Um eine 10%ige Veränderung des organischen Kohlenstoffvorrates mit statistischen Mitteln nachzuweisen, würden auf der untersuchten Fläche Proben von mehr als 300 Beprobungspunkten benötigt.

Auf Grundlage der beschriebenen Untersuchungsergebnisse konnten folgende Schlussfolgerungen gezogen werden: Ein großer Teil des organischen Kohlenstoffs in Mineralböden unter Wäldern der gemäßigten Breiten wird in Unterböden gespeichert, hat ein hohes Radiokohlenstoffalter und liegt in Form von O/N-alkyl C und Alkyl C vor. Die Streuung des Radiokohlenstoffalters in Mineralböden ist nicht alleine durch die chemische Zusammensetzung der organischen Kohlenstoffvorräte erklärbar. Vielmehr wird die Langzeitstabilisierung von organischem Kohlenstoff in Mineralböden höchstwahrscheinlich durch Interaktionen mit der Mineralphase, zum Beispiel durch Adsorption an Eisenoxide, kontrolliert. Aufgrund der hohen räumlichen Variabilität der im Boden gebundenen Kohlenstoffvorräte sind aufwendige Beprobungen notwendig, um kleine Veränderungen der Kohlenstoffvorräte in Mineralböden festzustellen.

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Abbreviations

AAS	Atomic Absorption Spectrometry
(Ac/Al) _s	Acid-to-aldehyde ratio of syringyl units
Al _d	Dithionite-extractable aluminium
Al _o	Oxalate-extractable aluminium
AMS	Accelerator Mass Spectrometry
BET	Brunauer-Emmett-Teller Method for surface area measurement
B.P.	Before Present
CECe	Effective Cation Exchange Capacity
CV	Coefficient of Variation
CPMAS	Cross Polarisation Magic Angle Spinning
DOC	Dissolved Organic Matter
E _{oc}	Enrichment ratio of OC
E _{VSC}	Enrichment ratio of CuO-oxidation products (Vanillyl, Syringyl- and Cinnamyl units)
FAO	Food and Agriculture Organization of the United Nations
Fe _d	Dithionite-extractable iron
Fe _o	Oxalate-extractable iron
γ (h)	Semivariance for distance class h
γ_{GR} (h)	General relative semivariance for distance class h
γ_M (h)	Semivariance in madograms for distance class h
Γ (h)	Crossvariance for distance class h
IC	Inorganic Carbon
ISSS	International Society of Soil Science
MDD	Minimum Detectable Difference
MDD _{rel.}	Relative Minimum Detectable Difference
NMR	Nuclear Magnetic Resonance
OC	Organic Carbon
OM	Organic Matter
pmC	Percent Modern Carbon
Q	Ratio of C/N ratios before and after demineralisation
r_s	Spearman correlation coefficient
SOM	Soil Organic Matter
SOC	Soil Organic Carbon
SSA	Specific Surface Area
SSA _{oxides}	Specific Surface Area of mineral oxides
SSA _{silicates}	Specific Surface Area of silicates
T _{1ρH}	Spin-lattice relaxation time in the rotating frame of protons
T _{1ρC}	Spin-lattice relaxation time in the rotating frame of carbon
T _{CH}	Carbon-proton cross polarisation time
TC	Total Carbon
VCT	Variable Contact Time
VSC	Sum of CuO-oxidation products (Vanillyl, Syringyl- and Cinnamyl units)
WRB	World Reference Base for soil resources

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1. Introduction and state of the art

In temperate forest ecosystems, more than 60% of the total carbon reserves (~159 Gt) are stored in forest floor and mineral soil (Watson et al., 2000). Some of the carbon is located in relatively labile pools and can rapidly be used by microbes and respired back to the atmosphere. Other pools of soil C are either resistant to microbial utilization and/or physically protected, so that the carbon can reside in the soil as organic matter (OM) for long periods of time (Pregitzer, 2003). Soil organic matter (SOM) in bulk soils is a heterogeneous mixture of labile, stable and inert SOM (Wang and Hsieh, 2002). Thus, many researchers have attempted to separate SOM pools of different turnover using chemical and physical means in order to study stabilisation of SOM.

1.1. Composition of soil organic matter in particle size fractions

The application of physical fractionation as a tool to separate SOM pools of different turnover has increased steadily over the past 25 years (Hedges and Oades, 1997; Christensen, 2001). This development arises from an increasing awareness of the importance of the interaction between SOM and inorganic soil components for the long-term protection of SOM against microbial decomposition (Sollins et al., 1996; Baldock and Skjemstad, 2000; Six et al., 2002; Lützwow et al., 2005). Different density and particle size fractionations have been used to study the protection offered by the soil matrix and soil minerals. Density fractionation is based on the isolation of SOM which is not firmly associated with the mineral part of the soil. The light fraction is taken to include labile plant and animal residues that turn over rapidly, whereas the heavy fraction is expected to comprise organo-mineral complexes in which SOM is stabilised (Christensen, 1992; Golchin et al., 1994; Golchin et al., 1995). Particle size fractionation, in contrast, relies on the concept that SOM associated with particles of different size and mineralogical composition differs in structure and function and, therefore, plays different roles in SOM turnover (Kögel-Knabner, 2000; Christensen, 2001).

C/N ratios and data on the chemical composition of SOM in particle size fractions show that decomposition of SOM increases from coarse to fine particle size fractions (Spycher et al., 1983; Kögel-Knabner and Ziegler, 1993; Zech and Guggenberger, 1996). Analyses from Eutrochrepts under spruce and mixed deciduous forest exhibit

that carbohydrates in sand are mainly of plant origin, whereas microbial-synthesised carbohydrates show a significant enrichment in clay (Guggenberger et al., 1994). Compared to bulk soils, clay of various soils under temperate and tropical forests is depleted and sand enriched in lignin oxidation products (Guggenberger and Zech, 1994; Solomon et al., 2002; Schöning et al., 2005b). Using results from solid state ^{13}C nuclear magnetic resonance (^{13}C CPMAS NMR) spectroscopy, Baldock et al. (1992) found increasing amounts of alkyl C from large (250-2000 μm) to small particle sizes (<2 μm) in arable soils, in peat and in soils under tropical forests. They suggested a selective preservation mechanism or an in-situ synthesis of alkyl C in the clay fraction. The textural differences in A horizons have been ascribed to the breakdown of coarse vascular plant fragments within the sand fraction and sequential conversion of vascular plant tissues via microbial biomass to residual “metabolites” (Hedges and Oades, 1997).

Although both, the A horizons and the subsoil horizons are relevant in the context of carbon storage (Batjes, 1996), most of the previous studies on the composition of SOM in particle size fractions of forest soils have been limited to A horizons (e.g. Baldock et al. (1992), Guggenberger et al. (1994), Guggenberger et al. (1995), Quideau et al. (2001a), Chen & Chiu (2003)). In subsoils, the input of SOM mainly derives from plant roots and from translocated dissolved SOM (Kögel-Knabner, 2002; Lützwow et al., 2005). Similar to various A horizons (Baldock et al., 1992), alkyl C compounds such as cutin/suberin-derived hydroxyalkanoic acids are preserved in the fine particle size fractions of B horizons of a Dystric Cambisol and a Haplic Podzol (Rumpel et al., 2002; Rumpel et al., 2004). Comparable studies with particle size fractions from subsoil horizons of Luvisols have not been conducted until now.

1.2. Radiocarbon age of soil organic matter in particle size fractions

Accelerated mass spectroscopy (AMS) has made it possible to ^{14}C date organic carbon (OC) fractions that were too small to be dated by the conventional decay counting method (Wang and Hsieh, 2002). However, although particle size fractionation is frequently applied to forest soils, information on the radiocarbon age of SOM associated with sand, silt, and clay sized separates is surprisingly rare. In two lysimeters, which were covered by pine and oak for a period of >50 years, highest mean residence time for OC in A horizons was determined in the coarse clay and the fine silt fraction (Quideau et al., 2000). Similar results obtained from two arable soils are presented by Anderson

& Paul (1984). In contrast, ^{14}C -data of particle size fractions from two Mollisols under different land use show age maxima in the medium and fine clay fractions (Scharpenseel et al., 1986). Moreover, the lowest ^{14}C contents in particle size fractions of forested Oxisols and Ultisols were detected alternately in sand, silt and clay fractions. Therefore, it was recommended to use density and chemical separation methods instead of particle size fractionation (Trumbore and Zheng, 1996). The study of Trumbore and Zheng (1996) is the only one in which radiocarbon contents of subsoil fractions were published so far. However, carbon dating of bulk soil samples from subsoil horizons of four Luvisols revealed maximum radiocarbon ages between 2,340 and 3,320 years which indicated a high degree of stabilisation of SOM in subsoils (Becker-Heidmann et al., 1996).

Reports combining results of composition of SOM with results of carbon turnover are rare. Gleixner et al. (2002) performed studies on the molecular residence time of SOM from bulk soils and found a very high life time for N-containing and polysaccharide-derived pyrolysis products. Quideau et al. (2000) combined ^{14}C radiocarbon dating, ^{13}C CPMAS NMR spectroscopy and particle size fractionation to investigate soils under oak and a pine forest. The turnover rates of SOM under pine corresponded to an increase in the alkyl C/ O/N-alkyl C ratio from the fresh litter to the clay fraction (Quideau et al., 2000). Some studies related the carbon turnover assessed by the ^{13}C abundance to chemical characteristics. Data on the degree of microbial alteration match well with the increasing age in particulate OM fractions and density fractions of fine silt associated carbon (Six et al., 2001). Combining ^{13}C CPMAS NMR and ^{13}C abundance data of occluded organic materials, Golchin et al. (1995) found that the O-alkyl C content of occluded organic materials was inversely related to their stabilities whereas their aromatic C content was directly related to their stabilities.

1.3. Interactions between iron oxides and soil organic matter

Isotope studies have shown that SOM is stabilised in fine particle size fractions of A horizons (Anderson and Paul, 1984; Scharpenseel et al., 1986; Schöning et al., 2005b). The stabilisation of SOM in fine fractions can be attributed to adsorption and chemical binding of OC on mineral surfaces as well as aggregate formation which lead to a reduced decomposition rate of SOM relative to similar unprotected carbon material (Baldock and Skjemstad, 2000). Among other mechanisms, the adsorption of SOM on

Fe oxide surfaces contributes to a decreased turnover of SOM (Sollins et al., 1996). Several correlations between Fe oxides and SOM emphasise the importance of Fe oxides with respect to SOM storage. The OC concentrations in mineral horizons of the main soil orders under temperate forests, such as Spodosols, Vertisols, Mollisols, Alfisols, Inceptisols and Entisols, are closely related to dithionite-extractable Fe (Kaiser and Guggenberger, 2000). Correlation was also found for OC and the oxalate-extractable Fe in silt fractions of an Alfisol and an Oxisol (Shang and Tiessen, 1998). Finally, in subsoil horizons of a loamy Podzol the amounts of resistant OC, as determined after oxidation with $\text{Na}_2\text{S}_2\text{O}_8$, increased with increasing concentrations of dithionite-extractable Fe (Eusterhues et al., 2003). Oades (1989) highlighted the importance of interaction between SOM and Fe oxides with respect to the accessibility of organic compounds to organisms. In incubation studies, Ferrihydrite reduced the decomposition of carbohydrates from beech litter by 15% (Miltner and Zech, 1998). Organic compounds interact with minerals mainly through the O and N atoms of their functional groups, since both O and N atoms have lone electron pair(s) (Deng and Dixon, 2002). Interactions between organic materials and Fe oxides involve ligand exchange reactions, anion exchange and non-coulombic interactions (Greenland, 1970).

Solid state ^{13}C NMR spectroscopy allows examining for association between iron oxides and SOM. The solid state NMR technique relies on the cross polarisation (CP) mechanism. In such an experiment, after polarisation of the ^1H spin system, the magnetisation is transferred to the ^{13}C spin system during a contact time after which the ^{13}C signal is detected. The time required for a complete transfer of magnetisation is called carbon-proton cross polarisation time (T_{CH}). However, already during the magnetisation transfer, the excited ^1H spin system tries to relax to its thermal equilibrium and thus loses polarisation. The time required for a complete loss of ^1H magnetisation is called the spin-lattice relaxation time in the rotating frame ($T_{1\rho\text{H}}$). The values of $T_{1\rho\text{H}}$ can be determined by a variable contact time experiment in which the ^{13}C intensity is measured as a function of the contact time. Fe^{3+} may compromise the cross polarisation process by shortening $T_{1\rho\text{H}}$ values with the consequence that some ^{13}C nuclei relax before being observed. Therefore, ^{13}C in the vicinity of fast relaxing ^1H nuclei may be underestimated by cross polarisation unless very short contact times are applied (Kinchesh et al., 1995). Signal loss and broadening by Fe^{3+} have been reported for many spectra from soil samples of different origin (Vassallo et al., 1987; Goncalves

et al., 2003; Keeler and Maciel, 2003). According to Smernik and Oades (2000), the presence of paramagnetic compounds affects solid state NMR spectra via three mechanisms: Long range effects of paramagnetic centres operate on ^{13}C nuclei of the whole sample. They arise due to decreases in magnetic field homogeneity. Therefore, signal loss via this mechanism is equal for all resonances in the spectrum. In contrast, medium range (within coupled spin systems) and short range effects (within few bonds) can explain selective suppression of specific carbon species and can be used to identify carbon species which are intimately associated with paramagnetic iron.

1.4. Spatial variability of soil organic carbon stocks

The magnitude of SOM is controlled by the balance between OM production by the vegetation and decomposition of OM by soil organisms. It is strongly linked to various factors, including temperature, moisture, OC structure, texture, soil type and topography (Parton et al., 1987; Tan et al., 2004). The multitude of factors illuminates why spatial variability is an inherent constraint when detecting short term changes in soil OC stocks. Changes of soil OC stocks are often calculated as the difference between net ecosystem exchange determined by eddy covariance and changes in vegetation C stocks (Post et al., 2001). In order to verify these calculations direct measurements of soil OC stocks are required (Smith, 2004). Detection of temporal changes of soil OC stocks might be difficult, because changes are typically small in comparison to the total amount of soil OC. In forest land, for example, soil OC may be sequestered at a rate of around $0.053 \text{ kg OC m}^{-2} \text{ yr}^{-1}$ by means of forest regeneration, fertilization, species choice and reduced forest degradation, against a background of around 9.6 kg C m^{-2} in the top 1 m of temperate forest soils (Watson et al., 2000).

Spatial variability of OC concentrations and stocks in soils is scale dependent. The coefficient of variation (CV) in grassland soils in the USA decreased with scale and was 39% at the county-scale (Dundy County) and 63% at the national-scale (Conant and Paustian, 2002). A strong logarithmic relationship between relative plot size and variance of soil OC stocks was described by Conen et al. (2004). This relationship indicated that reducing the plot size by six orders of magnitude would only halve the variance. Regardless of this correlation, the percentage of the overall variance of total soil OC stocks determined for subplots in a $10,000 \text{ m}^2$ pine forest stand was only marginally lower than for 30 plots distributed across the whole state of Georgia (Palmer

et al., 2002). Changes of carbon dynamics in forests are often studied on the stand scale. At the stand scale, small scale spatial variability is of particular interest. In an old field soil, Amador et al. (2000) observed a high variability of OC stocks even at a centimetre scale, but the majority of studies upon spatial variability of soil OC neglects the small scale variability by sampling in distances ≥ 1 m (Riha et al., 1986; Järvinen et al., 1993; Conen et al., 2004).

Although some studies have been conducted on spatial variability of soil OC stocks beneath forest stands, many questions still remain open. So far, most research on spatial variability of OC stocks in forest soils has been carried out in conifer stands (e.g. Ruark & Zarnoch (1993), Liski (1995), Homann et al. (2001), Palmer et al. (2002), Conant et al. (2003), Conen et al. (2004), Oliver et al. (2004)). Only few studies on the spatial variability in soil under deciduous forests are available (e.g. Riha et al. (1986), Conant et al. (2003), Davis et al. (2004)). The dominant soils studied were Podzols (e.g., Liski (1995), Conen et al. (2004)). Up to now, available data have often precluded worldwide calculations of the less dynamic reserves of soil carbon (Batjes, 1996). In most studies on the variability of OC stocks in forest soils only the forest floor material and several underlying layers within the upper 0.3 m of mineral soil were considered (Hewitt et al., 1998; Homann et al., 2001; Conen et al., 2004). This may be due to high stone contents, which are often encountered in subsoils of forest soils, and compromise the sampling of volumetric samples.

2. Objectives

In view of above state of the art, the primary objective of this dissertation was to characterise the chemical composition of OC pools in mineral soils under temperate forest. Moreover, the spatial variability of soil OC stocks at an even aged beech forest stand was studied. The following topics were addressed:

Combined study of composition and radiocarbon age of SOM pools

As explained above, previous studies often focused either on SOM composition or on radiocarbon age. This study aimed to fill the gap between studies on the dynamics of SOM and the chemical composition of SOM. Thus, a combined analysis was performed on (1) OC pools in bulk soil samples and particle size fractions, (2) their radiocarbon contents, and (3) their chemical composition (^{13}C CPMAS NMR spectroscopy and lignin analysis) (Chapters 4 and 5).

SOM pools in subsoils

Up to present little information is available on OC in subsoils. Therefore in this study composition of OC pools of different stability throughout Cambisol and Luvisol profiles was elucidated. It was examined if young and old OC pools can be separated by particle size fractionation and if radiocarbon age in particle size fractions was related to the chemical composition of SOM (Chapter 5).

Interaction between iron oxides and SOM

Mineral oxides with high specific surface areas promote the stabilisation of SOM. This study aimed to identify associations between iron oxides and specific carbon species. For this purpose ^{13}C CPMAS NMR spectra of clay fractions before and after removal of Fe by demineralisation with hydrofluoric acid (HF) were compared to examine short and medium range effects of paramagnetic Fe (Chapter 6).

Small scale variability of SOC stocks

Organic carbon stocks are highly variable, which makes spatial estimates of OC stocks difficult. Few data are available on the spatial variability in Luvisols under beech forest. This holds true most notably for the variability of OC stocks in subsoils. The objective of this study was to analyse the small scale variability of OC stocks of an almost stone free Luvisol under a beech forest stand. This included (1) an estimation of the

magnitude of OC stocks in the forest floor and the complete solum including the subsoil, (2) an analysis of the spatial continuity with the smallest sampling distance being 0.2 m, and (3) an investigation of the fundamental factors that account for the spatial variability (Chapter 7).

3. Materials and Methods

3.1. Study sites

Soil samples were collected from managed forest sites in Collelongo/Italy (41°52'N/ 13°38'E), Hesse/France (48°40'N/ 07°05'E), Sorø/Denmark (55°29'N/ 11°38'E), Leinefelde/Germany (51°20'N/ 10°22'E), and Tharandt/Germany (50°56'N/ 13°29'E) (Table 1). Soils in Collelongo, Hesse, Sorø and Leinefelde were covered with European beech (*Fagus sylvatica* L.), whereas spruce (*Picea abies* L.) was the dominant tree species in Tharandt. The humus form was mull at the beech forest sites and moder at the spruce forest site. At Leinefelde and Tharandt samples were taken from chronosequences including subsites with different tree age classes. The selected sites

Table 1: Study sites

	Collelongo (I)	Hesse (F)	Sorø (DK)	Leinefelde (D)	Tharandt (D)
<i>Location</i>					
Latitude, longitude	41°52'N/ 13°38'E	48°40'N/ 07°05'E	55°29'N/ 11°38'E	51°20'N/ 10°22'E	50°56'N/ 13°29'E
Elevation (m a.s.l)	1550	300	40	450	380
<i>Climate</i>					
Rainfall (mm)	1180	820	660	725	820
Annual mean temperature (°C)	6.3	9.2	8.2	7.0	7.5
<i>Forest</i>					
Dominant species	<i>Fagus sylvatica</i> L.	<i>Fagus sylvatica</i> L.	<i>Fagus sylvatica</i> L.	<i>Fagus sylvatica</i> L.	<i>Picea abies</i> L.
Age (years)	109	34	60	30/62/111/ 153+16	5/24/97
<i>Soil</i>					
Humus type	Mull	Mull	Mull	Mull	Moder
Soil type	Leptosol	Luvisol	Phaeozem	Leptosol /Luvisol	Cambisol
Parent material	Limestone	Loess/ shell limestone	Calcareous glacial material	Limestone/ loess	Porphyry

were characterised by an altitude between 40-1550 m a.s.l., a mean annual temperature of 6.3-9.2 °C and a mean annual precipitation of 660-1180 mm. The parent material was lime stone in Collelongo and Leinefelde (30/1), shell limestone in Hesse, calcareous glacial material in Sorø, loess in Leinefelde (30/2, 62, 111 and 153+16) and porphyry in Tharandt (5, 24, 97).

3.2. Soil sampling

Samples to study composition and radiocarbon age of SOM were taken from one representative soil pit at each site. Only at the 30 years old stand in Leinefelde samples were taken from two profiles because of the great soil heterogeneity. All soil pits were sampled by horizons. Soil groups, classified according to ISSS-ISRIC-FAO (1998) and FAO (1990), comprised Cambisols, Leptosols, Luvisols and a Phaeozem (Table 1).

- Samples from A horizons of the beech forest sites were selected to study composition of SOM as determined by ^{13}C CPMAS NMR spectroscopy and lignin analysis in bulk soils and particle size fractions and radiocarbon age in particle size fractions (Chapter 4).
- Samples from A, E and B horizons from Haplic and Stagnic Luvisols in Hesse und Leinefelde as well as Dystric Cambisols in Tharandt were selected to study composition and radiocarbon age of SOM throughout soil profiles (Chapter 5).
- Clay fractions of the A horizons from all sites were taken to study associations between iron oxides and functional groups of SOM (Chapter 6)

The study on the spatial variability of OC stocks was conducted at a 10,000 m² beech forest site located at Leinefelde/Germany (51°20'N/ 10°22'E) (Anthoni et al., 2004; Bascietto et al., 2004) (Chapter 7). The forest has been managed as a shelterwood system since 1838 (Anthoni et al., 2004). The dominant vegetation consisted of 111 years-old, even aged beech trees (*Fagus sylvatica* L.). The forest stand exhibited a stand basal area of 35.2 m² ha⁻¹, a mean top height of 36.5 m, and a tree density of 224 trees·ha⁻¹ (Anthoni et al., 2004; Bascietto et al., 2004). Thus the average distance between beech trees was around 7 m.

Soils were first sampled at 9 primary stations. The primary stations were randomly chosen. At each primary station, 5 substations in distances of 0.2, 0.6, 1.8, 5.4 and 16.2 m and random direction were sampled (Fig. 1). Our sampling design allowed for the sampling of OC stocks which were representative for a 10,000 m² area with a reasonable number of samples. At the same time it considered the small scale variability of OC stocks since it included sampling distances of less than 5 m. The smallest sampling distance was restricted by the size of the sampling device, whereas the sampling distance of 16.2 m exceeded the crown diameter of the beech trees. Soil samples were taken from the forest floor and the solum. The forest floor was sampled from a 0.01 m² sampling frame. All coarse wood fragments >5 mm in diameter were removed. The solum was sampled down to the bedrock in depth increments of 0.12 m using a device for taking soil core samples (Hartge and Becher, 1971). We used 0.37·10⁻³ m³ cores to avoid increased bulk densities due to a compression of soil samples. At each sampling location the distance to the next tree was measured. The distance between the sampling points and the next tree varied between 0.5 and 4.5 m.

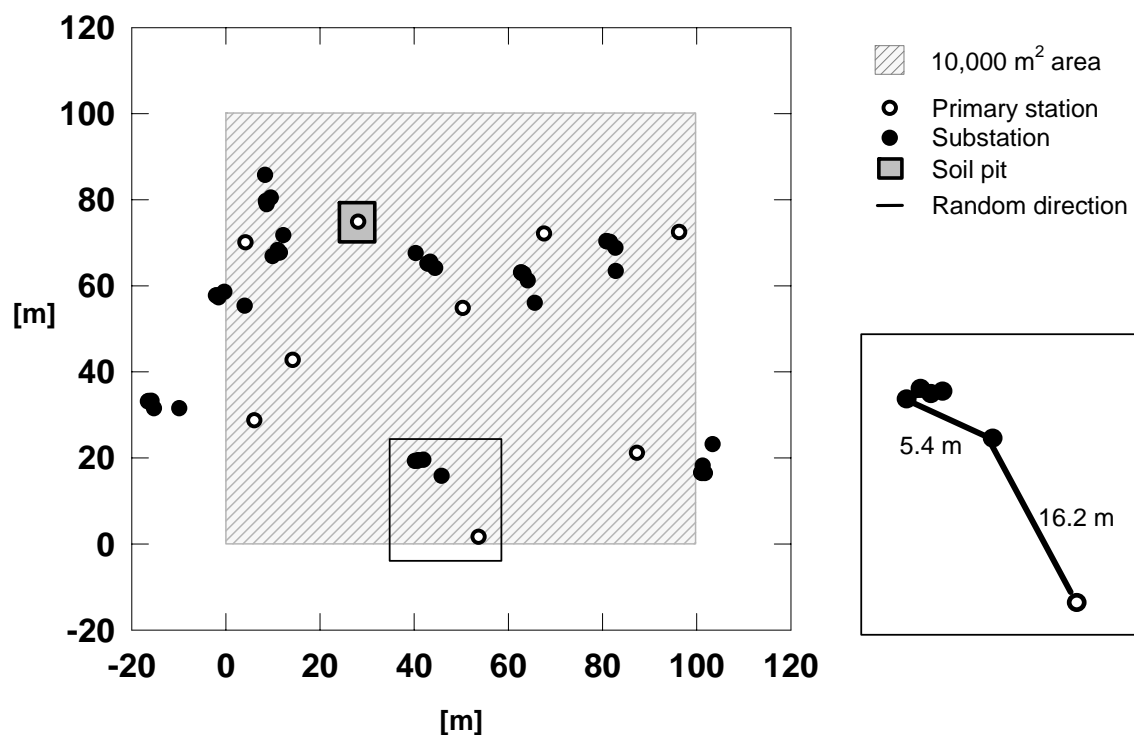


Figure 1: Location of sampling points at the site in Leinefelde/Germany

3.3. Basic soil parameters

3.3.1. Bulk density

Bulk density of the forest floor was calculated using the thickness of the forest floor (corrected for coarse wood fragments), the sampling area and the mass of the air dried forest floor. Bulk density of the mineral soil was calculated with the mass of the oven-dry soil (105°C) and the core volume (Hartge and Horn, 1989). Bulk density was corrected for roots (>2 mm) and stones taking into account a density of the parent material of 2.7 g cm⁻³ to calculate the bulk density of the fine earth.

