Carbon turnover in aggregated soils determined by natural ^{13}C abundance

Dissertation

zur Erlangung des Doktorgrades

der Mathematisch-Naturwissenschaftlichen Fakultäten

der Georg-August-Universität zu Göttingen

vorgelegt von

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Göttingen 2003

D 7

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Tag der mündlichen Prüfung: **27.06.2003**

Meinen Eltern gewidmet

Danksagung

Mein Dank gilt Herrn Prof. Dr. C. Leuschner für die Übernahme des Hauptreferates und Herrn Prof. Dr. M. Schaefer als Koreferenten.

Herrn Prof. Dr. Beese danke ich für die sehr guten Arbeitsbedingungen am Institut und inhaltliche Anregungen.

Meine beiden Betreuer, Herr PD Dr. Heiner Flessa und Herr Prof. Dr. Bernard Ludwig haben sich überaus engagiert und mit einer gelungenen Mischung aus Fördern, Fordern, Motivieren und Freiräume lassen für das Gelingen meiner Doktorarbeit eingesetzt. Ich habe sehr viel von ihnen gelernt. Dafür sage ich ganz herzlichen Dank!

Die sehr gute Arbeitsatmosphäre und die Hilfsbereitschaft unter den Kolleginnen und Kollegen trug wesentlich zum Gelingen dieser Arbeit bei. Herr Dr. Jens Dyckmans als mein ehemaliger Bürokollege hat mir durch seine große Hilfsbereitschaft den Start am Institut sehr einfach gemacht. Tamon Yamashita war im letzten Jahr nicht nur komplett in das Projekt mit eingebunden – sowohl wissenschaftlich als auch im Labor – sondern hat mir als mein gegenwärtiger Bürokollege auch viel über Japan beigebracht. Ihm und Dr. Jens Dyckmans, Dr. Martin Potthoff, Dr. Barbara Wick und Dr. Jürgen Prenzel danke ich für viele hilfreiche Diskussion. Dr. Norman Loftfield half bei der Mikrokosmenanlage und beim Trouble-Shooting am Dohrmann – auch dafür vielen Dank!

Kerstin Jespersen, leistete auch ungewöhnliche Laboreinsätze mit viel Einsatz. Lars Swecz und Reinhard Langel führten dankenswerterweise viele Isotopenmessungen für mich durch. Weiterhin danke ich den technischen Mitarbeiterinnen des Zentrallabors für ungezählte C- und N-Messungen.

Meine Eltern haben mich stets liebevoll bei meiner Arbeit unterstützt – ganz vielen Dank dafür. Mein lieber Freund Oliver Becker hat mich während der gesamten Zeit unterstützt und angespornt, er war in der heißen Abschlußphase unentbehrlich – ein großes Dankeschön!

Weiterhin danke ich der Deutschen Forschungsgemeinschaft, die meine Arbeit im Rahmen des Schwerpunktprogrammes 1090 „Böden als Quelle und Senke für CO_2“ förderte.

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Summary

Soil organic matter influences all soil functions and is a crucial factor in the global carbon cycle. Soils contain the largest active terrestrial carbon pool on earth, and through soil respiration, contribute an annual flux of CO_2 to the atmosphere that is 10 times greater than that from fossil fuel combustion. On the other hand, forests, agricultural lands, and other terrestrial ecosystems offer significant, but often temporary, mitigation potential.

The stabilization mechanisms of organic matter in soils are poorly understood. The objective of this study was to quantify soil carbon dynamics in soils from long-term monocultures with a change from a C_3-plant (rye or wheat) to a C_4-plant (maize) using natural ^{13}C abundance. Additionally, the carbon turnover under different static fertilizations was compared. The relationship between soil structure and the ability of soils to stabilize soil organic matter is a key element in soil C dynamics, thus the measurement of the enrichment of maize-derived carbon in physical soil fractions was one objective of the study. The microbial biomass is a source and sink of biologically mediated nutrients and responsible for transforming organic matter and nutrients within soils. The availability of soil organic carbon (SOC) to the microbial biomass influences its degradation and the nutrient availability for plants. Thus, the formation of the microbial biomass was investigated by determining its maize-derived percentages. In soil microcosm experiments the formation of dissolved organic carbon (DOC) and CO_2 from the soil was quantified. As carbon dynamics are influenced by nitrogen dynamics in the soil, the effect of fertilization on C sequestration was analyzed.

Two study sites in East and South Germany with differing soil properties and cultivation practices were chosen for the study. At the „Ewiger Roggen“ in Halle, the investigated plots were continuous rye (since 1878) and maize (since 1961) with and without mineral N fertilization. As the experimental plot was located close to a train station and nearby industrial areas, anthropogenic pollution by coal and soot was high. At an unpolluted site at Rotthalmünster in the rural district of Passau, the following sites were chosen: a continuous wheat plot with NPK-fertilization (since 1969), continuous maize plots (since 1979) with NPK-fertilization with or without organic fertilization, continuous grassland with NPK-fertilization (since 1961), and a spruce forest (~1920).

The method of natural ^{13}C abundance proved as a useful tool to determine the carbon turnover in soils. The results of the study indicated that young carbon turned over much faster than the older carbon in the soil. At Halle, after 40 years of maize monoculture, the enrichment of younger carbon was as low as 14.1% under NPK-fertilization and 9.5% without fertilization. The percentage of maize-derived carbon was higher at Rotthalmünster (35.1 – 35.8% maize-derived C) than at Halle due to the higher production of biomass, higher input of plant residues after harvest, higher NPK-fertilization, and the high percentage of silt and clay.

The stabilization of carbon and nitrogen was dependent on their position in the soil: The results of the size fractionation for the surface soils of the Halle site indicated that carbon and nitrogen enrichment were highest in the clay fraction, followed by the silt fractions. Carbon and nitrogen enrichment was relatively high in the coarse sand due to its high content of fresh organic matter. C/N ratios and maize-derived percentages indicated that the fine sand fraction and the coarse silt fraction were the most stable fractions.

In the topsoils of Rotthalmünster, tillage destroyed aggregates >1 mm: for the tilled soils of the maize sites, the most important fractions were the microaggregates (53-250 µm). For wheat (conservation tillage since 1998) the smaller macroaggregates (250-1000 µm) and for the grassland and forest soils the megaaggregates (>2000 µm) were most important. At the grassland and forest, surface soils were more aggregated than subsoils. Aggregates protect carbon from decomposition as carbon content in all aggregate fractions >53 µm was higher than in the silt and clay fraction (<53 µm). The amount of carbon stored in the microaggregates plus silt and clay was nearly constant and thus independent of the amount of SOC in the bulk soil, and hence cultivation. The amount of mega- and macroaggregates was highly dependent on the SOC, thus indicating that carbon is mainly lost from macroaggregates if soil cultivation commences. Water stable aggregates of the maize site of Rotthalmünster had lower maize-derived percentages in the microaggregates plus silt and clay than in the mega-and macroaggregates, thus proving the higher preservation of carbon in microaggregates.

The density fractionation for all soils of Halle and Rotthalmünster (excluding the forest site) suggested that in respect of the C-storage, of the light fractions occluded particulated organic matter (OPOM) with a density from 1.6 to 2.0 g cm^{-3} ($OPOM_{1.6-2.0}$) was most important, followed by the free particulate organic matter ($FPOM_{<1.6}$, density <1.6 g cm^{-3}), whereas the $