3.3.2. Sample preparation

After drying, soil samples were sieved to <2 mm. Prior to C and N analyses, ¹³C CPMAS NMR spectroscopy, and alkaline CuO oxidation, aliquots of bulk samples were ground to a size of <100 µm using a ball mill.

3.3.3. Determination of pH, particle size distribution and effective cation exchange capacity

The pH values were determined in duplicate with a glass electrode in the supernatant of a soil suspension obtained by mixing soil with 0.01 M CaCl₂ in a mass to volume ratio of 1:2.5. Determination of soil texture was carried out in duplicate according to Schlichting & Blume (1966). The proportions of fractions <63 µm were measured with a Sedigraph 5100 (Micromeritics Corp., Nocross, USA). The effective cation exchange capacity (CEC_e) and the base saturation (BS) were determined in triplicate corresponding to Trüby and Aldinger (1989).

3.3.4. Determination of C, N, Fe and Al

Determination of total carbon (TC) and nitrogen was performed in duplicate by dry combustion on a Vario EL elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The coefficient of variation of replicated analyses was below 4 %. Most samples were carbonate free. In those samples the TC concentration equalled the OC concentration. In the remaining samples the inorganic carbon (IC) concentrations of samples were determined after ignition of samples for 3 hours at 550°C. The OC concentration was calculated from the difference between TC and IC. For ¹³C CPMAS NMR spectroscopy, the carbonate of the samples from Collelongo was removed with

1M HCl. The total amounts of pedogenic Fe oxides, the dithionite-extractable Fe (Fe_d), were extracted using the strong reductant sodium dithionite (Mehra and Jackson, 1960). The poorly crystalline fraction of Fe oxides, the oxalate-extractable Fe (Fe_o), was extracted by acid ammonium oxalate (Schwertmann, 1964). Both, the dithionite and the oxalate extracts were analysed for Fe and Al (Al_d , Al_o) by atomic absorption spectrometry using an AAS UNICAM 939 (Unicam AAS-UV, Offenbach, Germany).

3.4. Particle size fractionation

Air dried <2 mm soil (30 g) was suspended in 150 ml deionised water with a soil mass (g) to water volume (ml) ratio of 1:5. An ultrasonic treatment with a Branson Sonifier 250 (Branson Ultrasonics Corp., Danbury, USA) was applied to break up aggregates. To prevent a redistribution of coarse particulate organic matter to finer size classes, ultrasonic dispersion was carried out in two steps as described by Amelung and Zech (1999). Macroaggregates were first destroyed with a low energy input of 60 J/ml. Particles >200 μm – including particulate organic matter – were then removed by wet sieving. A second, complete dispersion was achieved with an ultrasonic treatment using an energy input of 440 J/ml and a soil mass (g) to water volume (ml) ratio of 1:10. Subsequently, the 20-200 μm fraction was isolated by wet sieving. The remaining part of the sample was further separated in a 2-20 μm and <2 μm fraction by repeated gravitational sedimentation using Atterberg cylinders filled with deionised water. The clay fraction was recovered from the solution by pressure filtration (0.2 μm polypropylene filter) and freeze dried. All size separates >2 μm were oven dried at 40°C. Aliquots of particle size fractions taken for C and N analyses, radiocarbon dating, ^{13}C CPMAS NMR spectroscopy and lignin analysis (alkaline CuO-oxidation) were homogenised and ground with agate mortar and pestle to a size of <100 μm .

3.5. Radiocarbon dating

Radiocarbon activity was determined with the AMS facility at the Physics Department of the University of Erlangen, Germany. A complete description of the AMS facility was published by Kretschmer et al. (1997). Briefly, after dry combustion of the samples, a small aliquot of the arising carbon dioxide and nitrogen was bled into a mass spectrometer where the stable isotope ratios $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were measured. The remaining part of CO_2 was reduced to graphite by heating a mixture of H_2 and CO_2 with iron powder at 625°C. The graphite was pressed into targets and measured with the

AMS. The amount of radiocarbon enrichment is expressed in percent modern carbon (pmC) and in years before present (yrs B.P.) which refer to the 1950 ^{14}C activity. The average error was 0.5 pmC and 55 yrs B.P., respectively. All values were corrected for isotope fractionation using the $\delta^{13}\text{C}$ values. Samples from Collelongo were treated with 4% HCl during 24 hours to remove CaCO_3 prior to radiocarbon analysis (Mook and Streurman, 1983).

3.6. ^{13}C CPMAS NMR spectroscopy

3.6.1. Pre-treatment with HF (demineralisation)

Prior to NMR spectroscopy, bulk soil samples, $<2\ \mu\text{m}$ and $2\text{-}20\ \mu\text{m}$ fractions were treated with 10% hydrofluoric acid (HF) (v/v) to remove mineral material including paramagnetic compounds such as Fe and to concentrate the SOM (Schmidt et al., 1997). An HF concentration of 10% offers a reasonable compromise between maximal mineral dissolution efficiency and OC losses (Gélinas et al., 2001). Five gram of bulk soil samples and 1-2 g of particle size fractions were thoroughly mixed with 50 ml of 10% HF and stirred for 2 hours. The soil/HF samples were centrifuged for 10 min at 3000 rpm and the supernatant was removed and discarded. The demineralisation procedure was repeated on the same sample four times. Subsequently, the residual solid phase was rinsed with deionised water five times, freeze dried and homogenised with agate mortar and pestle. The Fe_d concentration after demineralisation was determined for clay fractions from Leinefelde (62, 111, 153+16) and from Hesse. The recovery of Fe_d after demineralisation ranged between 3 and 8% ($0.7\text{-}1.5\ \text{g Fe}_d\ \text{kg}^{-1}$ soil). OC and N determinations before and after demineralisation allowed the recovery of OC and N to be calculated (Eq. 1):

$$\text{OC(N) recov. (in\%)} = \frac{\text{OC(N) mass (HF treated sample)}}{\text{OC(N) mass (untreated sample)}} \cdot 100 \quad (1)$$

The HF soluble OC was calculated as the difference between OC mass in untreated and HF treated samples. The enrichment ratios of OC and N (Eq. 2) facilitate a comparison of the OC and N concentration before and after demineralisation:

$$E_{OC(N)} = \frac{\text{OC(N) conc. (HF treated sample)}}{\text{OC(N) conc. (untreated sample)}} \quad (2)$$

In addition, Q (Eq. 3), the ratio of OC/N weight ratios before and after demineralisation, was calculated and used to assess possible changes in SOM quality:

$$Q = \frac{\text{OC/N ratio (HF treated sample)}}{\text{OC/N ratio (untreated sample)}} \quad (3)$$

3.6.2. Standard ^{13}C CPMAS NMR measurements

Solid state ^{13}C CPMAS NMR spectra were obtained from bulk soils and particle size fractions. Due to low OC concentrations it was not possible to obtain spectra from the 20-200 μm fractions. Ground 200-2000 μm fractions containing negligible concentrations of paramagnetics were taken for ^{13}C CPMAS NMR spectroscopy without pre-treatment. All other samples were treated with 10% HF. Solid state ^{13}C CPMAS NMR spectra were acquired using a Bruker DSX 200 spectrometer (Bruker BioSpin GmbH, Karlsruhe, Germany) at a ^{13}C resonance frequency of 50.3 MHz. Samples were filled into zirconium dioxide rotors and spun in a magic angle spinning probe at a rotation speed of 6.8 KHz to minimise chemical anisotropy. A ramped ^1H pulse was used during a contact time of 1 ms to prevent Hartmann-Hahn mismatches. The total number of scans ranged from $8 \cdot 10^3$ to $333 \cdot 10^3$ with a constant recycle delay of 400 ms. Prior to Fourier transformation and phasing the spectra were processed with a line broadening of 50 Hz. Chemical shifts are referenced to tetramethylsilane (TMS = 0 ppm). Solid state ^{13}C CPMAS NMR spectra were divided into five chemical shift regions, representing alkyl C (0-45 ppm), O/N-alkyl C (45-110 ppm), C/H-aryl C (110-140 ppm), O-aryl C (140-160 ppm) and carbonyl C (160-220 ppm). The relative intensities of the chemical shift regions were determined by integration of ^{13}C CPMAS NMR spectra over given chemical shift ranges after phase and baseline correction. The variation of the relative intensities due to Fourier transformation, phase and baseline correction was lower than 4%. Changes of proportions of different carbon species in relation to the alkyl C proportion, which was the second most important carbon species, were investigated by calculating O/N-alkyl C, aryl C and carbonyl C quotients (Eq. 4). They were calculated from the O/N-alkyl C/alkyl C, aryl C/alkyl C and carbonyl C/alkyl C ratios before and after demineralisation:

$$\text{Quotient} = \frac{\frac{\text{O/N - alkyl C (aryl C, carbonyl C)}}{\text{alkyl C}} \text{ (HF treated sample)}}{\frac{\text{O/N - alkyl C (aryl C, carbonyl C)}}{\text{alkyl C}} \text{ (untreated sample)}} \quad (4)$$

Quotients >1 indicated, that during demineralisation the proportion of O/N-alkyl C, aryl C or carbonyl C increased relative to the alkyl C intensity. A decrease of the carbon species relative to alkyl C accounted for quotients <1. If the ratio between the carbon species and alkyl C was identical before and after demineralisation, the quotient equalled 1.

3.6.3. Variable contact time experiment

A variable contact-time (VCT) experiment was performed to compare spin-lattice relaxation times in the rotating frame ($T_{1\rho}H$) of the untreated and HF treated clay fraction from Hesse. This sample was chosen for a VCT experiment because of its high Fe_d/OC ratio (Table 12). Solid state ^{13}C CPMAS NMR spectra were acquired with an array of 17 different contact times varying from 0.03 ms to 4 ms. The values of $T_{1\rho}H$ in the vicinity of alkyl C and O/N-alkyl C were determined from the loss of ^{13}C magnetisation as a function of increasing contact times. Plots for carbonyl C and aryl C were not displayed, since low signal to noise ratios of the carbonyl C and aryl C signals in the spectra of the untreated sample did not allow for quantification. The curves of intensity of the different carbon species vs. contact time were fitted with a two component model using the sum of two Mehring terms (Mehring, 1983; Abelmann et al., 2004). The two component model considered that fast and slow relaxing components might be present in the sample. The fitting was performed with the software Mathcad 2000 Professional (Adept Scientific plc, Letchworth, UK) according to the procedure described by Abelmann et al. (2004). $T_{1\rho}H$ and $T_{1\rho}C$ values from experiments with coal samples (Abelmann et al., 2004) were found to be suitable as initial values for the modelling.

3.7. **Lignin analysis (Alkaline CuO oxidation)**

Lignin derived phenols were determined in duplicate using a modification of the CuO oxidation method developed by Hedges and Ertel (1982). The extraction by ethyl ether was replaced by an extraction with C_{18} columns introduced by Kögel and Bochter

(1985). Depending on OC concentrations between 50 and 500 mg of ground soil, 250 mg CuO, 50 mg $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 50 mg $\text{C}_6\text{H}_{12}\text{O}_6$ were weighed into teflon vessels and mixed with 15 ml 2 M NaOH. Subsequently, lignin was digested in a pressure bomb (Groteklaes GmbH, Jülich, Germany) under a nitrogen atmosphere at 172°C for 2 h. After cooling of the pressure bomb, samples were acidified to pH 2 with 6 M HCl and allowed to stand in the dark overnight. During this time humic acids precipitated and were separated by centrifugation. Aliquots of the supernatant, containing the lignin derived phenols, were extracted with C_{18} reversed phase columns. After drying of columns in a nitrogen stream for 1 h, the lignin derived phenols were extracted with five times 0.5 ml ethyl acetate. Ethyl acetate was evaporated in a nitrogen atmosphere, CuO oxidation products were dissolved in pyridine and derivatised with bis(trimethylsilyl)trifluoroacetamide. The lignin derived phenols were analysed on an Agilent 6890 gas chromatograph with a flame ionisation detector equipped with a HP5 fused silica capillary column (30 m length, 0.25 mm ID, 0.25 μm film thickness). 1 μl of samples was injected using the split mode (split ratio 1:50) at an injector temperature of 300°C. The initial column temperature was set to 100°C and the oven was programmed to 200°C at 5°C/min and to 300°C at 10°C/min. The final temperature was kept for 15 min. The detector temperature was 300°C. During the whole analysis a constant helium flow of 1.0 ml/min was maintained. The sum of vanillyl, syringyl and cinnamyl (VSC) units was taken to represent the lignin content. The coefficient of variation for the sum of VSC is usually 7 % (Kiem and Kögel-Knabner, 2003). The acid-to-aldehyde ratio of syringyl units was taken as an indicator for the degree of lignin modification (Ertel and Hedges, 1984).

3.8. Determination of specific surface area

The specific surface area (SSA) was determined by an Autosorb 1 surface area analyser (Quantachrome GmbH, Odelzhausen, Germany). Prior to determination of SSA, the samples were outgased in a He flow for 24 h at a temperature of 343 K to remove adsorbed water. The specific surface area was calculated from the adsorption isotherm of N_2 at 77 K, using the BET equation (Brunauer et al., 1938) and a 11 point measurement in the p/p_0 range of 0.05 to 0.30. SSA was first measured after removal of soil organic matter with 30% H_2O_2 to estimate the SSA of the total mineral matrix ($\text{SSA}_{\text{minerals}}$). After subsequent removal of dithionite extractable Fe oxides the SSA of silicates ($\text{SSA}_{\text{silicates}}$) was measured taking into account the mass loss due to the

dithionite extraction. Mineral oxides are often present as coatings that might mask a fraction of the silicate surfaces. However, an estimation of the SSA of mineral oxides (SSA_{oxides}) can be obtained by calculating the difference between SSA_{minerals} and $SSA_{\text{silicates}}$ (Borggaard, 1982; Kiem and Kögel-Knabner, 2002).

3.9. Statistics

3.9.1. Correlation analysis

Calculation of correlation coefficients was performed with the software package Statistica 6.1 (Statsoft Inc., Tulsa, USA). We used the Pearson's correlation coefficient (r) and the Spearman rank correlation coefficient (r_s), which is a distribution-free analogue of correlation analysis.

3.9.2. Analysis of spatial variation

The spatial variation of OC stocks was described by ordinary statistics and geostatistics. Mean, median, skewness, kurtosis and coefficient of variation (CV) of OC stocks were calculated as basic statistical parameters. The solum >0.12 m, i.e. the solum from a depth of 0.12 m down to the bedrock, was taken to estimate the OC stocks in the subsoil. OC stocks are presented in kg m^{-2} because extrapolation over large scales (e.g. using the unit Mg/ha) is complicated due to unknown correction factors for large roots, stumps, skeleton, and spatial variation. The minimum detectable difference (MDD) of OC stocks was calculated for the forest floor and the solum. MDD is defined as the smallest difference that can be detected between means of OC stocks (Eq. 5) (Zar, 1984):

$$MDD = \sqrt{\frac{s_p^2}{n} (t_{\alpha(2),v} + t_{\beta(1),v})^2} \quad (5)$$

where s_p^2 is the variance estimate, n is the sample size and t is the t-statistic at a given significance level (α), probability of type II error (β) and degree of freedom (v). In our study, we used a statistical power ($1-\beta$) of 0.90 and a significance level (α) of 0.05. As variability increases, the minimum number of samples needed to detect a given level of change increases. In order to enable a comparison of MDD values of depth increments with different magnitudes of OC stocks, the $MDD_{\text{rel.}}$ was calculated (Eq. 6) as follows:

$$MDD_{rel.} = \frac{MDD}{\bar{x}} \cdot 100\% \quad (6)$$

where MDD is the minimum detectable difference and \bar{x} is the mean OC stock. The magnitude of OC stocks in soils varies from location to location. The experimental semivariogram describes the rate of change of OC stocks as a function of the distance between sampling points and measures the degree of spatial continuity. Usually one distinguishes between directional (considering sampling points in one specific direction) and omnidirectional (considering sampling points in all directions) semivariograms (Webster and Oliver, 2001). Observations of OC stocks located close to one another often tend to be more similar compared to observations separated by a larger distance. Therefore the semivariance $\gamma(h)$ increases as distance between observations increases (Nielsen and Wendroth, 2003). The semivariogram was calculated in the following way (Eq.7):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [A_i(x_i) - A_i(x_i + h)]^2 \quad (7)$$

where $N(h)$ is the number of pairs of data points separated by the lag distance h . $A_i(x_i)$ and $A_i(x_i + h)$ represent values of A_i at the locations x_i and $x_i + h$. The experimental semivariogram was calculated for distances from 0 to 60 m taking into account distances between all pairs of sampling points. For this purpose, distances between sampling points were grouped into distance classes which cover 5 m each (1st class: 0-5 m, 2nd class: 5-10 m, and so on). In order to resolve the small scale variability, an additional semivariogram for the lag distances ≤ 16.2 m was calculated using the spatially explicit distances between primary stations and substations. Since sampling points are distributed all-over the study area, the semivariogram for the small lag distances is representative for the entire forest stand. For all semivariogram calculations, it was assumed that the intrinsic hypothesis of geostatistics holds. Most semivariograms reach an upper limit at which the semivariance remains nearly constant after the initial increase. The maximum semivariance is denominated as the sill variance. The range, in turn, is defined as the distance at which the variogram reaches the sill. The calculated values often appear to approach some positive value as the lag distance approaches zero, whereas theoretically the semivariance should be zero. This discrepancy is known

as the nugget variance and reflects the micro-heterogeneity and the measurement error. In addition to the traditional experimental semivariogram, more robust measures of spatial continuity such as madograms were plotted. Madograms are similar to traditional semivariograms, but they respond less sensitive to extreme data values. Instead of the square of differences, absolute differences between $A_i(x_i)$ and $A_i(x_i + h)$ were calculated (Eq.8) (Goovaerts, 1997):

$$\gamma_M(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} | [A_i(x_i) - A_i(x_i + h)] | \quad (8)$$

In order to examine spatial relations between different types of variables, the experimental crossvariogram is defined by an extension of the calculation of ordinary semivariograms (Eq.9) (Nielsen and Wendroth, 2003):

$$\Gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [A_i(x_i) - A_i(x_i + h)] [B_i(x_i) - B_i(x_i + h)] \quad (9)$$

where $A_i(x_i)$ and $B_i(x_i)$ are the values of variable A_i and B_i at location (x_i) . $A_i(x_i + h)$ and $B_i(x_i + h)$ represent values of A_i and B_i at the location $x_i + h$. To enable a comparison of the spatial continuity of different variables that are characterised by different magnitudes of variability, the general relative variogram was calculated, which is the traditional semivariogram as described in (Eq. 7), standardised by the square mean of the data used for each lag distance (Eq. 10) (Goovaerts, 1997):

$$\gamma_{GR}(h) = \frac{\gamma(h)}{\left(\frac{m_{-h} + m_{+h}}{2} \right)^2} \quad (10)$$

where m_{-h} is the mean of $A_i(x_i)$ values and m_{+h} is the mean of $A_i(x_i + h)$ values.

4. O/N-alkyl and alkyl carbon are stabilised in fine particle size fractions of soils under beech

Soil samples to study the composition of Ah horizons under beech (*Fagus sylvatica* L.) forest originated from sites in Collelongo/Italy, Hesse/France, Sorø/Denmark and Leinefelde/Germany (Table 2). In Leinefelde samples were collected from a chronosequence including stands with an average tree age of 30, 62, 111 and 153+16 years (153+16 refers to a mixture of 153 years old trees with 16 years old trees) (Table 2). In all figures of this chapter, the results of the chronosequence are presented separately (“Chronosequence Leinefelde”). For the comparison of “European Sites” the sites in Collelongo, Hesse, Sorø and the 62 years old stand from Leinefelde were selected. The 62 years old stand from Leinefelde versus the other Leinefelde sites was chosen to be included in the “European Sites comparison”, because it represents a stand with neither very young nor very old trees. The humus form at all sites was mull. The thickness of the Ah horizons varied between 0.07 and 0.25 m. Soil types comprised Rendzic Leptosols in Collelongo and Leinefelde (30/1), Stagnic Luvisols in Hesse and in Leinefelde (30/2, 62 and 153+16), a Haplic Luvisol in Leinefelde (111), and a Stagnic Phaeozem in Sorø (ISSS-ISRIC-FAO, 1998). Soil pH ranged from 4.1 in Hesse to 6.9 in Collelongo. According to the Soil Science Society of America nomenclature (SSSA, 2001) the soil texture in the Ah horizons corresponded to sandy clay loam in Sorø, silt clay loam in Hesse and Leinefelde (30/2, 62 and 111), silty clay in Leinefelde (30/1 and 153+16) and clay in Collelongo.

4.1. Major proportion of total OC is stored in clay fractions

The OC concentrations in the A horizons samples ranged from 31 to 96 g kg⁻¹ in the bulk soils and from 8 to 406 g kg⁻¹ in the particle size fractions (Table 3). To facilitate a comparison of carbon enrichments in fractions of soils with different OC levels in the bulk soils, enrichment factors for OC (E_{OC}) were calculated (g kg⁻¹ of OC in fraction/ g kg⁻¹ of OC in bulk soil) (Table 3). Most of the <2 µm and 200-2000 µm fractions were enriched, whereas most of the 2-20 µm and 20-200 µm fractions were depleted in OC. The OC stocks in the total Ah horizons ranged from 1.8 to 8.1 kg m⁻² (Table 3). The Ah horizons at Collelongo, Leinefelde (30/1) and Sorø which were thicker than 0.15 m exhibited the highest carbon stocks (more than 4.9 kg m⁻²).

Table 2: Characteristics of Ah horizon samples from 8 beech forest sites

Site	Latitude/ Longitude	Climate	Stand age	Soil Classification (WRB) ^c	Thickness of Ah horizon	pH (CaCl ₂)	Texture			
							2000 µm - 200 µm	200 µm - 20 µm	20 µm - 2 µm	<2µm
			years		m		%			
Collelongo/ Italy	41°52'N/ 13°38'E	mediterranean/ montane	109	Rendzic Leptosol	0.19	6.9	2	7	32	59
Hesse/ France	48°40'N/ 07°05'E	temperate/ suboceanic	34	Stagnic Luvisol	0.08	4.1	1	28	40	31
Sorø/ Denmark	55°29'N/ 11°38'E	temperate/ oceanic	60	Stagnic Phaeozem	0.25	4.1	23	39	14	24
Leinefelde/ Germany	51°20'N/ 10°22'E	temperate/ continental	30/1 ^a	Rendzic Leptosol	0.15-0.20	5.5	<1	16	28	56
			30/2 ^a	Stagnic Luvisol	0.08	5.1	<1	27	35	38
			62	Stagnic Luvisol	0.08	4.7	<1	24	45	31
			111	Haplic Luvisol	0.07	4.5	1	23	40	36
			153+16 ^b	Stagnic Luvisol	0.08	5.0	<1	15	43	42

^a Two profiles representing the main soil types were sampled and designated as Leinefelde 30/1 and 30/2.

^b 153 years old trees mixed with 16 years old trees. The proportion between old and young trees is about 20:80.

^c WRB: World Reference Base for soil resources, ISSS-ISRIC-FAO (1998)

The variability of carbon stocks on volume basis (22 to 41 kg m⁻³) was lower than on horizon basis. The highest proportions of the total OC stock of the respective Ah horizons were accumulated in the <2 µm and 2-20 µm fractions. The contribution of the 200-2000 µm fraction to the total OC stocks was higher under the young stands in

Table 3: OC concentrations, OC enrichment ratios (E_{OC}), OC stocks and C/N ratios in bulk soils and particle size fractions of Ah horizons

Site (Stand age)	Fraction µm	OC g kg ⁻¹	E_{OC}	OC stock kg m ⁻²	OC stock kg m ⁻³	% of bulk soil OC stock %	C/N
Collelongo (109)	Bulk soil	96		7.7	41		11.8
	200-2000	154	1.7	0.4	2	5	29.4
	20-200	102	1.1	0.7	4	9	20.1
	2-20	88	0.9	2.8	15	36	12.4
	<2	88	0.9	3.8	20	50	9.7
Hesse (34)	Bulk soil	31		1.8	22		13.4
	200-2000	109	3.5	0.3	5	18	27.8
	20-200	9	0.3	0.1	3	8	16.5
	2-20	14	0.4	0.4	7	21	12.0
	<2	51	1.6	0.9	17	53	6.7
Sorø (60)	Bulk soil	45		8.1	32		12.8
	200-2000	17	0.4	0.8	3	10	15.4
	20-200	8	0.2	0.7	3	8	11.7
	2-20	84	1.9	2.5	10	31	13.4
	<2	163	3.6	4.1	17	51	10.7
Leinefelde (30/1)	Bulk soil	47		4.9	29		11.1
	200-2000	114	2.8	0.8	4	16	18.4
	20-200	30	0.6	0.5	3	11	20.7
	2-20	43	0.9	1.1	7	23	16.3
	<2	62	1.3	2.4	15	50	9.5
Leinefelde (30/2)	Bulk soil	48		3.0	38		14.4
	200-2000	406	8.4	0.7	9	22	30.2
	20-200	15	0.3	0.3	3	9	18.7
	2-20	26	0.5	0.7	9	23	17.3
	<2	74	1.5	1.4	17	46	10.9
Leinefelde (62)	Bulk soil	49		3.1	38		13.8
	200-2000	203	4.1	0.3	4	11	20.7
	20-200	20	0.4	0.3	4	10	19.1
	2-20	42	0.9	1.2	15	40	17.0
	<2	75	1.5	1.2	15	39	8.6
Leinefelde (111)	Bulk soil	32		1.9	27		12.9
	200-2000	214	6.7	0.3	4	13	22.3
	20-200	15	0.5	0.3	4	14	20.4
	2-20	24	0.7	0.6	8	30	17.5
	<2	60	1.9	0.8	12	43	8.9
Leinefelde (153+16)	Bulk soil	34		2.1	27		13.1
	200-2000	245	7.2	0.4	4	16	25.6
	20-200	9	0.3	0.1	1	5	24.3
	2-20	23	0.7	0.6	8	30	21.4
	<2	45	1.3	1.0	13	49	8.7

Leinefelde (30/1, 30/2 and 153+15) and in Hesse. In almost all samples the C/N ratios were decreasing in finer particle size separates (Table 3). Only the C/N ratios of the 200-2000 μm fractions under the 30 years old stand in Leinefelde (30/1) and of the 20-200 μm fraction of Sorø did not fit in this trend.

The wide range of E_{OC} 's (Table 3), also shown by Christensen (1996) and Amelung et al. (1998), suggests that carbon pools of different structure and function were separated by particle size fractionation. The distribution of OC stocks between the particle size fractions was similar to that described for acid forest soils by Kaiser et al. (2002). A major proportion of OC was stored in the clay fractions (Table 3), but the contribution of the clay fraction to the total OC stock in Ah horizons was lower than in arable soils, where contributions of 50% and more are common (Christensen, 1996). This is most probably due to a comparatively high proportion of plant residues in forest soils, which are mainly associated with the 200-2000 μm fraction (Balesdent et al., 1998). The greater relative proportions of OC in the 200-2000 μm fractions of the young stands in Leinefelde and Hesse suggest that a high tree density in young stands affected the soil OC stock by providing higher litter inputs to the coarse fraction. However, a relation between bulk soil OC stocks and stand age was not observed (Table 3). The comparison of OC stocks per square meter and per cubic meter showed that the main factor controlling the magnitudes of the total OC stocks in the bulk soil was the thickness of the Ah horizon. As previously described, e.g. by Baldock et al. (1992), Balesdent et al. (1998) and Guggenberger et al. (1994), the C/N ratios decrease in the fine fractions of forest soils (Table 3). This is usually ascribed to a higher contribution of microbial derived compounds to SOM (Amelung et al., 1998; Haider, 1999; Schmidt and Kögel-Knabner, 2002).

4.2. Decreasing lignin contents with progressing decomposition

Solid state ^{13}C CPMAS NMR spectra of particle size fractions of the Ah horizons from the four European beech forest sites are presented in Fig. 2. Main resonances occurred at 30, 56, 72, 105, 130, 150 and 173 ppm. Resonances at 72 ppm and 105 ppm are most probably assigned to C2, C3, C5 and C1 in cellulose and non-crystalline polysaccharides (Preston et al., 1998). The resonance at 30 ppm is typical for methylene C in long chain aliphatic compounds, the features around 56, 130 and 150 ppm are attributed to methoxyl, H-/C-substituted and phenolic C in lignin and tannins (Kögel-

Knabner, 1997). N-alkyl of amino acids may also contribute to the signal at 56 ppm. High signal intensities at 130 ppm often arise from the presence of condensed aromatic C structures, such as in charred organic matter, but may also be explained by C in C-C double bonds. Carbonyl C in carboxyl, amide, and ester groups of various compounds contributes to the peak at 173 ppm.

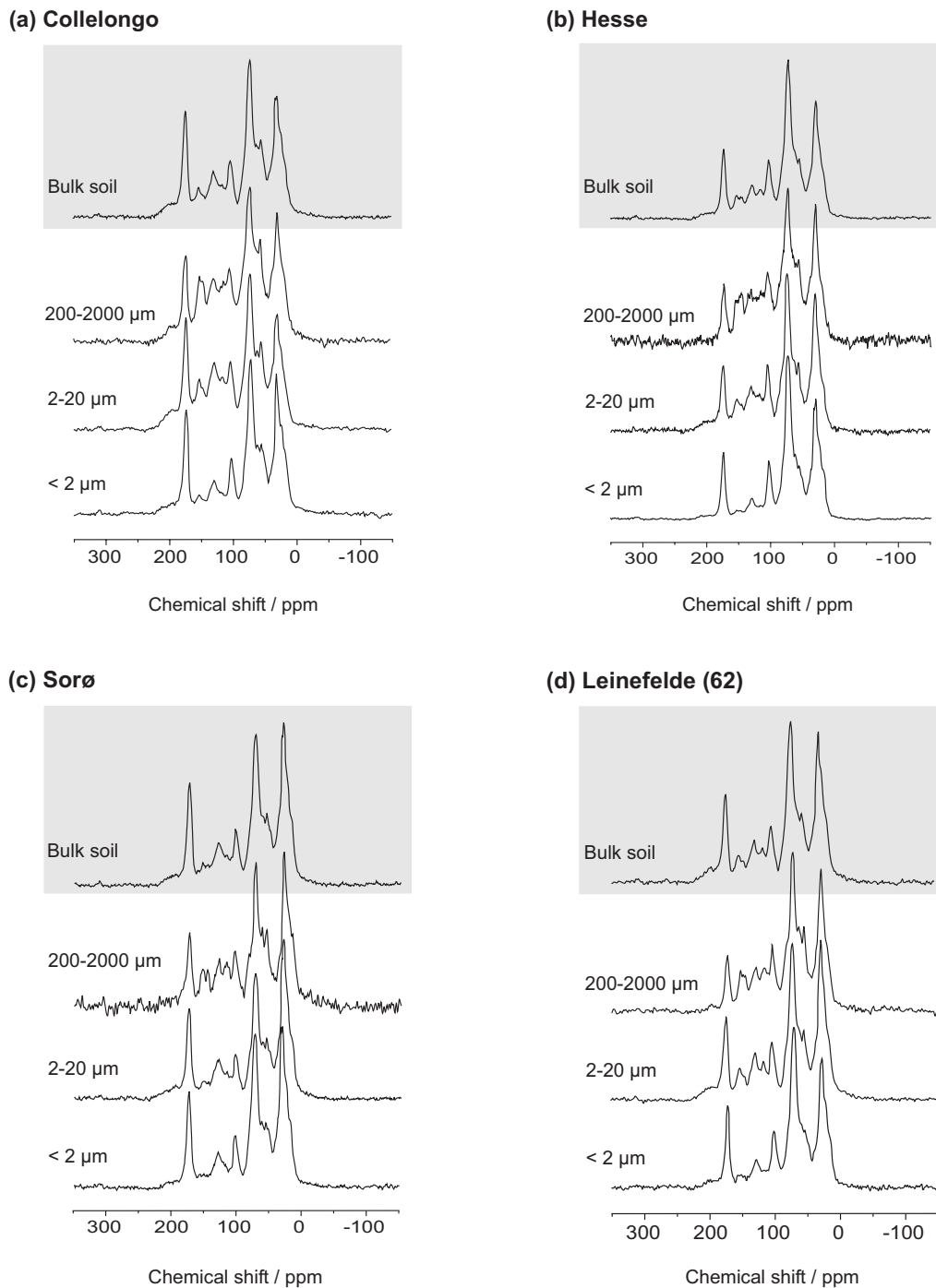


Figure 2: ^{13}C CPMAS NMR spectra of bulk soils and particle size fractions of Ah horizons from the sites in Collelongo (a), Hesse (b), Sorø (c) and Leinefelde (62 years old stand) (d)

Table 4 presents the relative intensities of the chemical shift areas. Integration of the chemical shift regions showed high relative intensities of O/N-alkyl C (37 to 53%) and alkyl C (22 to 34%) in the bulk soils as well as in the particle size fractions. Lower intensities were found for aryl C (9-22 %) and carbonyl C (7-17%). The highest variations between the relative intensities of particle size fractions were detected for O/N-alkyl C and aryl C (Table 4). The contribution of O/N-alkyl C in all A horizons decreased from the 200-2000 μm fraction (42-52%) to the 2-20 μm fraction (37-45%) and increased from the 2-20 μm fraction to the <2 μm fraction (42-53%). Relative intensities of aryl C declined from 19-21% in the 2000-200 μm fractions to 9-12% in

Table 4: Relative signal distributions of OC species in bulk soils and particle size fractions of Ah horizons determined by ^{13}C CPMAS NMR spectroscopy

Site (Stand age)	Fraction μm	Alkyl C	O/N-alkyl C	Aryl C	Carbonyl C
		(0-45 ppm)	(45-110 ppm)	(110-160 ppm)	(160-220 ppm)
		—————% OC—————			
Collelongo (109)	Bulk soil	26.1	42.9	15.4	15.5
	200-2000	22.1	43.2	18.1	16.5
	2-20	21.6	40.5	21.5	16.4
	<2	28.8	45.6	11.6	14.0
Hesse (34)	Bulk soil	26.4	48.6	14.5	10.5
	200-2000	24.7	47.6	21.3	7.6
	2-20	26.7	44.3	17.7	11.3
	<2	29.4	53.2	8.9	8.5
Sorø (60)	Bulk soil	31.3	41.3	13.6	13.7
	200-2000	29.1	41.9	19.2	9.8
	2-20	33.3	37.4	13.8	15.4
	<2	33.6	42.3	10.8	13.3
Leinefelde (30/1)	Bulk soil	24.9	47.9	13.5	13.7
	200-2000	21.6	46.1	20.8	11.4
	2-20	26.6	41.6	18.1	13.6
	<2	22.2	52.6	11.1	14.1
Leinefelde (30/2)	Bulk soil	26.0	47.8	14.2	12.0
	200-2000	23.0	50.9	18.7	7.4
	2-20	27.3	43.1	18.5	11.2
	<2	27.1	49.6	11.8	11.5
Leinefelde (62)	Bulk soil	29.9	42.1	14.3	13.7
	200-2000	26.6	47.1	19.1	7.2
	2-20	31.0	40.4	15.6	13.0
	<2	27.1	51.5	11.0	10.8
Leinefelde (111)	Bulk soil	31.5	43.9	13.1	11.5
	200-2000	27.9	43.3	19.2	9.6
	2-20	31.9	40.2	15.2	12.7
	<2	29.7	49.9	9.0	11.4
Leinefelde (153+16)	Bulk soil	27.2	47.2	13.9	11.7
	200-2000	23.7	51.9	17.0	7.4
	2-20	26.0	45.4	17.4	11.1
	<2	25.2	52.3	11.3	12.5

the $<2 \mu\text{m}$ fractions. The relative proportion of O-aryl C is correlated with the C/N ratios at the Chronosequence Leinefelde as well as at the European Sites (Fig. 3 a,b). The relation between O-aryl C intensity and C/N ratio in particle size fractions is non-linear. Similar to the relative intensity of O-aryl C the proportion of H/C-aryl C decreased with progressing turnover at the Chronosequence Leinefelde as well as at the European Sites. This leads to nearly linear relations between O-aryl C and H/C-aryl C intensities (Fig. 4 a,b).

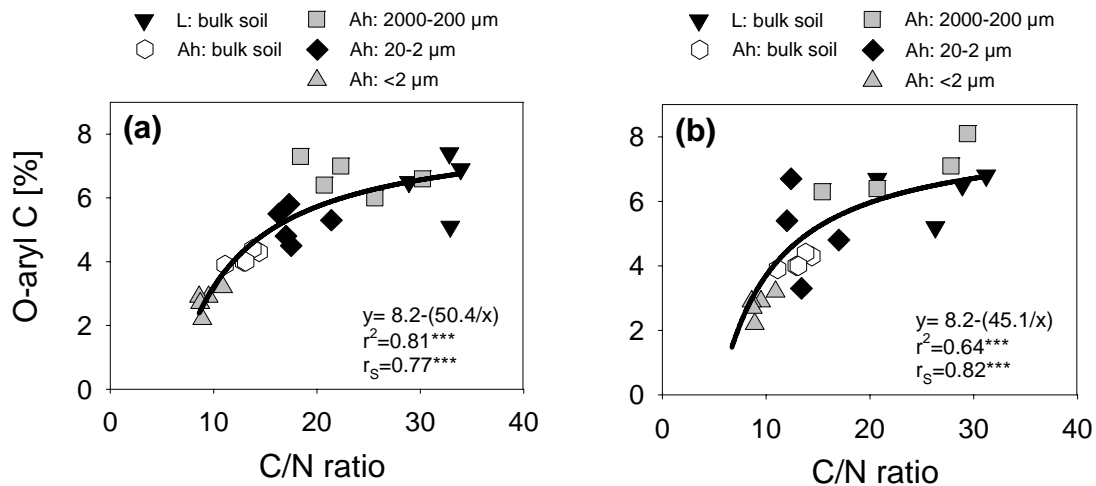


Figure 3: Relative intensity of O-aryl C in relation to C/N ratios in L horizons (L) and in bulk soil samples and particle size fractions of Ah horizons (Ah) (a) from the Chronosequence Leinefelde and (b) from the sites in Collelongo, Hesse, Sorø and Leinefelde (62 years old stand)

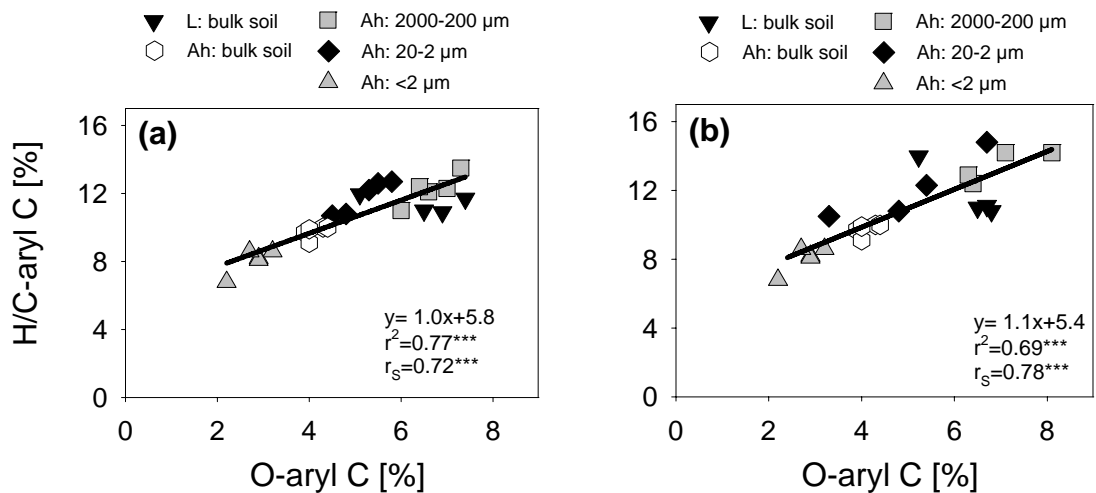


Figure 4: Relative intensity of H/C-aryl C in relation to relative intensity of O-aryl C in L horizons (L) and in bulk soil samples and particle size fractions of Ah horizons (Ah) (a) from the Chronosequence Leinefelde and (b) from the sites in Collelongo, Hesse, Sorø and Leinefelde (62 years old stand)

The contents of CuO oxidation products normalised to OC are given in Table 5. The sum of CuO oxidation products VSC in the bulk soils ranged between 10 and 22 g kg⁻¹ OC. The highest concentrations of CuO oxidation products were present in the

Table 5: Concentrations, enrichment ratios (E_{VSC}) and stocks of phenolic CuO-oxidation products (VSC) and acid-to-aldehyde ratios of syringyl units ($(Ac/Al)_s$) in bulk soil and particle size fractions of Ah horizons

Site (stand age)	Fraction μm	VSC g kg ⁻¹ OC	E_{VSC}	VSC stock 10 ⁻³ kg m ⁻²	% of bulk soil VSC stock %	$(Ac/Al)_s$ 10 ⁻¹
Collelongo (109)	Bulk soil	10		53		3.3
	200-2000	27	2.8	7	13	2.6
	20-200	12	1.2	6	11	4.2
	2-20	14	1.6	27	51	3.6
	<2	5	0.6	14	25	3.7
Hesse (34)	Bulk soil	17		32		2.3
	200-2000	30	1.8	10	32	1.9
	20-200	34	2.0	5	17	2.5
	2-20	25	1.5	10	31	2.6
	<2	6	0.4	6	20	5.2
Sorø (60)	Bulk soil	8		83		5.1
	200-2000	15	1.8	20	25	3.3
	20-200	20	2.4	23	28	5.3
	2-20	6	0.7	26	32	6.5
	<2	2	0.2	13	16	9.1
Leinefelde (30/1)	Bulk soil	13		73		2.9
	200-2000	29	2.2	20	27	2.8
	20-200	36	2.7	20	28	2.3
	2-20	19	1.4	21	29	2.8
	<2	5	0.4	12	16	3.3
Leinefelde (30/2)	Bulk soil	18		55		2.3
	200-2000	39	2.2	24	44	1.4
	20-200	37	2.0	7	16	2.6
	2-20	21	1.2	11	25	2.4
	<2	7	0.4	6	15	2.5
Leinefelde (62)	Bulk soil	19		59		2.7
	200-2000	49	2.6	17	28	2.4
	20-200	38	2.0	12	20	2.5
	2-20	19	1.0	23	40	3.0
	<2	6	0.3	7	12	3.2
Leinefelde (111)	Bulk soil	22		42		3.2
	200-2000	42	1.9	11	25	2.8
	20-200	40	1.8	11	26	3.5
	2-20	28	1.3	16	38	3.7
	<2	6	0.2	5	11	4.5
Leinefelde (153+16)	Bulk soil	15		32		2.9
	200-2000	32	2.1	11	34	2.5
	20-200	26	1.7	2	7	3.4
	2-20	22	1.5	13	42	3.2
	<2	6	0.4	6	17	4.1

fractions from 2 to 2000 μm . The SOM of the 200-2000 μm fractions had VSC concentrations between 15 and 49 g kg^{-1} OC, the 20-200 μm fractions between 12 and 40 g kg^{-1} OC and the 2-20 μm fractions between 6 and 28 g kg^{-1} OC. In contrast only 2-7 g kg^{-1} OC was determined in the <2 μm particle size class. The highest lignin stocks occurred either in the 2-20 μm fractions or the 200-2000 μm fractions, the lowest either in the <2 μm fractions (due to low concentrations of VSC components) or in the 20-200 μm fractions (due to the low carbon stocks). However, at Hesse and Sorø, the contents of CuO products in the 20-200 μm fractions were higher than in the 200-2000 μm fractions. With the exception of the 2-20 μm fraction in Sorø, enrichment factors (E_{VSC}) of the coarse fractions were >1 , whereas the clay fractions showed enrichment factors <1 . With the exception of Collelongo and Leinefelde 30/2, the acid-to-aldehyde ratios were lowest in the 200-2000 μm fraction and highest in the <2 μm fractions. The VSC concentrations, as determined by alkaline CuO oxidation, correlated with the signal intensities of O-aryl C (140-160 ppm) (Fig. 5 a,b).

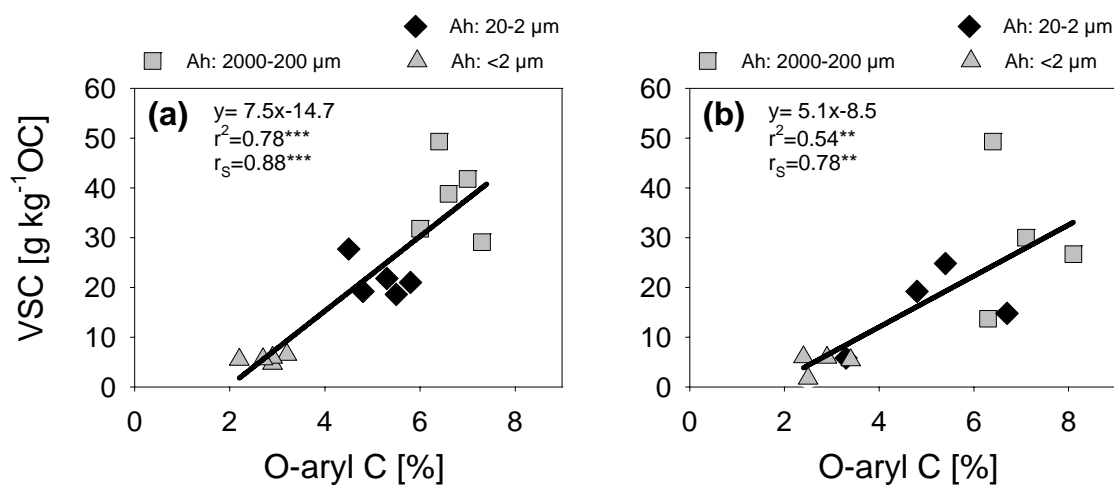


Figure 5: Relative intensity of O-aryl C in relation to concentrations of alkaline CuO oxidation products (VSC) in the particle size fractions of Ah horizons (a) from the Chronosequence Leinefelde and (b) from the sites in Collelongo, Hesse, Sorø and Leinefelde (62 years old stand).

At Leinefelde the amounts of lignin in the particle size fractions increased with increasing OC concentrations in the respective fractions (Fig. 6). Similar relations are expected for the other sites, but the number of data pairs was not sufficient to compile similar plots.

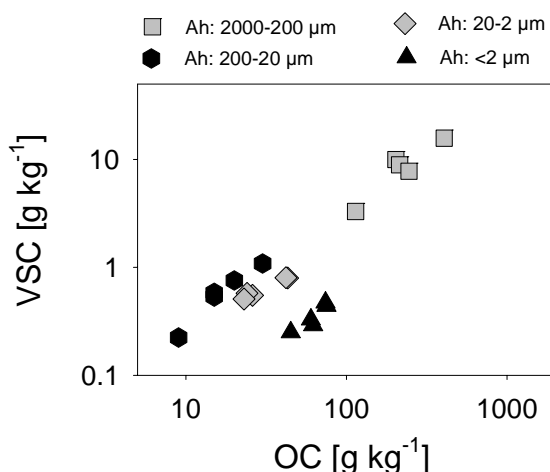


Figure 6: Alkaline CuO oxidation products (VSC) in relation to OC concentration in the particle size fractions of Ah horizons from the Chronosequence Leinefelde.

The O/N-alkyl C contribution decreased from sand to silt fractions, but increased again in the clay fractions. This trend of O/N-alkyl C proportions in the particle size fractions (Table 4, Fig. 2) is consistent with results from Beudert et al. (1989), Preston et al. (1994) and Skjemstad et al. (1996), but contrary to various other ¹³C CPMAS NMR studies showing clay fractions to consist predominantly of alkyl C (Baldock et al., 1992; Zech and Guggenberger, 1996; Quideau et al., 2000). Preston et al. (1994) discussed that higher O/N-alkyl C proportions in clay fractions might be attributed to a lower decomposition. However, this falls short of explaining the differences in O/N-alkyl C proportions between the <2 μm fractions and 2-20 μm fractions of our soils; all <2 μm fractions of this study were characterised by higher O/N-alkyl C proportions in comparison to the 2-20 μm fractions, whereas, at the same time, low C/N ratios indicated an increased decomposition stage. Most of the carbon assimilated by fungi and bacteria during decomposition ends up with microbial structures containing a significant proportion of O/N-alkyl C (Baldock et al., 1990; Golchin et al., 1996). Therefore the increasing proportion of O/N-alkyl C in the <2 μm fraction may arise from microbial sugars (Baldock et al., 1997; Schmidt and Kögel-Knabner, 2002). Higher mass ratios of (galactose+mannose)-to-(arabinose+xylose) in clay fractions of different origin support this assumption (Guggenberger et al., 1994; Guggenberger and Zech, 1999; Kiem and Kögel-Knabner, 2003).

The aryl C signals, mainly ascribed to lignin and tannin, decreased with decreasing particle size (Table 4, Fig. 2). This is indicative of either a complete decomposition or transformation with a loss of the phenolic and aromatic structures. The clear decrease

was more apparent as no or only little charred OC was incorporated into the soils that would result in overlapping of ^{13}C CPMAS NMR signal intensities in the aryl C region. In contrast to many other studies (Skjemstad et al., 1996; Mahieu et al., 1999; Kiem et al., 2000) low aryl C signal intensities around 130 ppm were found, particularly in the $<2\ \mu\text{m}$ and 2-20 μm fractions. This agreed well with results of Skjemstad et al. (1997). They detected high amounts of charred organic matter in Australian grassland soils which were under aboriginal fire management presumably for thousands of years, whereas adjacent forested soils which were not subjected to regularly burning, contain little charred OC. Schmidt et al. (1999) reported a substantial variability of charred OC content in German soils, ranging from 0–45% of the total OC in A horizons.

Lignin and tannin contain O-aryl C as well as H/C-aryl C as structural units. The narrowing C/N ratios together with decreasing O-aryl C proportions (Table 3, Table 4, Fig. 3 a,b) confirmed the decreasing proportion of O-aryl C with progressing degree of decomposition. The O-aryl C intensities in the 200-2000 μm fractions and the L horizons were similar (around 6%). This demonstrated that SOM in 200-2000 μm fractions was strongly influenced by relatively fresh and only slightly decomposed plant material. The C/N ratios and the O-aryl C intensities in the $<2\ \mu\text{m}$ fractions decreased when compared to coarse fractions. In spite of different climate, stand ages, soil types and textures at the sampling sites, similar O-aryl C intensities at specific stages of decomposition were detected. This indicated that site specific conditions did not affect the relation between O-aryl C intensity and C/N ratio. The decrease of O-aryl C intensity was accompanied by a decrease of H/C-aryl C intensity. At all sites the O-aryl C intensity was positively correlated with the H/C-aryl C intensity (Fig. 4 a,b) indicating that the H/C-aryl C signal can in the main part be assigned to phenolic compounds like lignin and tannin. In addition, alkenes are assumed to contribute to the H/C-aryl C signal (Kögel-Knabner, 1997). They likely explain the higher H/C-aryl C intensities in comparison to the respective O-aryl C intensities.

The VSC values pointed out a high range of lignin concentrations in each particle size class (Table 5). The contents of VSC and the corresponding enrichment factors underlined that lignin oxidation products were accumulated in coarse particle size fractions, whereas the clay fractions were depleted in lignin oxidation products. Similar trends for the VSC contents from coarse to fine fractions were previously described by

Beudert et al. (1989), Kögel-Knabner & Ziegler (1993) and Guggenberger et al. (1994). The increasing degree of lignin degradation from coarse to fine fractions is supported by the acid-to-aldehyde ratios (Table 5). There is no correlation between age of the forest stand and the acid-to-aldehyde ratios across the chronosequence suggesting that the stand age did not affect the degradation status of lignin.

The results of the wet chemical lignin analysis confirmed the trend for O-aryl C found by ^{13}C CPMAS NMR spectroscopy (Fig. 5 a,b). Thus, we assume that the signal at 150 ppm can almost entirely be assigned to lignin and/or tannin. However, the correlation was stronger if taking only values from the Chronosequence Leinefelde indicating that other O-aryl C components like tannins contributed in different extent to the O-aryl C intensities at the European Sites. The correlations between the results of alkaline CuO oxidation and ^{13}C CPMAS NMR spectroscopy underlined that the removal of aromatic carbon due to HF treatment was negligible or at least did not affect the bulk functional group characterisation by ^{13}C CPMAS NMR spectroscopy. Distinct relations between the VSC concentration and the OC concentration existed for the particle size fractions of Leinefelde, the increase of lignin with increasing OC concentrations being lowest in the clay fraction (Fig. 6). A similar trend was reported for a number of bulk forest soils by Kögel-Knabner (2000). The relative contribution of lignin to SOM in the particle size fractions appeared to be independent from the OC concentration in the specific particle size fractions. The higher the magnitude of the OC stocks in the individual particle size fractions, the higher was the magnitude of the VSC stocks. This indicated that the magnitudes of the lignin stocks in bulk soil samples were mainly controlled by the particle size distribution.

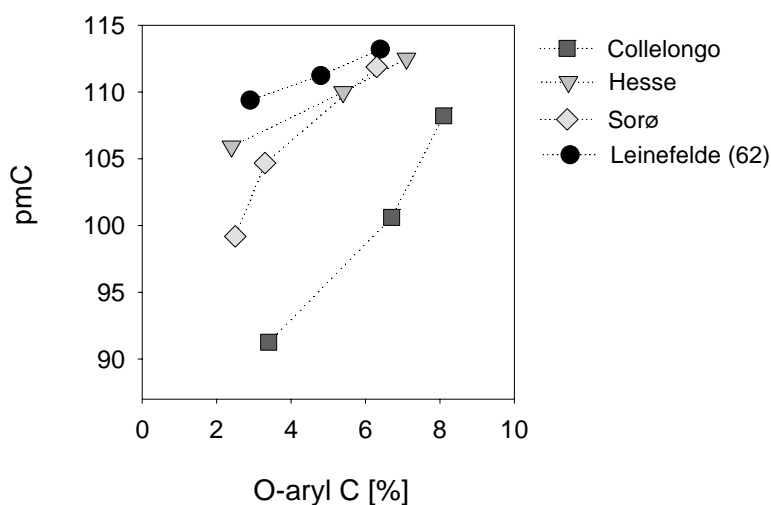
4.3. Chemical composition and turnover

The pmC values in the particle size fractions of the Ah horizons ranged from 91 to 113 (Table 6). Compared to the pmC values in the coarse fractions, lower pmC values were found in the clay fraction. The SOM of most particle size fractions showed pmC values higher than 100 and therefore the SOM in these fractions was younger than 50 years on average. Only the SOM of clay fractions in Collelongo and Sorø was clearly older and had pmC values of 91 and 99, which is equivalent to 734 and 70 years before present, respectively.

Table 6: Percent modern carbon in particle size fractions of Ah horizons

Site (Stand age)	Fraction	pmC
	μm	%
Collelongo (109)	200-2000	108.2
	20-200	112.1
	2-20	100.6
	<2	91.3
Hesse (34)	200-2000	112.5
	20-200	110.3
	2-20	110.0
	<2	105.9
Sorø (60)	200-2000	111.9
	20-200	110.1
	2-20	104.7
	<2	99.2
Leinefelde (62)	200-2000	113.2
	20-200	110.0
	2-20	111.2
	<2	109.4

Positive, site specific relations were found between the O-aryl C intensities and the pmC values at all sites (Fig. 7). Fractions containing the youngest carbon were enriched in O-aryl C, whereas the fractions with the oldest carbon were depleted in O-aryl C. A completely different pattern was obtained for the relation between the O/N-alkyl C intensity and the percentage of modern carbon (Fig. 8), with a strong increase of O/N-alkyl C content in the fine fractions with long turnover times.

**Figure 7:** Relative intensity of O-aryl C in relation to pmC values in <2 μm , 2-20 μm and 200-2000 μm fractions of Ah horizons

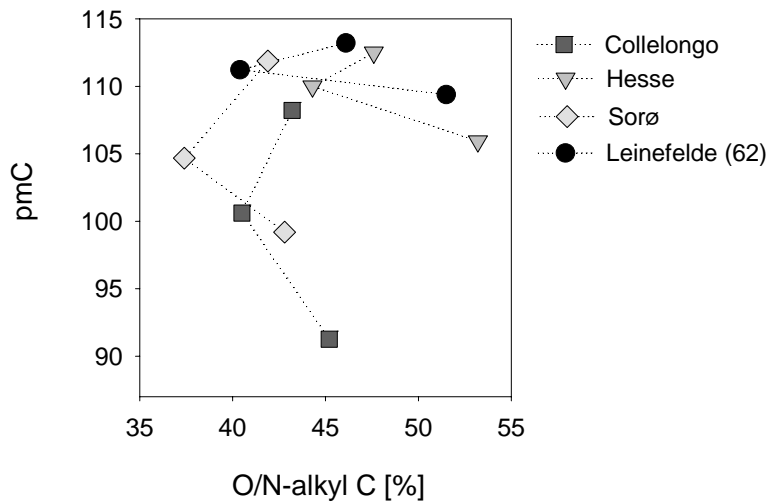


Figure 8: Relative intensity of O/N-alkyl C in relation to pmC values in <2 μm , 2-20 μm , 200-2000 μm fractions of Ah horizons

The pmC values of the fractions (Table 6) were in the same magnitude as pmC values measured in particle size fractions under oak forest in southern California (Quideau et al., 2000). Percentages modern carbon >100 reflected the enhancement of ^{14}C concentrations in the atmosphere after 1950 by bomb carbon. Lower pmC values in the clay fractions indicated higher proportions of components originating from plant material grown before 1950, whereas the coarse fractions (2000-20 μm) had a higher uptake of bomb carbon ^{14}C owing to the high contribution of recent material from leaves and roots (Table 6). In contrast to results of Trumbore and Zheng (1996), a consistent trend for the radiocarbon contents in particle size fractions of A horizon was found. The lowest amount of active material was always in the fine fractions. This is in line with results reported by Anderson & Paul (1984) who separated SOM from arable soils in pools with different turnover using a physical fractionation approach. But in contrast to their results the SOM of the clay fractions obtained in our study (Table 6) was consistently older than in the silt fractions. This was also found by Scharpenseel et al. (1986). The disagreement in the location of the most resistant SOC may be due to different stabilisation mechanisms in the different soil and vegetation types investigated (Guggenberger et al., 1994; Six et al., 2001), but may also be ascribed to distinctions in the isolation procedure for silt and clay. Scharpenseel et al. (1986) reported differences in the radiocarbon age of the clay fraction depending on the fractionation procedure. Lower radiocarbon contents were obtained, when clay fractions were isolated first after dispersion, whereas higher radiocarbon contents were found, when the clay fractions was isolated after the other fractions. Amelung & Zech (1999) exhibited that high energy inputs in the ultrasonication may lead to a redistribution of C

from the coarse to the fine fractions, which was avoided in the two-step procedure (Amelung and Zech, 1999) applied here. These results emphasise the importance of optimising the currently used fractionation procedures and the need for information on turnover of fractions obtained for a larger number of soils.

The relations between O-aryl C and pmC as well as O/N-alkyl C and pmC (Fig. 7; Fig. 8) underline the different behaviour of lignin and polysaccharides during humification (Kiem and Kögel-Knabner, 2003) and point to a specific stabilisation mechanism of O/N-alkyl C in the clay fraction. Organic carbon pools with a higher degree of turnover are characterised by an accumulation of O/N-alkyl C and are depleted in aryl C, although aromatic compounds such as lignin are considered highly recalcitrant. Lignin is recalcitrant in early stages of decomposition and is decomposed at slower rates than plant polysaccharides (Haider 1999), but in the long term lignin is completely decomposed in soils. In some soils it may accumulate in the silt-sized fractions (Baldock et al., 1992), due to retarded decomposition. However, there seems to be no stabilisation of lignin or other phenolic compounds as a result of interactions with clay minerals confirming results of Kiem & Kögel-Knabner (2003). Plant-derived polysaccharides are also degraded in soils, but polysaccharides of most likely microbial origin accumulate in the fine fractions of some soils. Kiem and Kögel-Knabner (2003) show positive relations between the polysaccharide C and the surface area and propose interactions of sugars with mineral surfaces in fine separates as a possible mechanism for the long term stabilisation of polysaccharide-type carbon. The stabilisation of O/N-alkyl C compounds in the clay fraction is supported by results of Gleixner et al. (2002) who detected old polysaccharide components in SOM from agricultural soils. However, clay fractions from other soils have a chemical composition dominated by alkyl C (Baldock et al., 1992). These differences remain to be investigated, to better understand the C stabilization mechanisms in different soils.

5. Chemical composition of young and old organic carbon pools throughout Luvisol and Cambisol profiles

Soils samples to study the composition of OC pools throughout Luvisol and Cambisol profiles were obtained from managed beech (*Fagus sylvatica* L.) forest sites in Hesse/France and Leinefelde/Germany as well as from the managed spruce (*Picea abies* L.) forest site in Tharandt/Germany (Table 7). In Leinefelde and Tharandt samples were collected from forest chronosequences. Soil types, classified according to ISSS-ISRIC-FAO (1998), comprise Haplic Luvisols and Stagnic Luvisols in Leinefelde and Hesse as well as Dystric Cambisols in Tharandt (Table 7). In all samples pH values were <5.2. According to SSSA (2001) the soil texture varied from silt loam in soil horizons from Tharandt to clay in Bt horizons from Leinefelde.

5.1. Organic carbon in coarse particle size fractions decreases with depth

OC concentrations of bulk soils and particle size fractions throughout Luvisol and Cambisol profiles at Hesse, Leinefelde and Tharandt are listed in Table 8. The OC concentrations ranged from 1 to 120 g kg⁻¹ in the bulk soil and from 1 to 245 g kg⁻¹ in the particle size fractions. The <2 µm fractions (3-195 g kg⁻¹) and the 200-2000 µm fractions (9-245 g kg⁻¹) exhibited the highest OC concentrations in almost all horizons. Only the 2-20 µm and 20-200 µm fractions from Tharandt (97) had OC concentrations marginally greater than the OC concentration of the 200-2000 µm fraction. The OC concentrations in bulk soil samples and particle size fractions generally decreased from the A horizons (9-245 g kg⁻¹) to the base of the profiles (1-166 g kg⁻¹). Some particle size fractions of the clay-rich Bt horizons from Leinefelde (111, 153+16) did not follow this trend. Taking into account bulk density, horizon thickness and percent by weight of particle size fractions, the bulk soil OC stocks and the distribution of OC on particle size fractions was calculated (Table 8). OC stocks ranged between 0.6 kg m⁻² in the Btw horizon of Leinefelde (111) and 5.6 kg m⁻² in the Bw horizon of Tharandt (97). In all soils more than 51% of the total OC was found in transition and subsoil horizons. With the exception of A horizons from Leinefelde (62) and Tharandt (97), the highest proportion of OC was in the <2 µm fractions, which contained between 27-86% of the bulk soil OC. In all soils profiles, the proportion of OC stored in the <2 µm fraction increased from the A horizon (27-53%) to the AE, B, EB and E horizons (44-86%) (Fig. 9).

Table 7: Characteristics of Cambisols and Luvisols from 2 spruce and 4 beech forest sites

Site (Stand age)	Soil classification (WRB) ^a	Horizon (FAO) ^b	Depth m	pH (CaCl ₂)	CECe cmol _c kg ⁻¹	Base saturation %	Fe _d g kg ⁻¹	Texture %			
								200-2000 μm	20-200 μm	<2μm	
Hesse (34)	Stagnic Luvisol	Ah	0.00-0.08	4.1	6.8	63.9	13.0	1	28	40	31
		AEhg	0.08-0.31	3.9	5.2	20.7	14.2	1	27	39	33
		Eg	0.31-0.58	4.0	5.1	24.2	14.7	1	26	39	34
		Btg	0.58-1.20+	4.0	10.4	53.6	17.2	1	20	37	42
Leinefelde (62)	Stagnic Luvisol	Ah	0.00-0.08	4.7	15.8	96.6	7.4	<1	24	45	31
		Eg	0.08-0.19	4.0	6.5	36.9	5.7	<1	29	39	32
		Btg	0.19-0.35	5.1	25.6	98.8	10.4	1	12	31	57
Leinefelde (111)	Haplic Luvisol	Ah	0.00-0.07	4.5	10.8	86.8	9.6	1	23	40	36
		EBw	0.07-0.26	3.9	7.6	22.0	9.0	1	35	37	28
		Bw	0.26-0.35	4.1	9.5	42.1	11.4	1	31	31	38
		Btw	0.35-0.40	5.0	31.2	99.0	20.4	1	12	18	70
Leinefelde (153+16) ^c	Stagnic Luvisol	Ah	0.00-0.08	5.0	16.1	97.7	7.9	<1	15	43	42
		Eg	0.08-0.20	4.4	10.2	73.2	9.2	<1	22	42	36
		Btg	0.20-0.55	5.2	33.8	99.3	16.2	<1	13	29	57
Tharandt (24)	Dystric Cambisol	Ah	0.00-0.06	3.0	14.4	6.1	6.8	11	20	41	28
		Bw	0.06-0.44	3.9	5.7	8.5	10.1	10	20	44	26
Tharandt (97)	Dystric Cambisol	Ah	0.00-0.01	2.9	12.6	21.4	9.9	n.d. ^d	n.d. ^d	n.d. ^d	n.d. ^d
		Bw	0.01-0.63	3.9	5.6	5.7	11.0	6	22	45	27

^a World Reference Base for soil resources, ISSS-ISRIC-FAO (1998); ^b Guidelines for profile description, FAO (1990); ^c 153 years old trees (20%) mixed with 16 years old trees (80%); ^d n.d. = not determined (lack of sample material for determination of particle size distribution)

In most samples OC was preferentially associated with the $<2 \mu\text{m}$ fractions (Table 8). This is in accordance with previous studies with forest soils (Rumpel et al., 2004), grassland soils (Amelung et al., 1998) and agricultural soils (Christensen, 1992). In the A horizons, however, a significant proportion of the bulk soil OC was in the 2-20 μm , 20-200 μm , and 200-2000 μm fractions (Table 8). The contribution of OC in the 20-2000 μm fractions to the total OC in the A horizons was much higher than in Ap-horizons of Danish arable soils with different carbon and clay contents where the percentage of SOM in 20-2000 μm fractions was in the range between 2 and 10% (Christensen, 1992).

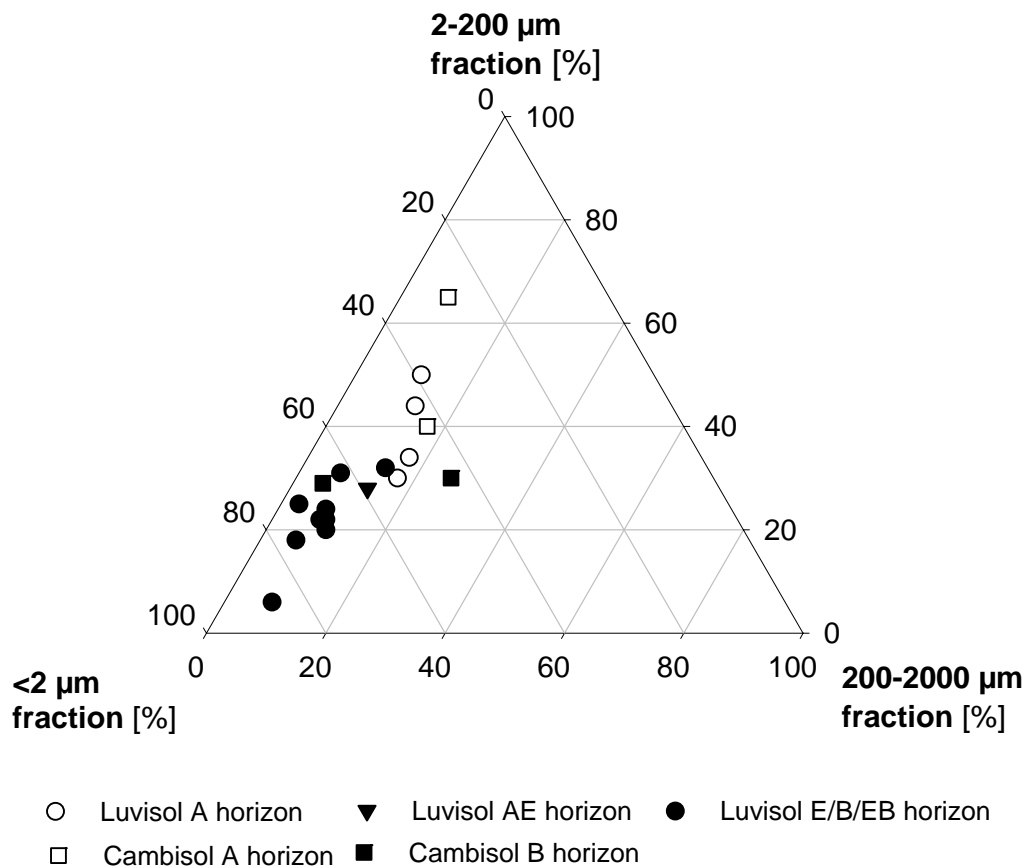


Figure 9: Distribution of organic carbon between particle size fractions in Cambisols and Luvisols

According to Christensen (1992), a major part of SOM in sand fractions consists of partly decomposed, particulate plant and animal remains which are not involved in organo–mineral complexes. Thus, the high proportion of the OC in 20-2000 μm

Table 8: OC concentrations in bulk soil and particle size fractions, OC stocks in bulk soils and distribution of OC between particle size fractions in Cambisols and Luvisols

Site (stand age)	Horizon (FAO) ^a	OC concentration				OC stock					
		Bulk soil		Particle size fractions		Bulk soil		Distribution on particle size fractions			
		200-2000 μm	20-200 μm	2-20 μm	<2 μm	200-2000 μm	20-200 μm	2-20 μm	<2 μm		
		g kg ⁻¹ soil				kg m ⁻²					
		%									
Hesse (34)	Ah	31	109	9	14	51	1.8	17	8	21	53
	AEhg	14	79	2	8	29	2.3	13	4	24	59
	Eg	7	26	1	3	14	1.7	8	5	17	70
	Btg	1	19	1	1	3	0.9	10	4	17	70
Leinefelde (62)	Ah	49	203	20	42	75	3.1	11	10	40	39
	Eg	12	231	2	7	33	1.7	14	3	28	54
	Btg	8	166	2	4	10	1.6	6	3	15	76
Leinefelde (111)	Ah	32	214	15	24	60	1.9	13	14	30	43
	EBw	11	129	1	5	33	2.4	9	4	18	69
	Bw	7	78	1	3	15	0.7	8	3	21	68
	Btw	12	40	2	4	15	0.6	8	2	3	86
Leinefelde (153+16)	Ah	34	245	9	23	45	2.1	17	5	30	49
	Eg	12	104	3	8	24	1.5	7	5	25	62
	Btg	8	62	4	5	11	2.9	3	7	18	72
Tharandt (24)	Ah	69	59	36	34	136	2.5	17	15	25	43
	Bw	20	54	9	10	54	5.6	26	11	19	44
Tharandt (97)	Ah	120	107	112	108	195	0.7	8	23	42	27
	Bw	12	9	5	5	39	4.9	5	8	21	66

^a Guide lines for profile description, FAO (1990)

fractions of the A horizons suggest a higher proportion of particulate organic matter (POM) in forest soils compared to agricultural soils. These results agree well with a study on the dynamics in a forest-cultivation sequence, where POM was affected the most by cultivation (Balesdent et al., 1998).

Generally, the contribution of 2-200 μm and 200-2000 μm fractions to the total OC decreased with depth whereas the contribution of the <2 μm fractions increased (Fig. 9). This is in line with a study of Kaiser et al. (2002) who showed that the contribution of the sand fraction to the total OC in a Cambisol and Podzol covered by spruce and beech forest decreased from 12-21% in the topsoils to 3-6% in the C horizons. We suppose that the decrease of OC in coarse particle size fractions reflects a decreasing litter input with increasing soil depth.

5.2. Young OC fraction is isolated by particle size fractionation

Table 9 presents the percentage modern carbon (pmC) and the radiocarbon ages of particle size fractions from Hesse (34), Leinefelde (62) and Tharandt (97). We tried to analyse all particle size fractions for radiocarbon content, but the OC contents in the 20-200 μm fractions from Hesse (34) were too small even for analysis by AMS. The OC in the 200-2000 μm fractions from all sites and horizons had pmC values >100 and was modern. In addition, also the OC in <2 μm , 2-20 μm and 20-200 μm fractions of the A horizons from Hesse (34) and Leinefelde (62) and the <2 μm fraction of the transition horizon from Hesse (34) was modern with pmC values >101 .

All other fractions had pmC values between 55 and 98 corresponding to radiocarbon ages between 189 and 4745 yrs before present (B.P.). In most particle size fractions pmC values decreased with increasing soil depth. The decline was much more pronounced in the <2 μm , 2-20 μm and 20-200 μm fractions compared to the 200-2000 μm fraction (Table 9).

The highest pmC values, in the topsoil as well as in the subsoil horizons, were always obtained in the 200-2000 μm fractions (Table 9). This confirmed a study which showed that the youngest OC in Aquic Hapludolls is located in the 20-2000 μm fractions (Scharpenseel et al., 1986). Radiocarbon ages in soils are strongly related to the input of

Table 9: Percent modern carbon (pmC) and radiocarbon age in particle size fractions of Cambisols and Luvisols

Site (Stand age)	Horizon (FAO) ^a	pmC in particle size fractions				Radiocarbon age in particle size fractions			
		200-2000 μm	20-200 μm	2-20 μm	<2 μm	200-2000 μm	20-200 μm	2-20 μm	<2 μm
		%							
		Years B.P.							
Hesse (34)	Ah	112.51	110.31	110.00	105.93	modern	modern	modern	modern
	AEhg	107.60	n.d. ^b	97.67	101.24	modern	n.d. ^b	189	modern
	Eg	103.04	n.d. ^b	91.57	91.48	modern	n.d. ^b	708	715
	Btg	103.72	n.d. ^b	n.d. ^b	55.40	modern	n.d. ^b	n.d. ^b	4745
Leinefelde (62)	Ah	113.21	109.95	111.23	109.39	modern	modern	modern	modern
	Eg	105.31	81.03	93.82	92.52	modern	1698	512	625
	Btg	102.85	85.05	86.46	75.80	modern	1301	1169	2226
Tharandt (95)	Ah	110.12	97.06	93.07	95.18	modern	239	577	397
	Bw	100.14	91.53	90.13	90.00	modern	711	834	846

^a Guidelines for profile description, FAO (1990)

^b n.d.= not determined (OC content too low)

young, relatively undecomposed and labile carbon (Krull and Skjemstad, 2003). During a 4-year exposure of a beech spruce ecosystem to elevated atmospheric CO₂, about 60% of the CO₂-derived new soil C was incorporated into sand fractions of an acidic loam and a calcareous sand (Hagedorn et al., 2003). Our results underline that the 200-2000 µm fractions of our soils were dominated by fresh litter input and that our fractionation procedure was suitable to isolate a young OC fraction in topsoils and subsoils.

In topsoils, the oldest OC was identified in the <2 µm fraction of the Luvisols and in the 2-20 µm fraction of the Cambisol (Table 9). This suggests that the location of the oldest SOC depends on soil type and/or soil texture which has to be confirmed with a larger number of soils. Using ¹⁴C dating, the oldest carbon in the Ap horizon of cultivated Udic Haploborolls and a Typic Argiboroll was detected in the silt (Anderson and Paul, 1984). In contrast, two Aquic Hapludolls under cultivation and forest showed age maxima in the middle and fine clay fractions in the lower part of the A horizons (Scharpenseel et al., 1986). Accordingly, Balesdent et al. (1998) showed, that the turnover determined by concentrations of ¹³C in the 0-0.3 m surface layer of a forest-cultivation sequence, was most rapid in the POM 200-2000 µm fraction, intermediate in the 2-50 µm fraction and slowest in the <2 µm fraction.

In subsoil horizons, the 20-200 µm fractions had a similar age as <2 µm and 2-20 µm fractions (Table 9). We could not detect a consistent trend for the <2 µm, 2-20 µm or 20-200 µm fraction to be the oldest fraction which partly confirms results of Trumbore and Zheng (1996). However, contrasting to the study of Trumbore and Zheng (1996) we were able to separate young and stabilised organic matter with our fractionation procedure. The changing location of the oldest OC may be astonishing since the residence time of ¹⁴C labelled ryegrass correlated with the surface area in incubation experiments (Saggar et al., 1996) and the surface area of clay fractions is usually higher than the surface areas of silt and sand fractions (Eusterhues et al., 2005). However, first we have to bear in mind that ¹⁴C data of the 20-200 µm fractions of subsoil horizons from Leinefelde were near the limit of quantification. In addition, the OC concentrations in the 2-20 µm and 20-200 µm fractions of the transition and subsoil horizons were much lower than in the <2 µm fractions (Table 8). Thus, the surface area of the 2-20 µm and 200-200 µm fractions may be sufficient to protect a relevant proportion of OC against degradation.

All A horizon particle size fractions of the Cambisol at the Tharandt (97) site had lower pmC values than respective particle size fractions of the Luvisols from Hesse (34) and Leinefelde (62) (Table 9). This is in accordance with results of Harrison et al. (2000), who observed a higher mean residence time in mineral soil samples from the 0-0.05 m layer under spruce (35-340 yrs) than under beech (65-140 yrs). The lower pmC values in the A horizon from Tharandt (97) can probably be ascribed to the delay in the incorporation of fresh plant litter in the mineral soil due to decreased biological activity (Quideau et al., 2001b; Rumpel et al., 2002). The results of this study suggest that the type of forest floor which was mull at the Luvisol sites and moder at the Cambisol site affects the radiocarbon age in A horizons.

In this study the ^{14}C activity in the individual particle size fractions decreased with depth (Table 9). Similar results were obtained with bulk soil samples from Mollisols (Scharpenseel et al., 1986), Kastanozems (Becker-Heidmann et al., 1988), Inceptisols (Torn et al., 1997), and a Cambisol (Rumpel et al., 2002). The decrease of pmC values with depth was much more pronounced in the $<200\ \mu\text{m}$ fractions compared to the coarse fraction. These results indicate that OC in the 200-2000 μm fractions consists of labile material throughout the profile, whereas stabilisation mechanisms act to an increasing extent in all other fractions. The data showed that the difference in radiocarbon content between the stabilised and the labile 200-2000 μm fractions increases with depth, which can be explained by decreasing input of fresh organic material into the subsoil horizons.

5.3. Significant proportion of OC in clay fraction is HF soluble

Bulk soils, $<2\ \mu\text{m}$ and 2-20 μm fractions had to be treated with HF before ^{13}C CPMAS NMR analysis. OC recoveries after HF treatment of bulk soils are given in Table 10. The OC recoveries in bulk soils varied between 39 and 88% of the total OC. In Fig. 10 a) the proportion of OC in $<2\ \mu\text{m}$ fractions is plotted versus the OC recovery in bulk soils after HF treatment. The data showed a strong correlation between both parameters ($r_s=0.90$; $p<0.01$). A weaker correlation was obtained between OC recovery after HF treatment and Fe_d concentration in bulk soils ($r_s=0.54$; $p<0.05$). Table 11 presents the OC recoveries after HF treatment of the $<2\ \mu\text{m}$ and 2-20 μm fractions from Hesse (34), Leinefelde (62) and Tharandt (97). On average, the OC recovery after HF treatment was significantly higher ($78\% \pm 4\%$) in 2-20 μm fractions compared to $<2\ \mu\text{m}$ fractions ($56\% \pm 5\%$).

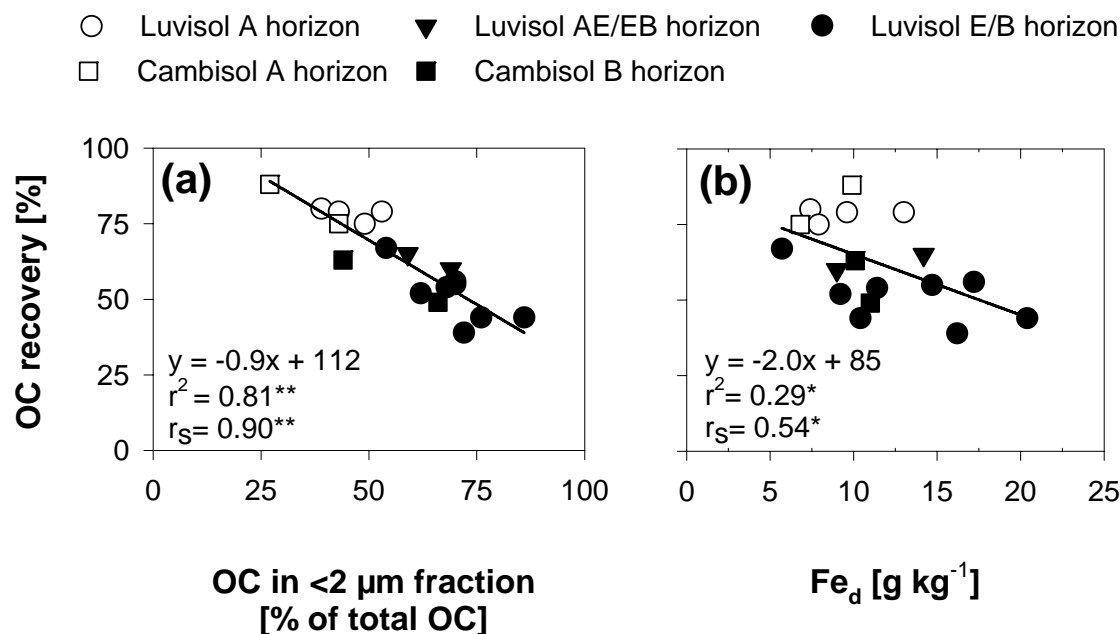


Figure 10: OC recovery after HF treatment of bulk soil samples of Cambisols and Luvisols against (a) %OC in the <2 μm fraction and (b) dithionite-extractable iron (Fe_d)

HF treatment has been successfully applied to remove mineral particles and to concentrate SOM in A horizons and compost samples (Schmidt et al., 1997; Schmidt and Gleixner, 2005). In subsoils, however, a large fraction of HF soluble OC is removed during the demineralisation procedure (Dai and Johnson, 1999; Eusterhues et al., 2003). OC losses after HF treatment ranged between 39 and 67% of the total OC in Typic Haplorthods (Dai and Johnson, 1999) and between 45 and 92% of the total OC in a Dystric Cambisol and a Haplic Podzol (Eusterhues et al., 2003). The small OC recovery in subsoils was attributed to a loss of low molecular OC adsorbed to iron oxides and clay minerals before HF treatment (Rumpel et al., 2002; Eusterhues et al., 2003). This explains the higher OC losses in <2 μm compared to 2-20 μm fractions (Table 11). Since radiocarbon age and HF recovery were positively correlated in bulk soils, a relation between ^{14}C and the HF soluble OC was suggested in previous studies (Eusterhues et al., 2003). Our results, however, showed that the loss of OC was much more pronounced in <2 μm fractions compared to 2-20 μm fractions (Table 11), even though they had similar pmC values (Table 9). This is line with results of Certini et al. (2004), who could not find a clear trend between molecular weight and residence time in Umbrisols. A relation between radiocarbon age and OC recovery after HF treatment could not be confirmed with our soils.

5.4. Dominance of O/N-alkyl carbon and alkyl carbon throughout soil profiles

Fig. 11 shows ^{13}C CPMAS NMR spectra of particle size fractions acquired from bulk soils and particle size fractions from Hesse (34), Leinefelde (62) and Tharandt (97).

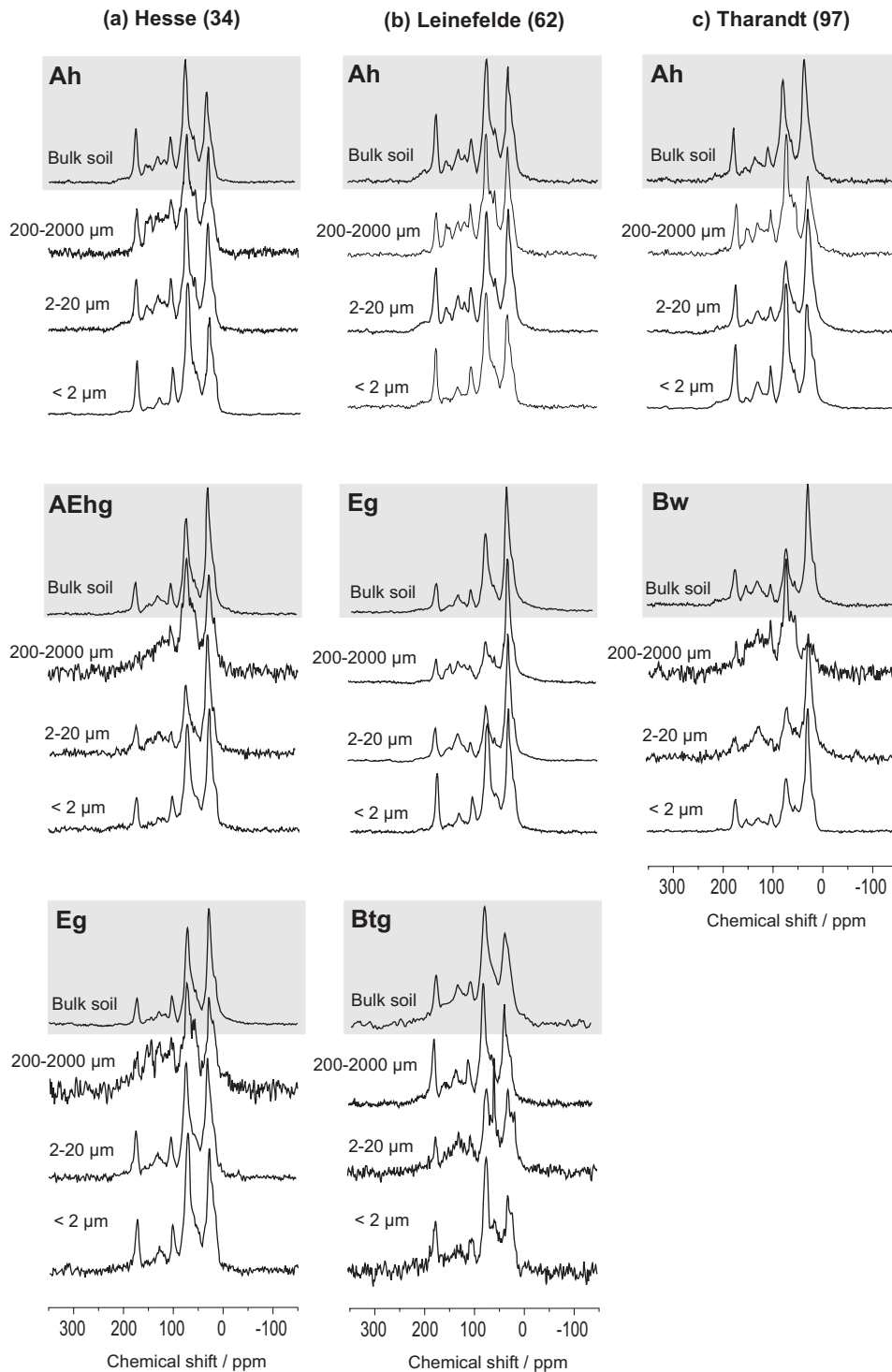


Figure 11: ^{13}C CPMAS NMR spectra of particle size fractions acquired from bulk soils and particle size fractions of a Cambisol and two Luvisols. ^{13}C CPMAS spectra of the bulk soil and the particle size fractions of the Btg horizon from Hesse could not be obtained, since the OC content was too low.

^{13}C CPMAS NMR spectra of the 20-200 μm fractions can not be presented, since they contained too little carbon to provide well-resolved spectra. The main signals in all ^{13}C CPMAS NMR spectra were observed at 30, 72, 105, 130, 150 and 173 ppm. The resonance centred at 30 ppm indicated the presence of methylene C in long chain aliphatic compounds, commonly derived from lipids, proteins, suberin and cutin (Kögel-Knabner, 1997). Resonances centred at 72 ppm and 105 ppm may be attributed to proteins and to C2, C3, C5 and C1 in cellulose and non crystalline polysaccharides (Preston et al., 1998). The smaller signals around 130 and 150 ppm can be assigned to H-/C-substituted and phenolic C typically present in lignin and tannin (Kögel-Knabner, 1997), but the signal at 130 ppm may also arise from charcoal or from olefinic C. Carboxyl, amide, and ester groups contribute to the peak at 173 ppm.

Table 10: OC recovery after HF treatment and distributions of OC species in bulk soils of Cambisols and Luvisols as determined by ^{13}C CPMAS NMR spectroscopy

Site (Stand age)	Horizon (FAO) ^a	Recovery after HF treatment	%			
			Alkyl C (0-45 ppm)	O/N-alkyl C (45-110 ppm)	Aryl C (110-160 ppm)	Carbonyl C (160-220 ppm)
Hesse (34)	Ah	79	26	49	15	11
	AEhg	65	41	41	11	8
	Eg	55	29	43	16	12
	Btg	56	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b
Leinefelde (62)	Ah	80	30	42	14	14
	Eg	67	37	39	13	11
	Btg	44	30	43	15	12
Leinefelde (111)	Ah	79	32	44	13	12
	EBw	60	42	42	8	7
	Bw	54	40	40	12	9
	Btw	44	32	47	10	11
Leinefelde (153+16)	Ah	75	27	47	14	12
	Eg	52	32	42	15	11
	Btg	39	27	38	21	14
Tharandt (24)	Ah	75	34	36	15	15
	Bw	63	33	38	17	12
Tharandt (97)	Ah	88	32	39	15	14
	Bw	49	43	29	16	11

a Guidelines for profile description, FAO (1990)

b n.d.= not determined (OC content too low)

The distribution of OC species in bulk soil samples throughout the profiles is summarised in Table 10. The most abundant C species in spectra of HF treated samples were O/N-alkyl C (29-49%) and alkyl C (26-43%) type. Only minor amounts of OC were present as aryl C (8-21%) and carbonyl C (7-15%). Correlation analysis revealed that the proportion of non HF soluble alkyl C in subsoils was significantly related to pH values ($r_s = -0.75$; $p < 0.05$) but not to parameters such as clay content or Fe_d concentration.

Non HF soluble Alkyl C [%]

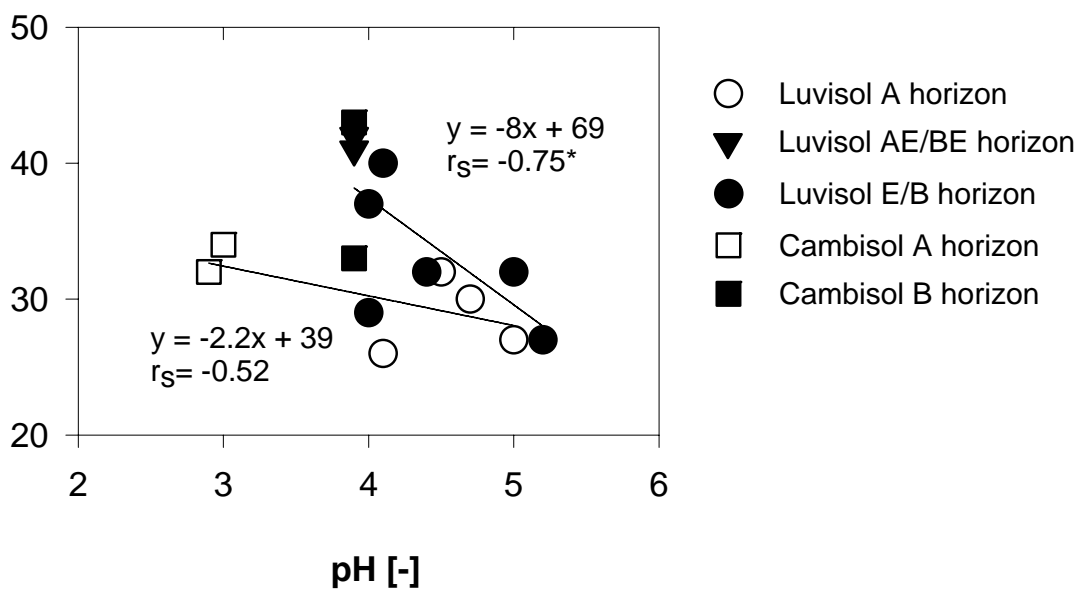


Figure 12: Alkyl C in HF treated samples of Cambisols and Luvisols against pH in topsoil and transition/subsoil horizons

The distribution of OC species in particle size fractions from Hesse (34), Leinefelde (62) and Tharandt (97) is given in Table 11. Similar to bulk soils, particle size fractions were dominated by O/N-alkyl (28-53%) and alkyl C (14-48%). In all horizons, the proportion of aryl C is decreasing from 16-26% in the 200-2000 μm fraction to 7-13% in the <2 μm fraction. Additionally, the consistent trend of higher O/N-alkyl C intensities in the <2 μm fractions compared to the 2-20 μm fractions was observed. However, one has to notice that OC recoveries in the <2 μm fractions were much lower than in the 2-20 μm fractions. Therefore ^{13}C CPMAS NMR spectra of <2 μm fractions may not be representative for the total OC in clay fractions.

Table 11: OC recovery after HF treatment and distribution of OC species in particle size fractions of a Cambisol and two Luvisols as determined by ^{13}C CPMAS NMR spectroscopy

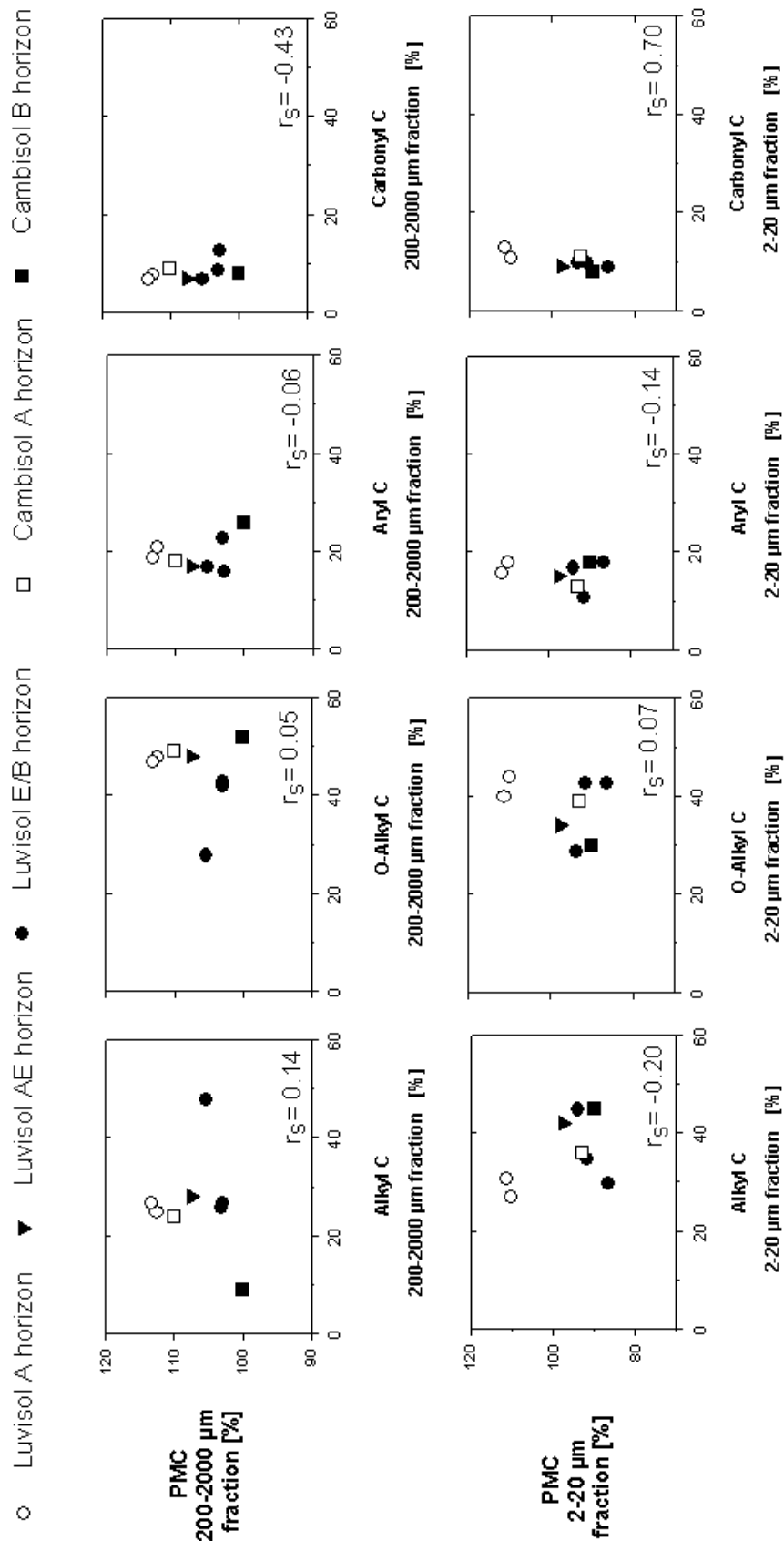
Site (Stand age)	Horizon (FAO) ^a	Fraction μm	Recovery after HF treatment	Alkyl C	O/N-alkyl C	Aryl C	Carbonyl C
				(0-45 ppm)	(45-110 ppm)	(110-160 ppm)	(160-220 ppm)
			%				
Hesse (34)	Ah	200-2000	-	25	48	21	8
		2-20	92	27	44	18	11
		<2	70	29	53	9	9
	AEhg	200-2000	-	28	48	17	7
		2-20	86	42	34	15	9
		<2	58	38	46	7	8
	Eg	200-2000	-	26	42	23	9
		2-20	95	35	43	11	10
		<2	48	33	48	9	10
Btg	200-2000	-	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	
	2-20	71	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	
	<2	46	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	
Leinefelde (62)	Ah	200-2000	-	27	47	19	7
		2-20	73	31	40	16	13
		<2	69	27	51	11	11
	Eg	200-2000	-	48	28	17	7
		2-20	77	45	29	17	10
		<2	52	36	44	9	11
	Btg	200-2000	-	27	43	16	13
		2-20	72	30	43	18	9
		<2	40	26	46	13	15
Tharandt (95)	Ah	200-2000	-	24	49	18	9
		2-20	77	36	39	13	11
		<2	82	31	43	13	13
	Bw	200-2000	-	14	52	26	8
		2-20	62	45	30	18	8
		<2	42	45	34	11	10

a Guidelines for profile description, FAO (1990)

b n.d.= not determined (OC content too low)

Non HF treated 200-2000 μm fractions and OC recoveries >72% in HF treated 2-20 μm fractions, allowed to examine for relations between the pmC values and the chemical composition in the soil profile (Fig. 13). No significant correlations between pmC values and O/N-alkyl C, alkyl C, aryl C or carbonyl C proportions in 2-20 μm and 200-2000 μm fractions, respectively, were observed.

Figure 13: PmC values against alkyl C, O/N-alkyl C, aryl C and carbonyl C intensities in 2-20 μm and 200-2000 μm fractions of a Cambisol from Tharandt (97) and of Luvisols from Hesse (34) and Leinfelde (62)



The structure of the SOM was dominated by alkyl C and O/N-alkyl C in bulk soils, labile, and stabilised SOM fractions throughout the soil profiles, whereas aryl C and carbonyl C were of minor importance (Table 10; Table 11). Beyer (1996) and Rumpel et al. (2002) reported a similar dominance of alkyl and O/N-alkyl C in bulk soil samples from Podzols and Cambisols. Alkyl C and O/N-alkyl material in the coarse fractions is suggested to derive from leave, needle and root litter (Lorenz et al., 2004). Alkyl C and O/N-alkyl C material in fine fractions most probably derived from bacteria and fungi decomposing the plant litter (Baldock et al., 1990; Golchin et al., 1996). The contribution of aromatic carbon to the stabilized organic matter in our soils samples was rather small. In the literature, however, we found a couple of examples where high contributions of aromatic compounds occurred (Zech and Guggenberger, 1996; Golchin et al., 1997; Krull and Skjemstad, 2003). In those soil profiles most probably significant amounts of black carbon were present and give signals primarily between 110 and 145 ppm (Haumaier and Zech, 1995; Nelson and Baldock, 2005). Several studies showed, that plant derived aromatic compounds like lignin are not stabilised in the mineral soil over a long period (Zech and Guggenberger, 1996; Schöning et al., 2005b). Only 28 and 20% of the total lignin but 47 and 75% of the total OC was stored in the Podzol and Cambisol subsoils, where OC was characterised by a high degree of stabilisation (Rumpel et al., 2002). Therefore high alkyl C and O/N-alkyl C proportions throughout the soil profile appear to be characteristic for forest soils that were not subjected to regular burning.

Using diffuse reflectance Fourier transform infrared spectroscopy, Capriel et al. (1995) showed, that organic matter in sandy soils from southern Germany (n=92) contained more aliphatic C (signal in the spectral region 2800-3000 cm^{-1}) compared to soils rich in clay. With the soils of this study, however, a significant correlation between sand content and alkyl C could not be found. In fact, the proportion of alkyl C was correlated to the pH (Fig. 12). A negative correlation ($r=-0.72^{**}$) between pH and alkyl C was also noted for 12 typical soils under agricultural use from north-western Germany (Beyer, 1993). Although analysis of alkyl C by sequential chemical degradation of forest soil profiles together with CG MS analysis can not completely explain the alkyl C contents determined by ^{13}C CPMAS spectroscopy (Kögel-Knabner et al., 1992; Winkler et al., 2005), there are indications for an accumulation of selected alkyl C species in soils with a low pH level. According to Nierop et al. (2003) higher alkyl C contributions in acid

soils may be explained by an accumulation of ester-bound aliphatic moieties like suberin. Moreover, a higher proportion of OC in acid soils occurs in the form of lipids or lipid-like constituents, which contribute between 1 and 20% to the total SOM (Stevenson, 1994).

The contribution of O/N-alkyl C increased from the 20-2 μm fraction to the <2 μm fraction (Table 11). This pattern was observed not only in topsoil but also in subsoil and transition horizons. In subsoil clay fractions, however, one has to bear in mind the high OC losses during demineralisation with HF which amounted >42% of the total OC mass (Fig. 10). Therefore, the chemical composition of the soluble molecular material that is removed together with the HF solution remains to be studied to assure the ^{13}C CPMAS NMR results for clay fractions. However, generally the OC losses during HF treatment are explained by a preferred loss of easily soluble amino acids and amino sugars (Gélinas et al., 2001; Mathers et al., 2002). Thus, the O/N-alkyl C proportion in untreated clay fractions would be even higher. This would strengthen the described trend of O/N-alkyl C intensities between particle size fractions. Higher mass ratios of (galactose + mannose) -to- (arabinose + xylose) in clay fractions of A horizons under forest indicate that O/N-alkyl C proportions in <2 μm fractions were in the most part attributed to carbohydrates of microbial origin (Guggenberger et al., 1994). In clay fractions of topsoils intimate associations between iron oxides and O/N-alkyl C are evident and probably contribute to a stabilisation of O/N-alkyl C (Schöning et al., 2005a). We expect that similar processes act in the subsoil horizons, although data for microbial carbohydrates in particle size fractions of subsoils and their interaction with the mineral phase are missing so far. Another pattern apparent between particle size fractions is the decrease of relative intensities of aryl C along with decreasing particle size (Table 11). This indicates a complete decomposition and/or transformation of plant derived aromatic compounds like lignin and tannin in clay fractions. Again a similar pattern for the distribution of carbon species in particle size fractions of topsoils and subsoils was observed.

In previous studies, the selective stabilisation preservation of the rigid alkyl C compounds was suggested (Baldock et al., 1992; Kögel-Knabner et al., 1992). Accordingly, in the surface layer of a lysimeter under pine, there was a gradual increase in turnover rate progressing from the floatable to the clay fraction, and differences in

turnover rates among fractions corresponded to an increase in alkyl C/ O/N-alkyl C ratio (Quideau et al., 2000). All these results were discussed in the context of different particle size fractions from one horizon. In our study, however, we took a step forward and compared the composition of SOM and turnover in the same particle size fractions from different horizons. However, we could not find any relation between chemical composition and radiocarbon content (Fig. 13). This confirms a study of Wattel-Koekkoek and Buurman (2004) with NaOH and Na₄P₂O₇ extracts from clay fractions from Nitosols and Vertisols, where the variance in different OC types in liquid state ¹³C NMR spectra did not explain variance in ¹⁴C activity. Our results revealed that bulk chemical composition may have an impact on the degradation of SOM at the short term, as shown in particle size fractions of A horizons. In subsoils, however, mechanisms like the adsorption and chemical binding to mineral surfaces or the physical encapsulation appeared to be more important controls in respect to stabilisation of SOM.

6. Intimate association between iron oxides and O/N-alkyl carbon in clay fractions

Soil samples to study associations between iron oxides and SOC were collected from A horizons of managed forest sites in Collelongo/Italy, Hesse/France, Sorø/Denmark, Leinefelde/Germany and Tharandt/Germany (Table 12). Soils in Collelongo, Hesse, Sorø and Leinefelde were covered with European beech (*Fagus sylvatica* L.), whereas spruce (*Picea abies*) was the dominant tree species in Tharandt. Soil groups, classified according to ISSS-ISRIC-FAO (1998), comprised Cambisols, Leptosols, Luvisols as well as a Phaeozem. The A horizon thickness was between 0.01 to 0.25 m. According to SSSA (2001), the soil texture varied from sandy clay loam to clay. The pH of the soils ranged from very acid (Tharandt, pH 2.9-3.0) to almost neutral (Collelongo, pH 6.9). The clay fractions of the A horizons were isolated by particle size fractionation. They were characterised by OC concentrations between 50 and 233 g kg⁻¹, whereas the dithionite extractable iron concentrations ranged from 13 to 29 g kg⁻¹.

6.1. Effect of demineralisation on organic carbon and nitrogen

In order to remove the mineral material including the paramagnetic Fe, the clay fractions were treated with 10%HF. The HF treatment was accompanied by a loss of mass, OC and N. Table 2 gives the recovery of mass, OC and N after demineralisation (Eq. 1), the OC and N enrichment factors (Eq. 2) and the Q-values (Eq. 3). After demineralisation, 13 to 42% of the initial mass of the samples was retained. The recovery of OC ranged from 60 to 93%, whereas the N recovery ranged from 50 to 80%. Due to higher relative mass losses compared to OC and N losses, OC and N were strongly concentrated in the HF treated samples. The enrichment factors of OC (2.2-5.5) and N (1.9-4.3) reflected this feature.

In all samples the N recovery was lower than the OC recovery leading to Q-values >1. However, some untreated samples showed a high variability of N concentrations. A positive linear correlation between OC and N indicated that the recovery of N showed a pattern comparable with that of the OC recovery ($r_s=0.87$, $p<0.01$).

Table 12: Characteristics of samples to study association between Fe oxides and SOM

Site	Latitude/ Longitude	Soil classification (WRB) ^a	Bulk soil		Clay fraction						
			pH (CaCl ₂)	Clay fraction ^b g kg ⁻¹	OC	C/N	Fe _d	Al _d	Fe _o	Al _o	Fe _d /OC
Collelongo	41°52'N/ 13°38'E	Rendzic Leptosol	6.9	520	88	9.7	25.3	8.6	4.4	16.9	3.0
Hesse	48°40'N/ 07°05'E	Stagnic Luvisol	4.1	288	50	8.4	21.7	4.7	6.1	4.0	4.3
Sorø	55°29'N/ 11°38'E	Stagnic Phaeozem	4.1	141	163	10.7	13.0	7.2	4.5	8.4	0.8
<i>Chronosequence Leinefelde</i>											
Leinefelde 30-1	51°20'N/ 10°22'E	Rendzic Leptosol	5.5	441	62	9.5	28.1	5.0	4.6	7.9	4.6
Leinefelde 30-2	51°20'N/ 10°22'E	Stagnic Luvisol	5.1	287	74	10.9	23.6	4.9	3.7	5.2	3.2
Leinefelde 62	51°20'N/ 10°22'E	Stagnic Luvisol	4.7	253	75	8.6	19.2	4.5	4.6	4.4	2.6
Leinefelde 111	51°20'N/ 10°22'E	Haplic Luvisol	4.5	236	60	8.9	25.9	5.6	6.4	6.3	4.3
Leinefelde 153+16	51°20'N/ 10°22'E	Stagnic Luvisol	5.0	366	45	8.7	16.7	3.3	4.7	4.7	3.7
<i>Chronosequence Tharandt</i>											
Tharandt 5	50°56'N/ 13°29'E	Dystri-Stagnic Cambisol	3.0	188	233	13.8	20.8	6.0	5.5	4.9	0.9
Tharandt 24	50°56'N/ 13°29'E	Dystric Cambisol	3.0	178	136	16.8	28.7	9.6	8.7	7.5	2.1
Tharandt 97	50°56'N/ 13°29'E	Dystric Cambisol	2.9	175	195	16.5	28.4	6.4	13.0	5.9	1.5

^a WRB: World Reference Base for soil resources; ISSS-ISRIC-FAO (1998)

^b clay = <2 μm

Table 13: Recovery of mass, organic carbon (OC) and nitrogen (N) after demineralisation of Ah horizon clay fractions with 10% hydrofluoric acid (HF)

Site	Mass recovery	OC recovery	E_{OC}^a	N recovery	E_N^b	Q^c
	%	%		%		
Collelongo	22	66	3.0	64	2.9	1.0
Hesse	13	70	5.5	50	3.9	1.4
Sorø	30	74	2.5	66	2.2	1.1
<i>Chronosequence Leinefelde</i>						
Leinefelde 30-1	14	60	4.4	59	4.3	1.0
Leinefelde 30-2	17	77	4.6	67	3.9	1.2
Leinefelde 62	20	69	3.5	55	2.8	1.3
Leinefelde 111	15	61	4.0	55	3.8	1.1
Leinefelde 153+16	20	65	3.3	57	2.9	1.2
<i>Chronosequence Tharandt</i>						
Tharandt 5	42	93	2.2	80	1.9	1.2
Tharandt 24	20	71	3.5	65	3.3	1.1
Tharandt 97	33	82	2.5	72	2.2	1.1

^a $E_{OC} = \text{g kg}^{-1}$ of OC after demineralisation / g kg^{-1} of OC before demineralisation

^b $E_N = \text{g kg}^{-1}$ of N after demineralisation / g kg^{-1} of N before demineralisation

^c $Q = \text{OC/N ratio after demineralisation} / \text{OC/N ratio before demineralisation}$

Fig.14 shows the absolute dithionite extractable Fe content versus HF soluble OC. The amount of HF soluble OC was higher in samples with a higher concentration of dithionite extractable Fe oxides ($r_s=0.38$, $p<0.25$). If the sample from Sorø was considered as outlier the correlation between Fe content and HF soluble OC became considerably stronger ($r_s=0.88$, $p<0.01$).

OC was strongly concentrated during the demineralisation, indicated by high E_{OC} values (Table 13). However, it was not possible to avoid some OC losses during the demineralisation. The average OC recovery of $71.6 \pm 0.8\%$ in the clay fractions was quite low compared to recoveries of bulk soil samples from the surface layer. To give an example, Skjemstad et al. (1994) reached OC recoveries of 83% to 90% in different

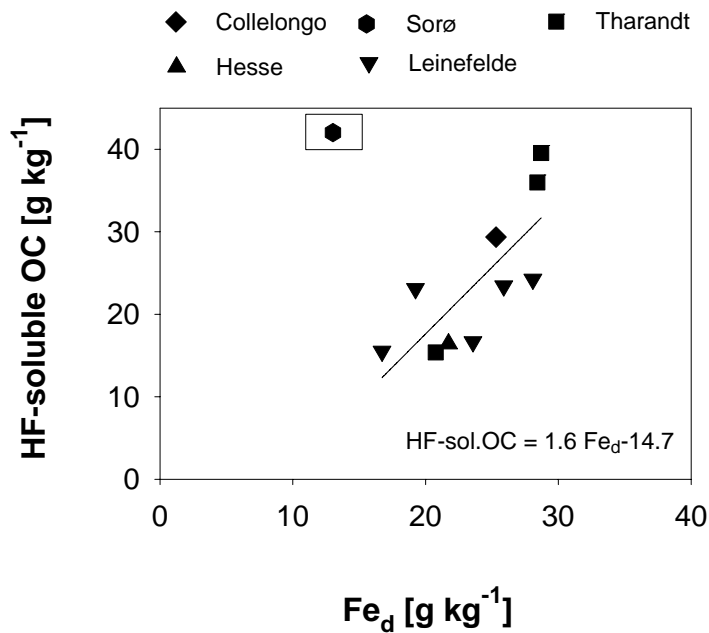


Figure 14: Concentration of dithionite extractable Fe oxide in relation to the 10% hydrofluoric acid (HF) soluble OC in A horizon clay fractions. The sample from Sorø was considered as an outlier.

Australian soils (Hapludoll, Kandiusstox, Pellustert, Natrustalf, Rodoxeralf) using 2% HF. Schmidt et al. (1997) already described a lower OC recovery in HF treated clay fractions from a Phaeozem with 77% in the clay fraction and 79 to 89% in the silt fractions. Increasing values of OC losses during demineralisation in Collelongo, Hesse, Leinefelde and Tharandt fitted together with increasing amounts of dithionite extractable Fe (Fig. 14). This suggests that part of the HF soluble OC was stabilized by Fe oxides. Oades et al. (1987) found a dominance of carbohydrates in dithionite extracts and they suggested a substantial interaction of carbohydrates with Fe oxides. A correlation between dithionite soluble Fe and HF soluble OC was previously observed by Eusterhues et al. (2003) for subsoil samples. The correlation for our samples indicated that additional factors, for example the chemical composition of the SOM or the diversity and proportions of different Fe oxides, influence the dissolution of SOM by HF. The high OC losses at Sorø may be explained by high proportions of acid soluble, free particulate organic matter at this site.

After demineralisation, the recoveries and enrichment ratios of N were lower than the corresponding recoveries and enrichment ratios of OC (Table 13). This was previously

observed for some of the Ferrasols analysed by Goncalves et al. (2003). The higher N losses during HF treatment may be explained by a preferred loss of easily soluble amino acids and amino sugars (Gélinas et al., 2001; Mathers et al., 2002) that were protected through sorption before HF treatment. Their signals are expected between 0 and 60 ppm and around 176 ppm in the ^{13}C CPMAS NMR spectra.

6.2. Selective signal loss

Fig. 15 presents the ^{13}C CPMAS NMR spectra of clay fractions before and after demineralisation. The main signals were at 30, 72, 103, 129 and 173 ppm, corresponding to unresolved methyl, methylene and methane carbon (30), ring and anomeric carbohydrate carbons (72 and 103), C- and H-substituted aromatic carbon and olefines (129) and carboxyl, amide and ester carbons (173) (Preston et al., 1984). All spectra were characterised by high signal to noise ratios, which enabled integration of the chemical shift regions for quantification. However, the spectra of non HF treated samples had broader resonance lines resulting in a stronger overlapping of signals at 103 ppm and 129 ppm.

The relative intensity distribution in the spectra of the samples before and after demineralisation is given in Table 14. The dominating signal intensity occurred in the region assignable to O/N-alkyl C and alkyl C type. Before demineralisation, the relative intensity of O/N-alkyl C was in the range between 33 and 46% and that of alkyl C was in the range between 28 and 40%. The relative intensities of the aryl C and carbonyl C signals were < 16%. After demineralisation, the spectra of the samples from Collelongo, Hesse, Sorø and Leinefelde (30/1, 30/2, 62, 111, 153+16) showed an increase of the relative O/N-alkyl C intensity (+3 to +20%). At the same time a decrease in other chemical shift regions, particularly in the alkyl C region (-2 to -11%), was apparent. Unlike other samples, the Tharandt (5, 24, 97) samples showed no increase of O/N-alkyl C intensity and no significant change of the relative alkyl C intensity after demineralisation.

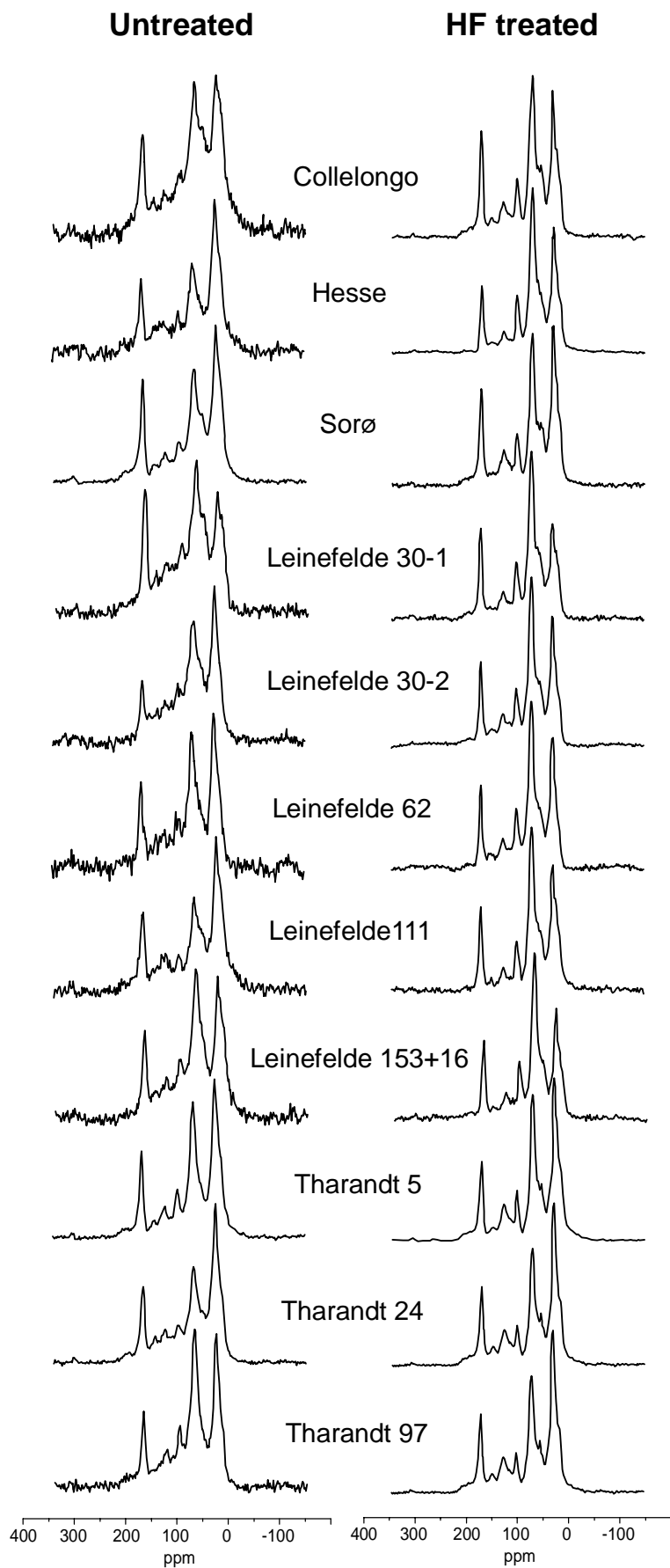


Figure 15: Solid state ^{13}C NMR spectra of A horizon clay fractions before and after demineralisation with 10% hydrofluoric acid (HF).

Table 14: Relative signal intensity distribution in the ^{13}C CPMAS NMR spectra of A horizon clay fractions before and after demineralisation with 10% hydrofluoric acid (HF).

Site	Alkyl C		O/N-Alkyl C		Aryl C		Carbonyl C				
	Un-treated (1)	HF treated (2)	Δ (2)-(1)	Un-treated (1)	HF treated (2)	Δ (2)-(1)	Un-treated (1)	HF treated (2)			
Collelongo	33	29	-4	42	46	4	12	12	13	14	1
Hesse	40	29	-11	33	53	20	14	9	13	9	-4
Sorø	36	34	-2	39	42	3	11	11	14	13	-1
<i>Chronosequence Leinefelde</i>											
Leinefelde 30-1	28	22	-6	43	53	10	13	11	16	14	-2
Leinefelde 30-2	33	27	-6	41	50	9	14	12	13	12	-1
Leinefelde 62	30	27	-3	43	52	9	14	11	14	11	-3
Leinefelde 111	40	30	-10	34	50	16	13	9	13	11	-2
Leinefelde 153+16	31	25	-6	43	52	9	14	11	14	13	-1
<i>Chronosequence Tharandt</i>											
Tharandt 5	37	37	0	41	39	-2	10	11	11	12	1
Tharandt 24	39	38	-1	36	35	-1	13	13	12	14	2
Tharandt 97	30	31	1	46	43	-3	13	13	11	13	2

To enable a comparison of the relative change of proportions of the different C species with the change of the relative alkyl C intensity the quotients of O/N-alkyl C, aryl C and carbonyl C before and after demineralisation were calculated (Eq. 4; Table 15). After demineralisation, the O/N-alkyl C/alkyl C ratios of the samples from Collelongo, Hesse and Leinefelde (30/1, 30/2, 62, 111, 153+16) increased leading to O/N-alkyl C quotients between 1.3 and 2.2. In contrast, the O/N-alkyl C/alkyl C ratios of samples from Sorø and Tharandt (5, 24, 97) and the aryl C/alkyl C and carbonyl C/alkyl C ratios of all samples remained nearly unchanged after demineralisation as shown by quotients of 1 ± 0.2 .

Table 15: Quotient of relative signal intensity ratios of A horizon clay fractions before and after demineralisation with 10% hydrofluoric acid (HF).

Site	O/N-Al/Al ^a (HF treated)	Ar/Al ^b (HF treated)	Ca/Al ^c (HF treated)
	O/N-Al/Al (untreated)	Ar/Al (untreated)	Ca/Al (untreated)
Collelongo	1.3	1.1	1.2
Hesse	2.2	0.9	0.9
Sorø	1.1	1.1	1.0
<i>Chronosequence Leinefelde</i>			
Leinefelde 30-1	1.6	1.1	1.1
Leinefelde 30-2	1.5	1.0	1.1
Leinefelde 62	1.3	0.9	0.9
Leinefelde 111	2.0	0.9	1.1
Leinefelde 153+16	1.5	1.0	1.1
<i>Chronosequence Tharandt</i>			
Tharandt 5	1.0	1.1	1.0
Tharandt 24	1.0	1.0	1.1
Tharandt 97	0.9	1.0	1.1

^a O/N-Al/Al = O/N-alkyl C/Alkyl C ratio

^b Ar/Al = Aryl C/Alkyl C ratio

^c Ca/Al = Carbonyl C/Alkyl C ratio

The low relative O/N-alkyl C intensity in the samples from Hesse and Leinefelde before demineralisation may be due to a shortening of $T_{1\rho H}$ of protons in the vicinity of O/N-alkyl C. Part of the O/N-alkyl C may be invisible unless very short contact times are applied. Therefore a variable contact time experiment was conducted with the sample from Hesse before and after demineralisation. Fig. 16 shows plots of the contact time versus the measured and modelled values of alkyl C and O/N-alkyl C intensities.

The untreated sample from Hesse was characterised by a very strong decrease of O/N-alkyl C intensity with increasing contact time. 44% of the maximum intensity was already lost at a contact time of 1 ms, usually employed to obtain ^{13}C CPMAS NMR spectra of soil samples. After demineralisation, the O/N-alkyl C intensity loss at the contact time of 1 ms was clearly smaller (7% of the maximum).

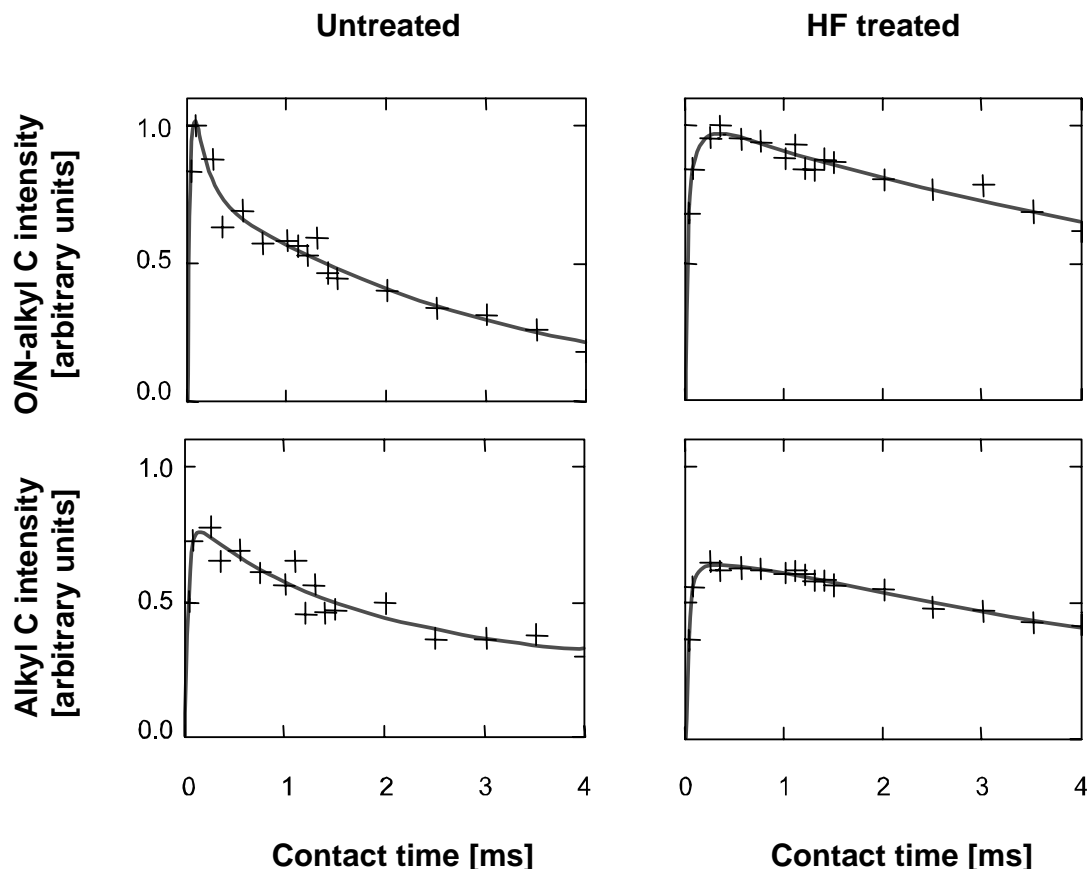


Figure 16: Cross polarisation behaviour of O/N-alkyl C and alkyl C in the A horizon clay fraction from Hesse before and after demineralisation with 10% hydrofluoric acid (HF): (+) measured intensity values, (—) modelled intensity values.

In comparison to O/N-alkyl C intensity, the loss of alkyl C intensity with increasing contact time in the untreated sample was much lower (20% of the maximum at a contact time of 1ms). Table 16 shows the values of T_{CH} and $T_{1\rho\text{H}}$ calculated from the slope of the functions of alkyl C and O/N-alkyl C intensities versus contact time. Additionally, the model performance parameters are given. The model fitted very well for the intensities of carbon species before and after demineralisation which was demonstrated by low maximum errors (<0.10), high coefficients of determination (>0.89) and high

modelling efficiencies (>0.89) (Table 16). T_{CH} was relatively short for all types of nuclei before and after demineralisation (<0.44 ms) (Table 16). Before demineralisation, the $T_{1\rho}H$ values of the slowly and fast relaxing protons in the vicinity of O/N-alkyl C were 3.21 ms and 0.13 ms, respectively. The considerable difference in relaxation behaviour of protons indicated inefficient spin diffusion which occurs if the different domains are physically separated. The difference between the $T_{1\rho}H$ values of slowly and fast relaxing protons in the vicinity of alkyl C was even more pronounced, although $T_{1\rho}H$ values were higher (18.38 ms and 1.35 ms) than those of protons in the vicinity of O/N-alkyl C (Table 16). After demineralisation, comparable $T_{1\rho}H$ values of around 8 ms were determined for O/N-alkyl C and alkyl C domains. This pointed to a more efficient spin diffusion and to a higher physical homogeneity of the HF treated sample.

Table 16: Results of modelling of cross polarisation behaviour for O/N-alkyl carbon (72 ppm) and alkyl carbon (30 ppm) of the A horizon clay fraction from Hesse before and after demineralisation with 10% hydrofluoric acid (HF).

Signal	Demineralisation	Cross polarisation behaviour						Model performance		
		Slow domain			Fast domain			ME ^d	CD ^e	MEF ^f
		M_0^a	T_{CH}^b	$T_{1\rho}H^c$	M_0	T_{CH}	$T_{1\rho}H$			
ppm			ms	ms		ms	ms			
72	Untreated	0.82	0.03	3.21	0.46	0.03	0.13	0.10	0.96	0.96
	HF treated	0.58	0.01	10.04	0.45	0.08	8.97	0.06	0.94	0.94
30	Untreated	0.42	0.03	18.38	0.42	0.04	1.35	0.10	0.89	0.89
	HF treated	0.63	0.04	7.28	0.09	0.44	7.28	0.02	0.99	0.98

^a M_0 : Equilibrium ^{13}C magnetisation (theoretically reachable maximum magnetisation)

^b T_{CH} : time required for a transfer of magnetisation from 1H to ^{13}C nuclei

^c $T_{1\rho}H$: Spin-lattice relaxation time in the rotating frame of protons

^d ME: Maximum error of model

^e CD: Coefficient of determination of model

^f MEF: Modelling efficiency

In the bulk of samples, demineralisation resulted in an increase of relative O/N-alkyl C proportions, while the relative intensities of alkyl C decreased (Table 14). These results are in accordance with findings of Knicker (2004), who showed a higher O/N-alkyl C intensity (+11%) and a lower alkyl C (-6%) and carbonyl C (-4%) intensity after demineralisation of a municipal solid waste sample. Integration of the different chemical shift regions results in relative intensity values. Therefore, the change of

signal intensities may have been caused by a preferential removal of alkyl C compounds during demineralisation or by a selective suppression of O/N-alkyl C intensity in the untreated samples. In previous demineralisation studies, samples with high OC concentrations showed, however, no loss of alkyl C. In mature compost the relative intensity of O/N-alkyl C declined (-7%) and the alkyl C intensity increased (+4%) (Schmidt et al., 1997). Two samples from organic horizons of Spodosols displayed decreases of 3 and 6% of O/N-alkyl C whereas the alkyl C remained constant (Dai and Johnson, 1999). Samples originating from litter of a mixed deciduous and a beech forest gave comparable spectra before and after demineralisation (Schmidt et al., 1997). In addition, mass balances calculations showed that the preferential loss of acid soluble amino acids can not explain the signal shift in ^{13}C CPMAS NMR spectra of the samples from Hesse and Leinefelde.

The calculated quotients of O/N-alkyl C, aryl C and carbonyl C (Table 15) supported the assumption that the change in relative signal intensities was ascribed to a selective O/N-alkyl C suppression in the untreated sample rather than to a preferential loss of alkyl C. The quotients of relative intensities of aryl C and carbonyl C normalised to the alkyl C intensity remained nearly constant (1 ± 0.2) for the samples before and after HF treatment (Table 15). Thus, the presence of paramagnetic Fe affected the intensities of aryl C, carbonyl C and alkyl C signal to the same extent.

Interactions between SOM and Fe^{3+} were considered as most likely explanation for the differences of relative intensities in ^{13}C CPMAS NMR spectra before and after demineralisation. The higher number of required scans and the lower signal to noise ratios in the spectra of untreated samples can be attributed to both, the effects of Fe^{3+} and the low OC concentrations (Fig. 15). However, no displacement of the main signals was found in the ^{13}C CPMAS NMR spectra. This is contrary to Parfitt et al. (1999) who observed displacements of NMR signals as result of interactions between allophane and SOM in Podzols. The lower quality of the ^{13}C CPMAS NMR spectra of the untreated samples is most probably linked to a decrease of the detectability of carbon. Using 2% HF and forest soil samples, Keeler and Maciel (2003) increased the percent carbon detected by ^{13}C CPMAS NMR, from 48 to 82%, while the Fe concentration of the soil was reduced from 10.5 to 2.5 g kg^{-1} soil. The effects of paramagnetics on ^1H during cross polarisation MAS experiments are usually known to be more intense than on ^{13}C

during direct polarisation MAS experiments because the high abundance of ^1H spins allows the redistribution of magnetisation by spin diffusion (Smernik and Oades, 1999). However, the occurrence of slowly and fast relaxing domains of protons with clearly different $T_{1\rho\text{H}}$ values underline that the untreated sample from Hesse was characterised by physically separated molecular domains (Table 16). The heterogeneity of the sample clearly prevented efficient spin diffusion between protons in the vicinity of different C species and allowed the selective suppression of NMR signals.

The results showed a selective effect of Fe on the O/N-alkyl C (Table 14, Fig.15). This was indicated by a stronger shortening of $T_{1\rho\text{H}}$ of O/N-alkyl C in comparison to that of other carbon species (Table 16). The selective suppression of O/N-alkyl C confirmed results of Pfeffer et al. (1984) who observed a preferential loss of proton polarisation associated with carbohydrates when investigating model sludge mixtures amended with FeCl_3 . A selective effect on the carbohydrate region of ^{13}C CPMAS NMR spectra was also shown for a Terric Humisol with a high concentration of paramagnetic Cu (Preston et al., 1984). A series of spectra acquired at different contact times showed increases in the relative contribution of the aromatic region and a large decrease in the carbohydrate region with increasing contact times. Smernik and Oades (1999) added Fe^{3+} to HF treated samples and found that differences of signal intensities are largest for both, the O/N-alkyl C and the carbonyl C region. In contrast to their results, differences in the intensities of carbonyl C were not found in the A horizon clay fractions used for this study. The absence of a difference in the relative carbonyl C intensities before and after demineralisation could partly be explained by the selective loss of amide and carboxyl C from amino acids. But it may also be explained by a high contribution of ester and amide groups to the carbonyl C of the studied soils. Upon esterification, a dramatic reduction in Cu binding to carbonyl groups was evident in peat samples (Schilling and Cooper, 2004b).

The selective association of Fe and O/N-alkyl C was in contrast to results of Kaiser et al. (2003). From a mixture of organic compounds in DOM, goethite preferentially adsorbed hydrophobic fractions, fulvic and humic acids rich in carboxyl and aromatic C against hydrophilic fractions characterised by high abundances of O/N-alkyl C. They suggest that the strong sorption of the hydrophobic fraction is a result of the presence of lignin decomposition products. The different results can

probably be explained by the low amounts of lignin products in the clay fractions of the samples used for this study (Schöning et al., 2005b). The selective signal loss of O/N-alkyl C did also not agree with Schmidt et al. (1997), Goncalves et al. (2003) and Jancke et al. (2002) who did not find any selective signal loss in untreated soil samples. However, Jancke et al. (2002) did not differentiate between alkyl and O/N-alkyl C and they were therefore not able to detect possible O/N-alkyl C suppressions in their soils. The results of Schmidt et al. (1997) and Goncalves et al. (2003) underline that the type of Fe oxide may be an important determinant for the interaction between SOM and Fe oxides and that the association between Fe oxides and O/N-alkyl C may be specific for certain soils.

6.3. Control parameter of signal loss

In clay fractions of soils under temperate forest, Fe^{3+} is generally the main paramagnetic compound. Thus, changes of relative intensities as result of demineralisation were expected to be proportional to the Fe concentrations. However, no correlation between Fe_d or Fe_o concentration in the untreated samples and the change of relative O/N-alkyl C intensity which is affected the most by iron oxides was obtained (Fe_d : $r_s = -0.12$, $p < 0.6$; Fe_o : $r_s = -0.18$, $p < 0.8$). With increasing OC concentrations an increasing proportion of OC is probably not directly associated with Fe. Therefore it was examined, whether a correlation between the Fe_d/OC ratio and the change of O/N alkyl C quotient existed. The O/N-alkyl C quotient was increasing with increasing values of Fe_d/OC ratio ($r_s = 0.89$; $p < 0.01$) or Fe_o/OC ratio ($r_s = 0.68$; $p < 0.05$) (Fig. 17).

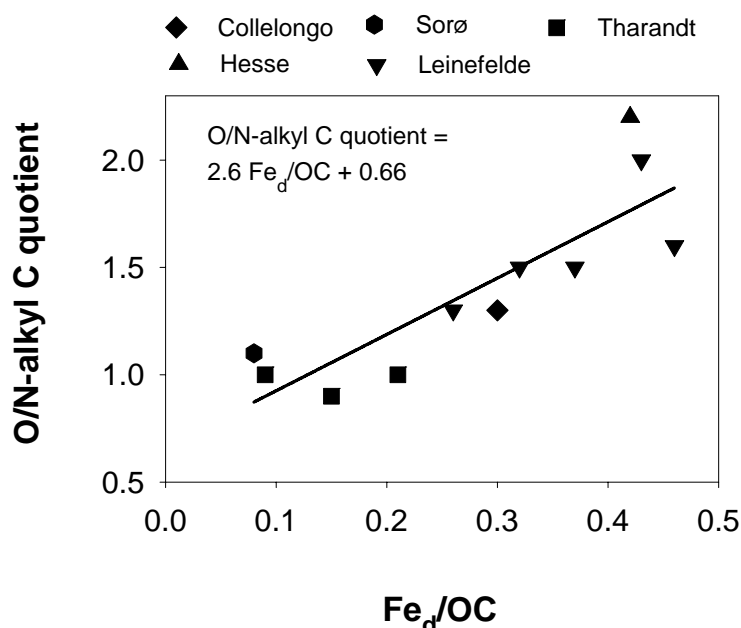


Figure 17: Ratio of dithionite extractable Fe and OC concentration in relation to O/N-alkyl C quotient of A horizon clay fractions (Eq. 4)

Fe oxides provide a high contribution to the SSA of mineral soil samples. In the samples from the beech forest sites in Collelongo, Hesse, Sorø and Leinefelde SSA_{oxides} (Table 17) was positively correlated with the concentration of Fe_d ($r_s=0.93$; $p<0.01$). Also, a correlation between the SSA_{oxides} normalised to the OC concentration and the O/N-alkyl C quotient was evident ($r_s=0.92$; $p<0.01$) (Fig. 18).

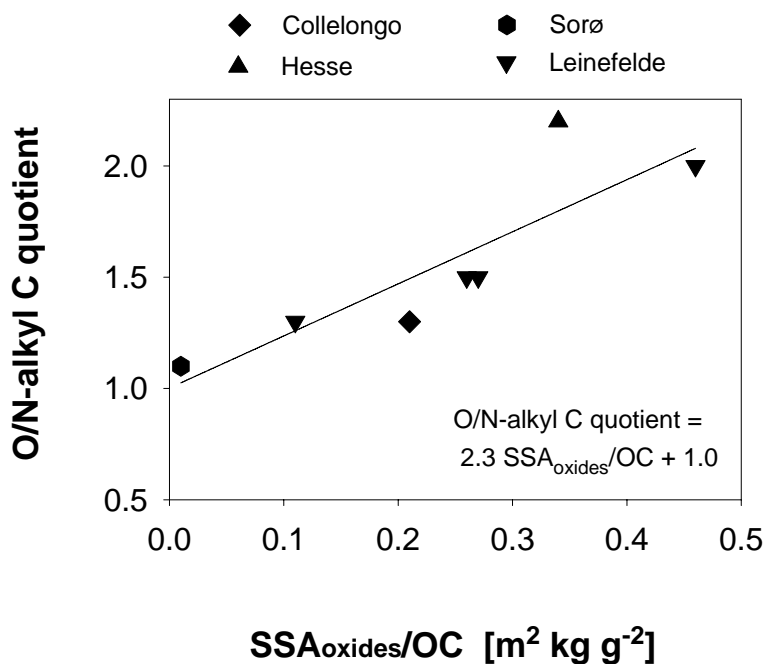


Figure 18: Ratio of specific surface area of oxides (SSA_{oxides}) and OC concentration in relation to O/N-alkyl C quotient of A horizon clay fractions (Eq. 4)

The relationship between the Fe_d/OC ratio and the signal change indicated that the Fe concentration is one important factor for the extent of signal loss (Fig. 17). For humic acids amended with different amounts of Fe^{3+} , Keeler and Maciel (2003) showed a negative, roughly linear relationship between the percent carbon observed in direct polarisation MAS experiments and the percent Fe. The importance of the concentration of paramagnetic material was also shown in experiments, where Cu was amended. $T_{1\rho}H$ was negatively correlated with increasing Cu content for all four regions of the spectra, but the effect was much larger and the correlation coefficient much higher for the carbohydrate region (Preston et al., 1984). However, paramagnetic compounds can be diluted by OC. This was indicated by the decrease of the extent of changes of the relative intensities with decreasing Fe_d/OC ratios (Fig. 17). The effects of paramagnetic Fe may, therefore, be masked in soils, especially with high OC contents,

Table 17: The specific surface area (SSA) of A horizon clay fractions from beech forest sites after removal of SOM (SSA_{minerals}) and after removal of SOM and dithionite extractable minerals ($SSA_{\text{silicates}}$)

Site	SSA_{minerals}^a	$SSA_{\text{silicates}}^b$	SSA_{oxides}^c
	$\text{m}^2 \cdot \text{g}^{-1}$		
Collelongo	67.5	47.5	20.0
Hesse	35.8	18.1	17.7
Sorø	14.5	13.3	1.2
<i>Chronosequence Leinefelde</i>			
Leinefelde 30-1	n.d. ^d	n.d.	n.d.
Leinefelde 30-2	49.6	28.7	20.9
Leinefelde 62	28.8	19.8	9.0
Leinefelde 111	48.3	20.5	27.8
Leinefelde 153+16	31.4	19.4	12.0

^a SSA_{minerals} = Specific surface area of minerals (after H_2O_2 treatment)

^b $SSA_{\text{silicates}}$ = Specific surface area of silicates (after H_2O_2 and dithionite extraction)

^c SSA_{oxides} = Specific surface area of oxides ($SSA_{\text{oxides}} = SSA_{\text{minerals}} - SSA_{\text{silicates}}$)

^d n.d. = not determined

and only observed in fine fractions with high concentrations of paramagnetics. Arshad et al. (1988) recommended an OC:Fe ratio >1 to obtain spectra of soil samples with a reasonable quality. However, in this study, ^{13}C CPMAS NMR spectra of clay fractions with OC:Fe ratios between 2.2 and 3.8 were considerably affected by Fe oxides (Table 14, Fig. 15). These results were in agreement with those of Schilling and Cooper (2004a), who could not obtain useful spectra of samples from untreated Ultisols with OC:Fe ratios of 2.1 and 1.8. These results indicate that soil samples with OC:Fe ratios >1 do not assure good quality ^{13}C CPMAS NMR spectra, and that much higher OC:Fe ratios may be necessary for some soil samples.

Fe oxides are characterised by a high surface area. Relationships between mineral specific surface area and OC concentration were found in A horizons of soils (Mayer, 1994; Kahle et al., 2002). In two sandy Luvisols from Germany and Poland the amount of refractory C was linearly related to the mineral surface area and the content of oxalate and dithionite extractable iron (Kiem and Kögel-Knabner, 2002). Coating of kaolinite, montmorillonite and illite with Fe oxides strongly increases the SSA (Zhuang and Yu, 2002). Eusterhues et al. (2005) estimated for particle size fractions $<6.3 \mu\text{m}$ of

a Dystric Cambisol and a Haplic Podzol a SSA between 4 and 145 m²g⁻¹ which decreases by 70%, on average, after removing dithionite-extractable minerals. Our results showed that the selective signal loss of O/N-alkyl C is dependent on the surface area that is offered by Fe oxides. The surface area, in turn, was proportional to the concentration of Fe oxides. The high SSA of Fe oxides seemed to promote the sorption of O/N-alkyl C.

7. Small scale spatial variability of organic carbon stocks in litter and solum of a forested Luvisol at Leinefelde

Samples to study spatial variability were obtained from the 111 years old beech forest stand in Leinefelde. At Leinefelde the underlying limestone was covered by loess deposited 10,000 years ago during the last glacial period. Some of the soil characteristics, studied at a representative soil pit, are presented in Table 18.

Table 18: General properties of a representative soil pit at the 111 yrs old beech stand in Leinefelde

Horizon (FAO) ^a	Soil depth	Bulk density	pH (0.01 M CaCl ₂)	Particle size distribution			CECe	Base saturation
				Sand	Silt	Clay		
	m	g cm ⁻³			%		cmol _c kg ⁻¹	%
L	+0.04-0.00	0.05	n.d. ^b	n.d.	n.d.	n.d.	n.d.	n.d.
Ah	0.00-0.07	0.86	4.5	2	62	36	11	87
EBw	0.07-0.26	1.12	3.9	6	66	28	8	22
Bw	0.26-0.35	1.25	4.1	8	54	38	10	42
Btw	0.35-0.40	1.08	5.0	4	26	70	31	99

^a Guidelines for profile description, FAO (1990)

^b n.d. = not determined

7.1. Magnitude of organic carbon stocks

At all 54 sampling points, soils were classified as Luvisols covered by mull-type forest floor. The average thickness of the litter ranged between 0.01 and 0.04 m, whereas the solum thickness was between 0.24 and 0.96 m. The thickness of the loess layer ranged between 0.20 and 0.90 m, whereas the clayey B horizon which derived from the weathering of the limestone had a thickness of <0.1 m. The summary statistics of OC stocks are listed in Table 19. The statistical distributions of OC stocks were positively skewed (Table 19). However, normality plots and medians showed that OC stocks in all layers matched the normal distribution. On average, 0.4 kg m⁻² OC was stored in the litter. The mean OC stock in the solum declined from 3.0 kg m⁻² in the 0-0.12 m layer to 0.7 kg m⁻² in the 0.72-0.84 m layer. The decrease of mean OC stocks with depth was accompanied by a decrease of standard deviation. The CV of OC stocks varied between

Table 19: Summary statistics of soil OC stocks

Sample	Soil depth	N	Mean	Median	Min	Max	Standard deviation	Skewness	Kurtosis	CV ^a
			kg m ⁻²							%
Litter	(+0.04/0.01)-0.00	51	0.4	0.4	0.1	0.8	0.2	0.9	0.6	38
Solum	0.00-0.12	54	3.0	2.7	1.8	5.9	0.9	0.9	0.8	30
	0.12-0.24	54	2.0	2.0	0.8	4.7	0.7	1.2	4.0	34
	0.24-0.36	50	1.4	1.3	0.4	2.8	0.6	0.6	-0.2	43
	0.36-0.48	29	1.1	1.0	0.4	2.0	0.4	1.0	0.3	39
	0.48-0.60	25	1.0	0.8	0.4	2.1	0.4	1.2	1.3	41
	0.60-0.72	14	0.9	0.7	0.6	2.2	0.4	1.9	3.8	49
	0.72-0.84	7	0.7	0.7	0.5	1.3	0.2	1.9	4.4	34
	0.84-0.96	1	0.6	0.6	-	-	-	-	-	-
Solum + litter	(+0.04/0.01) - (0.24/0.96)	51	7.9	7.7	4.2	14.5	2.1	0.6	0.8	27
Solum >0.12 m	0.12-(0.24/0.96)	54	4.5	4.1	1.5	9.8	1.8	0.8	0.5	40

^a CV = Coefficient of variation

27 and 49%, but we observed no relation between CV and soil depth. Frequency distributions of OC stocks in litter, in solum 0-0.12 m and in the solum >0.12 m are presented in Fig. 19. This figure illustrates that mean values as well as the range of OC stocks were increasing in the order litter, solum 0-0.12 m and solum >0.12 m. On average, the solum >0.12 m contained 4.5 kg OC m⁻².

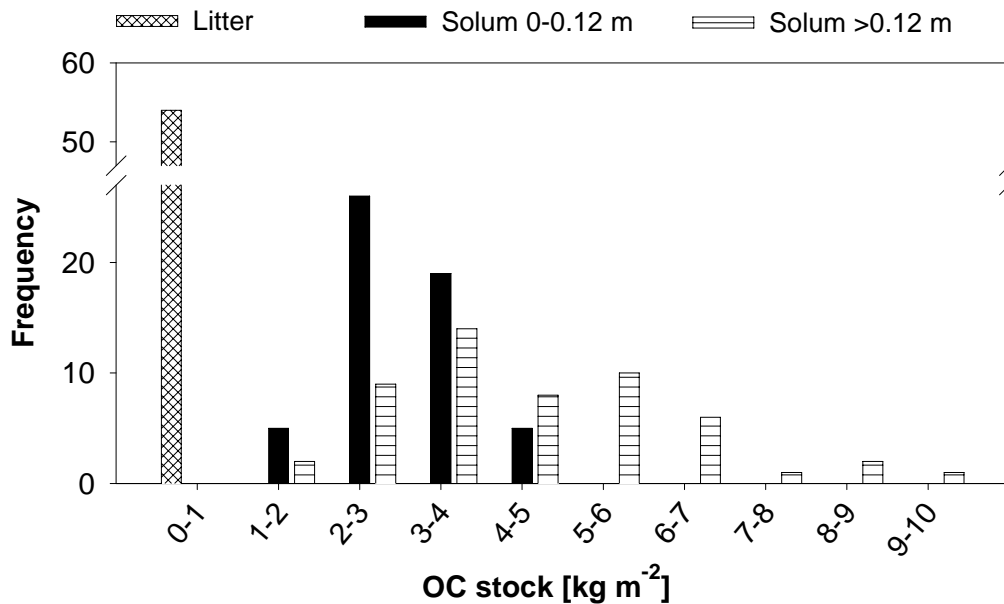


Figure 19: Frequency distribution of OC stocks in litter, solum 0-0.12 m and solum >0.12 m

The mean soil OC stock in the solum of the Luvisol at the site in Leinefelde was higher (Table 19) than the mean C stock of Luvisols ($n=604$) sampled all over the world (Batjes, 1996), which was 3.1 kg m⁻² for the depth interval of 0-0.3 m and 4.3 kg m⁻² for the depth interval of 0-0.5 m. Similar to other forest soils, e.g. Hapludults and Haplorthods under mixed deciduous and coniferous forest (Conant et al., 2003), the OC stock per depth interval decreased in the solum with increasing depth (Table 19). However, if one takes the thickness of horizons into account, a major proportion of the total OC was found in the solum >0.12m, i.e. in the subsoil (Table 19; Fig. 19). This is in line with Batjes (1996) who showed that only 48% of the total OC in the upper meter of Luvisols is held in the first 0.3 m. Although vertical distribution is strongly affected by the parent material (Batjes, 1996; Davis et al., 2004), soils at Leinefelde contained significantly more OC in the subsoil than loess soils in Rhode Island (Davis et al., 2004), where approximately 70% of soil OC was found in O and A horizons. This might be caused by the different thickness of A horizons, which was 0.18 m at the Rhode

Island site (Davis et al., 2004) and around 0.07 m at the site studied here. The OC stocks in forest floor and mineral soil layers showed substantial variation indicated by coefficients of variation $>30\%$ (Table 19). Coefficients of variation at our study site were only slightly lower than that of Luvisols sampled all over Central and Eastern Europe which were 57% for the 0-0.3 m layer ($n=48$) and 46% for the 0-1.0 m layer ($n=37$) (Batjes, 2002). This demonstrates the importance to study spatial structure of soil OC stocks on a stand scale.

7.2. Spatial structure of organic carbon stocks

A preliminary examination of directional semivariograms exhibited that there was no significant difference in the spatial structure of the directional semivariograms. Therefore, omni-directional experimental semivariograms were plotted for OC stocks in litter, solum 0-0.12 m and solum >0.12 m (Eq.7/ Fig. 20). The experimental semivariograms with a lag interval of 5 m showed only a weak spatial dependence of OC stocks. The same result was obtained after the calculation of madograms (Eq.8/ Fig. 21).

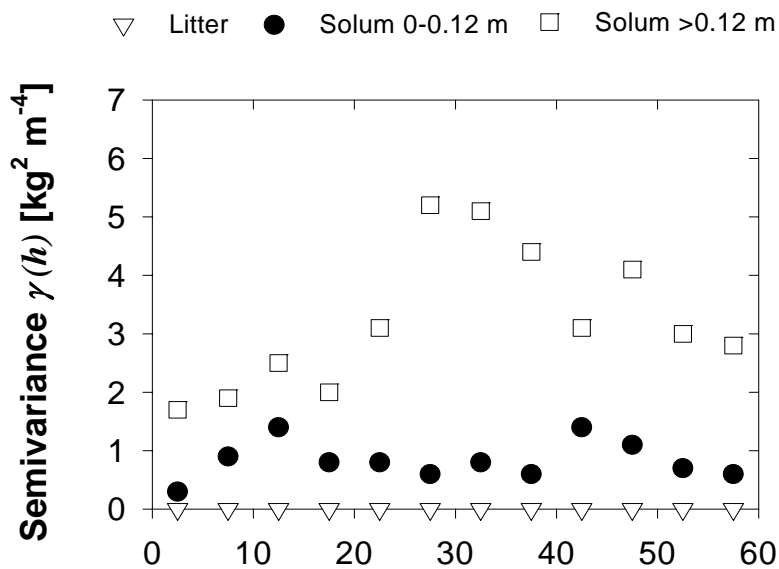


Figure 20: Semivariograms of OC stocks in litter, solum 0-0.12 m and solum >0.12 m with lag distance intervals of 5.0 m

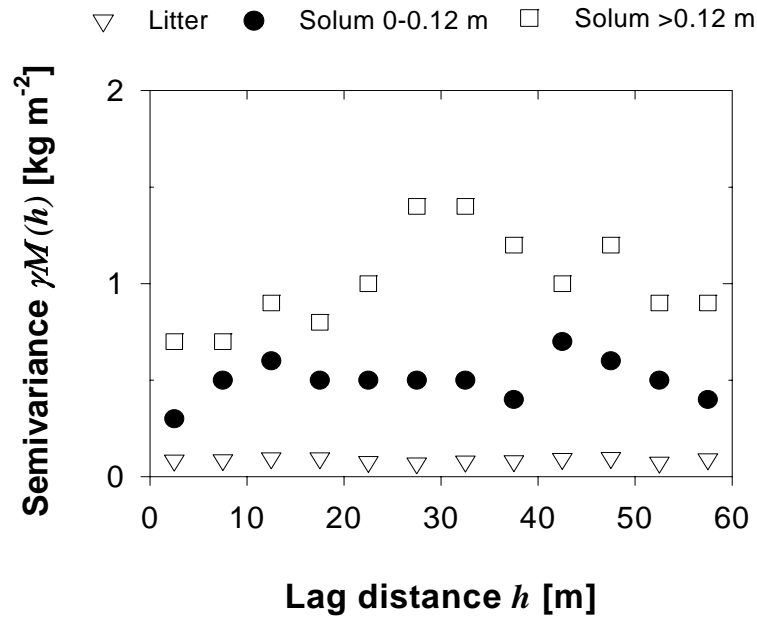


Figure 21: Madograms of OC stocks in litter, solum 0-0.12 m and solum >0.12 m with lag distance intervals of 5.0 m.

Experimental semivariograms (Eq.7) for OC stocks based on the semivariance of the fixed lag distances of 0.2, 0.6, 1.8, 5.4 and 16.2 m are presented in Fig. 22. Semivariograms for the litter revealed a pure nugget effect. Semivariograms for the

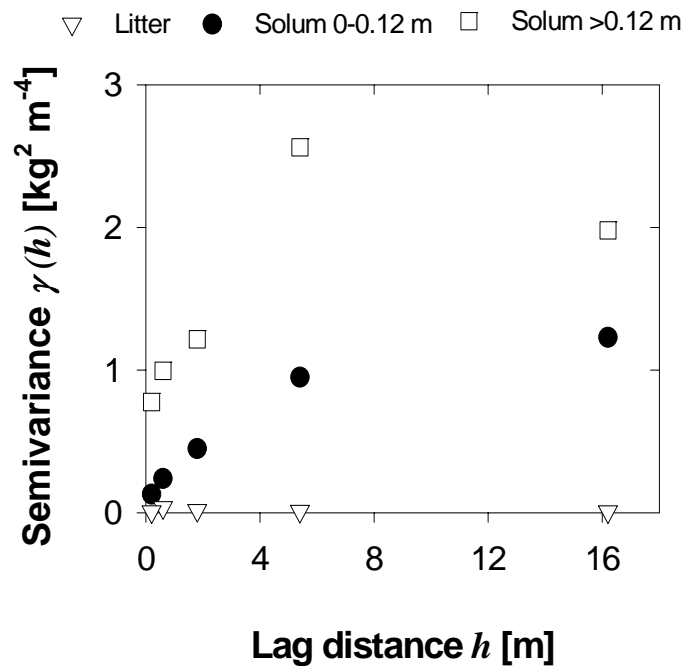


Figure 22: Semivariograms of OC stocks in litter, solum 0-0.12 m and solum >0.12 m with explicit lag distances of 0.2, 0.6, 1.8, 5.4 and 16.2 m.

solum 0-0.12 m and solum >0.12 m, in contrast, showed a considerable spatial dependence when smaller lag distances were chosen. Both semivariograms were characterised by a range of less than 5.4 m and a nugget variance that accounts for around 30% of the sill in the solum 0-0.12 m and for over 50% of the sill in the solum >0.12 m. Semivariograms were also calculated for the 0.12-0.24 m and the 0.24-0.36 m layer of the solum, but both revealed a pure nugget effect.

General relative semivariograms (Eq. 10) were used to compare the spatial pattern of bulk density, OC concentration and OC stock in the solum 0-0.12 m (Fig. 23a). OC concentration and OC stock showed a very similar spatial pattern in the solum 0-0.12 m, whereas bulk density exhibited a pure nugget effect. A crossvariogram (Eq. 9) confirmed that in the solum 0-0.12 m OC concentration and OC stock were spatially correlated (Fig. 23b).

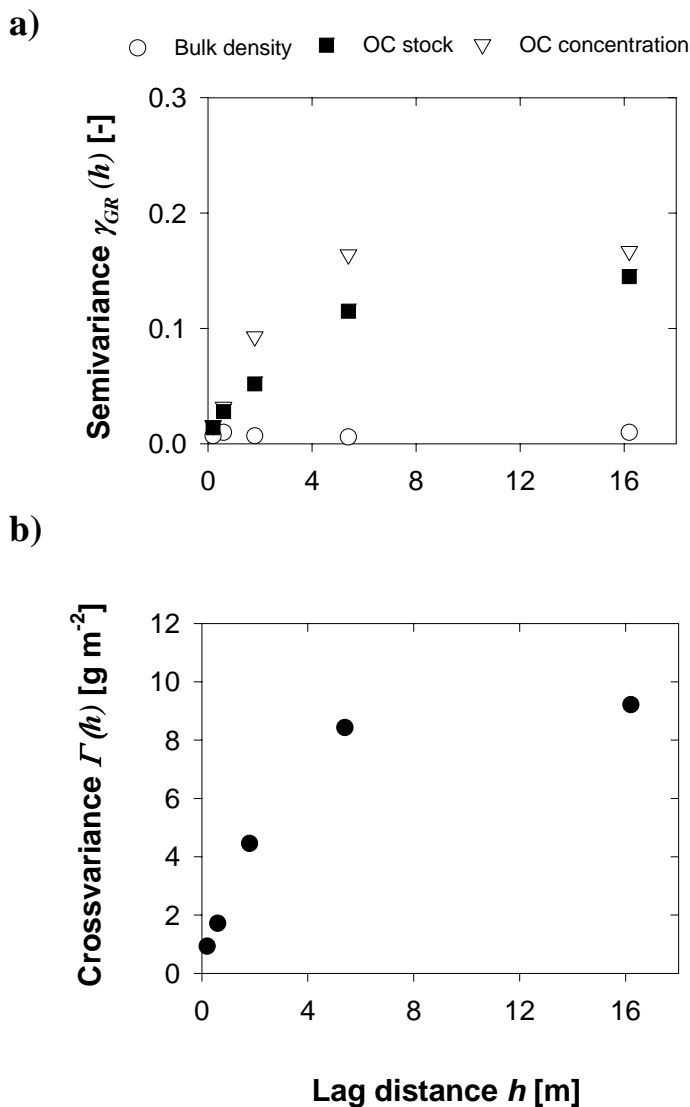
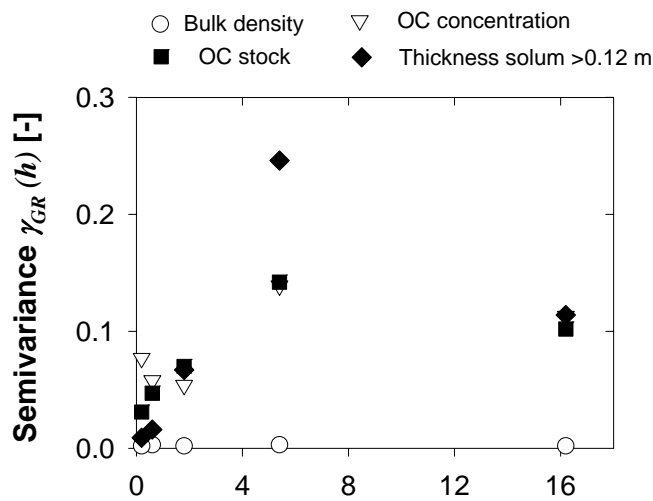


Figure 23: (a) General relative variograms for OC concentration, OC stock and bulk density in the solum 0-0.12 m; (b) Crossvariogram between OC stock and OC concentration in the solum 0-0.12 m.

General relative variograms (Eq. 10) calculated for the solum >0.12 m are presented in Fig. 24a. Here, OC concentration was calculated as an average OC concentration of the different depth increments. The thickness of the solum >0.12 m was also included in the plot. Contrary to the solum 0-0.12 m, OC stock and OC concentration appear to have a different spatial structure in the solum >0.12 m, whereas the spatial structure of soil thickness and OC stock was similar. A crossvariogram (Eq. 9) underlined a positive spatial relation between OC stock in the solum >0.12 m and the solum thickness (Fig. 24b).

a)



b)

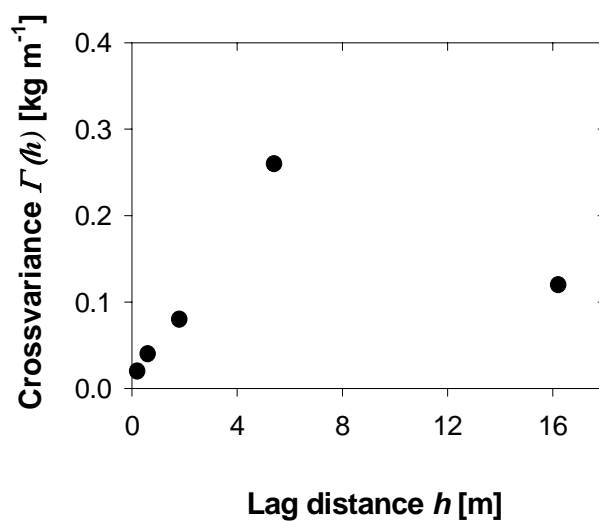


Figure 24: (a) General relative variograms for OC concentration, OC stock, bulk density and solum thickness in the solum >0.12 m; (b) Crossvariogram between OC stock and thickness of the solum >0.12 m.

In order to examine an effect of trees on the OC stocks, the distance of each sampling point to the nearest tree was correlated against the OC stock (Table 20). The coefficient of determination is between 0.03 in the litter layer and 0.35 in the 0.72-0.84 m layer. On a significance level of $p = 0.05$ it could not be found any significant relationship between distance to the nearest tree and the magnitude of the OC stocks. In crossvariograms, values of crossvariance changed between positive and negative values which indicated that no spatial correlation was evident.

Table 20: Relation between distance to the nearest tree and soil OC stock

Sample	Soil depth —— m ——	N	r^2
Litter	(+0.04/0.01)-0.00	51	0.003
Solum	0.00-0.12	54	0.003
	0.12-0.24	54	0.023
	0.24-0.36	50	0.099
	0.36-0.48	29	0.118
	0.48-0.60	25	0.035
	0.60-0.72	14	0.147
	0.72-0.84	7	0.350
	0.84-0.96	1	-
Solum + litter	(+0.04/0.01)- (0.24/0.96)	51	0.003
Solum >0.12 m	0.12-(0.24/0.96)	54	0.022

Comparisons of semivariograms and madograms indicated that spatial structure is similarly represented by both types of variograms (Fig. 20; Fig. 21). This confirmed a geostatistical study of soil OC concentrations in grassland of south eastern Ireland. In this study, more robust methods, e.g. using median values instead of average values in the calculation of the variogram, were tested and resulted in little improvement of the semivariograms (Zhang and McGrath, 2004). The semivariograms of all depth increments were characterised by a high nugget effect (Fig. 20), even though semivariograms included the very small lag distances of 0.2 and 0.6 m (Fig.22). This

either suggests undetected spatially dependent small scale variance or measurement errors. The small scale variability of OC stocks could not be further resolved in our study, since the determination of bulk density with $0.37 \cdot 10^{-3} \text{ m}^3$ cores required a sampling area of $6.4 \cdot 10^{-3} \text{ m}^2$. This may cause undetected small scale variability. High nugget variances were also obtained in a study with grassland soils, where 50% of the sill is nugget variance in consideration of lag distances of 0.3 m (Hewitt et al., 1998). A high small scale spatial variability OC stock is specific for soils covered by natural vegetation. Paz-Gonzales et al. (2000) compared variograms for OC concentrations in Umbrisols under cultivation and under natural vegetation (shrubs, pine trees and grass) and observed a higher micro-heterogeneity at the site with natural vegetation. Liski (1995), in turn, could show that OC stocks of podzols generally varied more under pine tree canopies than in an adjacent within stand opening area. Our results showed high values of nugget variance in the depth increments 0.12-0.24 m as well as 0.24-0.36 m. In these depth increments the spatial pattern of OC stocks is controlled by the distribution of root litter and the sorption of dissolved organic carbon (DOC). It was found that OC concentrations along preferential flow paths were 12-69% higher than in the soil matrix (Bundt et al., 2001). Usually, DOC sorption in carbonate-free subsoils is related to oxalate-extractable aluminium and dithionite-extractable iron (Kaiser et al., 1996). Therefore high small scale variability of pore distribution and distribution of aluminium and iron hydroxides are probably responsible for the high nugget variance in the depth increments below 0.12 m. Together with other studies our results indicated a short distance of spatial continuity of OC stocks in forest stands (Fig. 22). Liski (1995) showed, that the OC stock of soil layers and the thickness of the soil horizons in a spruce forest stand were spatially dependent within distances varying from about 1 m to 8 m. Correspondingly, with a minimum sampling distance of 5 m Järvinen et al. (1993) and Riha et al. (1986) could not identify any spatial autocorrelation of organic matter content for forest floor and mineral soil.

The semivariograms of OC stocks in the solum 0-0.12 m were similar to variograms of OC concentrations (Fig. 23a,b). These results are in accordance with Hewitt et al. (1998), who found a similar spatial structure for OC stocks and concentrations to a depth of 0.075 m in Pallic Orthic Brown soils under grassland. The semivariance of OC stocks is slightly lower than the nugget in semivariograms of OC concentrations. This may be explained by the phenomenon that soil samples with higher

OC concentrations are often characterised by lower bulk densities, which reduces variability of OC stocks compared to variability of OC concentrations (Huntington et al., 1989). Contrary to OC concentration, bulk density showed a complete lack of spatial variation indicated by an almost pure nugget effect in semivariograms (Fig. 23a). This can be attributed to small scale variations of bulk density resulting from the combined effect of parent-material and biological activity. Furthermore, the magnitude of relative variability of bulk density is significantly smaller than the magnitude of relative variability of OC concentrations. Applying descriptive statistics, Davis et al. (2004) could show lower coefficients of variation for bulk densities compared to those of the OC concentrations. Our results highlighted that the OC concentration was the main determinant for the variability of OC stocks in the solum 0-0.12 m.

Often terrain attributes such as slope and elevation were found to be main factors controlling variability in local C stores (Arrouays et al., 1998; Chaplot et al., 2001). However, although vegetation and micro-topography are quite homogeneous within our sampling area, a high spatial variability of OC carbon stocks was detected (Table 19, Fig. 22). General relative variograms and crossvariograms clearly indicate that OC stocks in the solum >0.12 m and soil thickness were spatially correlated (Fig. 24a,b). Homann et al. (2001) already emphasised the impact of O horizon thickness on the coefficient of variation of OC stocks. They showed that masses of OC and N in the O horizon of a Dystrachrept and Hapludults under Douglas fir and pine were twice as variable as in the mineral soil, because the O horizon depth varied, whereas the mineral soil values were for specified depths. The subsurface stratigraphy, in particular the surface characteristics of the underlying limestone and the thickness of the loess layer are probably the decisive factors for solum thickness and total OC stock at the study area in Leinefelde. At an agricultural site, it was shown that present terrain attributes often imperfectly explain variability of soil thickness: A multiple correlation indicated that micro-topography parameters accounted for only 9% of the variability of B horizon thickness, whereas a significant correlation to the depth of an intertill sand-gravel layer was evident (Kachanoski et al., 1985). In a study on the total C stocks in soils of the world, different relations between soil thickness and C stock were found for different parent materials (Batjes, 1996). This may explain, why Liebens and van Molle (2003) could not find any systematic relationship between OC stocks and pedon thickness (correlation coefficient was -0.1) for the region of Flanders/ Belgium. We suppose that

relations between soil thickness and OC stock are characteristic for variability studies on the forest stand level, where soils developed from the same parent material.

An effect of trees on the magnitude of OC stocks in litter and solum was not detectable in our study (Table 20). This result is in contrast to studies carried out at pine stands. In podzols, the F/H layer was thicker and contained more OC within 1-3 m radius from trees (Liski, 1995). In Typic Kandudults, C and N levels were always elevated in a region within 0.8 m of the tree stems, whereas variability of the estimates of C and N consistently decreased with increased proximity to the stem. This was explained by the soil OC derived from stemflow and bark sloughing (Ruark and Zarnoch, 1993). On the other hand, Riha et al. (1986) could not find any significant differences in organic matter concentration in the forest floor and surface layer of a Typic Fragiochrept and Typic Dystrochrept as a function of distance from maple, spruce and pine trees. Possible effects of trees at our site may be masked. In the study of Ruark and Zarnoch (1993) it was emphasised that measurements were conducted at a first-rotation stand growing on an abandoned farm site and that the surface plow layer could be considered to have been relatively homogeneous prior to forestation. This enabled the detection of spatial differences which were solely attributed to the influence of tree vegetation. Since soils contain a significant proportion of old OC, the spatial distribution of OC stocks at our site is probably not only influenced by the current but also by former vegetation patterns. Beside trees, site variables like soil respiration and soil texture may also affect spatial patterns of OC stocks. With a 1x1 m sampling grid, Gömöryová (2004) could not find any relationship between the position of beech trees and soil respiration in a forested Cambisol.

7.3. Minimum detectable difference (MDD) of organic carbon stocks

To estimate the MDD of OC stocks at our study area, we assumed that OC stocks at the sampling points, which are separated by a distance of 16.2 m, would have been sampled in two points in time (Table 21). According to the semivariograms in Fig. 4 this would assure the statistical independence of sampling points. MDD (Eq.5) for the distance of 16.2 m ranged between 0.15 kg m⁻² in the litter layer and 4.48 kg m⁻² in the complete soil profile (solum + litter). This corresponded to a MDD_{rel.} between 41 and 95% (Eq. 6). Layers with large OC stocks, such as the solum 0-0.12 m, tended to have larger variances and therefore higher absolute MDD values. If one would disregard the

statistical requirement of statistical independence and would resample points separated by a distance of 0.2 m (paired approach), this would result in smaller MDD for the solum layers. They would range between 0.15 kg m⁻² in the litter and 1.85 kg m⁻² in the complete soil profile. The maximum MDD_{rel.} would decrease from 95% at a sampling distance of 16.2 m to 49% at a sampling distance of 0.2 m.

Table 21: Absolute and relative minimum detectable difference of soil OC stocks taking into account sampling points separated by 16.2 and 0.2 m.

Sample	Soil depth	MDD		MDD _{rel.}	
		16.2 m	0.2 m	16.2 m	0.2 m
	— m —	— kg m ⁻² —		— % —	
Litter	(+0.04/0.01)-0.00	0.2	0.2	41	39
Solum	0.00-0.12	1.9	0.6	67	18
	0.12-0.24	1.7	0.8	95	39
	0.24-0.36	0.8	0.7	75	49
Solum + litter	(+0.04/0.01)- (0.24/0.96)	4.5	1.9	59	21
Solum >0.12 m	0.12-0.24/0.96	2.6	1.6	58	32

The MDD_{rel.} declines as a function of sample size. Figure 25a plots the MDD_{rel.} in relation to sample size taking into account the standard deviation of the sampling points separated by a distance of 16.2 m. The diagram shows that one would need more than 160 samples from the litter and even more than 300 samples from the solum to detect an OC stock difference of 10%. Fig. 25b, in contrast, shows the MDD_{rel.} in relation to sample size taking into account the standard deviation of points separated by a distance 0.2 m. Here, smaller sample sizes are sufficient to detect a certain OC stock change. An OC stock difference of 10% could be detected with 40 samples in the solum 0-0.12 m and with 140 samples from the solum >0.12 m and 160 samples from the litter.

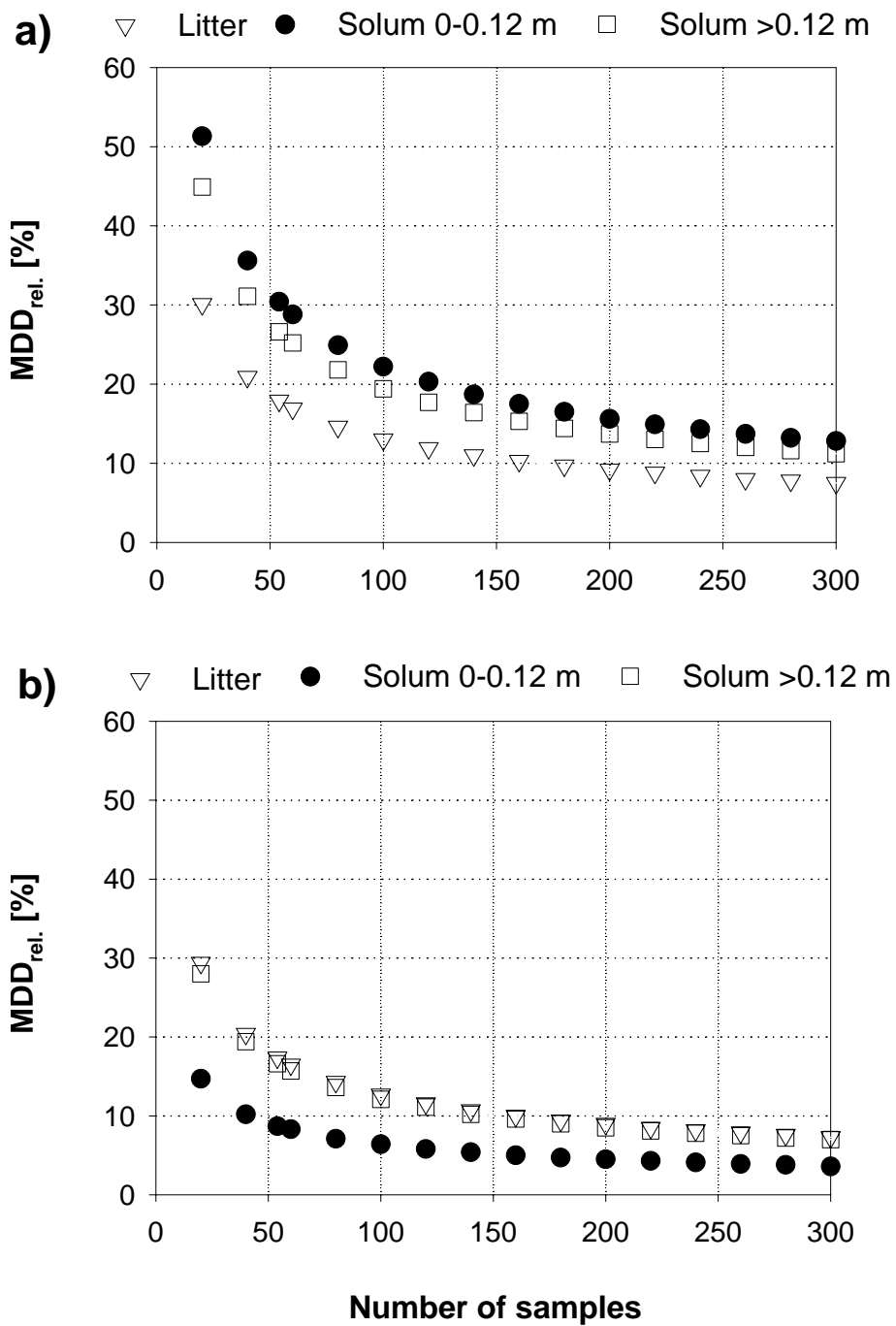


Figure 25: Relative minimum detectable difference of organic carbon stocks in relation to sample size (a) under consideration of statistically independent sampling points (distance between sampling points 16.2 m), and (b) under consideration of statistically dependent sampling points (distance between sampling points 0.2 m)

7.4. Implications for future sampling and monitoring

Information gained on the range of OC stocks can be used in the kriging interpolation, when samples are taken closer than the range (Liski, 1995). To construct a meaningful map of OC stocks in the solum at our study area, samples would have to be taken in a sampling grid of less than 5.4 x 5.4 m (Fig. 22). This would result in more than 343 sampling points in our study area. Determination of bulk density requires a destructive sampling and cores for a carbon stock change assessment have to be taken at two different locations. From the point of view of soil statistical independence, samples should be taken further from each other than the range of spatial dependence (Liski, 1995). Van Groenigen (2000) suggests to place sampling points at distances greater than the twofold range, in order to assure the resulting sampling scheme is still random. Relating these recommendations to our sampling area, future samples from the solum have to be taken in a distance of more than 10.8 m apart from each other to fulfil the criteria of statistical independence. For statistical independent sampling points, we calculated a minimum detectable difference of 4.5 kg m⁻² for OC stocks in the three uppermost solum layers (0.36 m) (Table 21). This is much higher, than the MDD values of OC stocks in the surface 0.4 m of Alfisols and Ultisols beneath switchgrass, which were between 0.53-1.27 kg m⁻² for a similar sample size (n = 8) (Garten and Wulschleger, 1999). Some studies, however, indicate higher MDD for OC stocks in soils beneath forest. Changes of OC stocks smaller than 0.49 and 3.14 kg m⁻² at second-growth and old-growth sites, respectively, could not be detected in the surface 0.3 m even with collection and analysis of samples from 100 microplots (Conant et al., 2003). Conant et al. (2003) suggested a sampling scheme that enables future resampling of the same forest microplots (2 x 5 m) to decrease the MDD. Assuming soil OC changes at 0.05 kg C m⁻² yr⁻¹, changes at two forest sites could be detected as much as eight years earlier if the same micro-plot was resampled (Conant et al., 2003). This was also demonstrated for micro-sites with calcareous Chernozems, where only paired temporal comparisons in 1 m distance showed an effective recovery of previously added coal C (Ellert et al., 2002). Ellert et al. (2002) emphasised, however, that these results assume that soil OC increases uniformly within a microplot and that soil OC increases are directly related to initial soil OC content. At the site in Leinefelde, future sampling in 0.2 m distance to the previous sampled points would decrease the OC stock change in the complete solum required for the detection of a statistical verified difference by more than 50%.

8. Conclusions

The present study helped to better understand the composition and spatial variability of SOM in mineral soils under temperate forest. Particle size fractionation allowed to separate OC pools with distinct chemical composition and radiocarbon age. The OC in the 200-2000 μm fractions consisted of labile material ($\text{pmC} > 100$) throughout the profiles, whereas $< 2 \mu\text{m}$ fractions revealed radiocarbon ages of up to 4745 years before present. These results showed that the 200-2000 μm fractions were dominated by fresh litter. In contrast, stabilisation mechanisms played a major role in the particle size fractions $< 200 \mu\text{m}$, particularly in the subsoils.

In the A horizons, SOM in coarse fractions showed a plant-like chemical composition (high lignin contents, high C/N ratios), whereas the SOM in fine fractions (clay) is probably dominated by compounds of microbial origin (depleted in lignin and aryl C, low C/N ratios). ^{13}C CPMAS NMR analyses of subsoil samples from Cambisols and Luvisols suggest that the same applies to the subsoil, but this has yet to be confirmed by wet chemical analyses.

The major components of labile and stable OC pools in topsoils and in subsoils of Cambisols and Luvisols were always O/N-alkyl C and alkyl C compounds. In contrast, the overall contribution of aryl C and carbonyl C to the stabilized OC was relatively small. Compared to Luvisols, Cambisols contained more alkyl C in topsoil and subsoil horizons which indicates an accumulation of alkyl C in acid forest soils.

The present study highlighted that chemically labile components such as carbohydrates and proteinaceous (O/N-alkyl C) compounds can persist in the mineral soils for long periods of time. The detailed chemical composition of O/N alkyl C and alkyl C in old fractions, particularly the relevance of different O/N alkyl C and alkyl C stabilisation mechanisms, remains to be studied to elucidate the long term turnover of OC.

As shown by CuO oxidation as well as ^{13}C CPMAS NMR spectroscopy, even recalcitrant structures, such as lignin, can be degraded in the short term. Although lignin may have an important role in the control of biodegradation rates at early stages of litter decay, it is not undergoing stabilisation by association with the clay minerals.

In the A horizons, relations were found between the radiocarbon age and functional groups in particle size fractions. These relations were site specific, probably due to the different mineral composition of the parent material and the resultant possibilities of physical and chemical preservation. This suggests that in the short term turnover of SOM is significantly controlled by the chemical composition of SOM. However, a relation between chemical composition and radiocarbon age in particles size fractions throughout soil profiles was not found. Thus, it was demonstrated that the chemical structure of SOM in the particle size fractions cannot explain the increase of radiocarbon age with increasing soil depth. This highlights the importance of mechanisms of protection offered by the soil matrix and soil minerals for the long term storage of SOM.

The ability of iron oxides to form intimate associations with O/N-alkyl C in clay fractions from Leptosols and Luvisols was demonstrated using ^{13}C CPMAS NMR spectroscopy. Such association most probably provides a specific mechanism of protection of O/N-alkyl C against biological attack. The association between O/N-alkyl C and iron oxides impacts the applicability of ^{13}C CPMAS NMR spectroscopy to study the SOM composition in clay fractions without previous removal of iron oxides. Due to the association with paramagnetic iron, part of the O/N-alkyl C in untreated clay fractions might be invisible in standard ^{13}C CPMAS NMR spectra acquired with a contact time of 1 ms. In contrast to available literature, clay fractions with OC:Fe ratios between 2 and 4 were affected by associations between Fe oxides and O/N-alkyl C. They had to be treated with HF to circumvent a selective suppression of the O/N-alkyl C signal.

The vertical distribution of OC stocks in Cambisols and Luvisols pointed towards the importance of subsoils as carbon reservoirs in temperate forest ecosystems. Though the concentration of OC in soils decreased with depth, the magnitude of OC stocks in subsoils was significantly higher than in litter and topsoil. A high proportion of OC is stored in subsoils for many years. OC stocks in the subsoils were mainly controlled by the parent material, soil texture, and horizon thickness, but were little affected by the present vegetation. To understand carbon storage not only at the very short time scale,

but also at the medium and long time scale, magnitude and variability of OC stocks in subsoils need to be considered in carbon balances.

Semivariograms indicated that the OC stock in a Luvisol may be extremely variable at distances shorter than 5 m even if it is homogeneously covered by beech forest. This suggests that studies on the spatial variability of OC stocks at the forest stand level should include sampling intervals of less than 5 m to avoid a pure nugget effect in variograms. No direct relationship was observed between the OC stock of individual samples and the proximity to individual beech trees. In contrast, soil thickness affected the magnitude of OC stocks and increased its variability. Our results suggest that information about the soil thickness is helpful when estimating spatial OC stocks in soils developed from the same parent material.

Considering statistical independence of sampling points, the minimum detectable difference ranged between 0.2 kg m^{-2} in the litter layer and 4.5 kg m^{-2} in the complete soil profile. In order to detect a change of 10% in OC stocks of the solum, more than 300 samples would be required. If one would disregard the statistical independence, the minimum detectable difference and number of samples necessary to detect a carbon change in the solum could be halved by taking samples in a distance of 0.2 m to the previously sampled points.

It can be concluded that considering small scale spatial variability and subsoil OC stocks is essential for monitoring soil OC stocks. Long term stabilisation appeared to be dominated by active stabilisation mechanisms rather than by chemical recalcitrance. The study of the quantitative relevance of different active stabilisation mechanisms in space and time is a key area of future research.

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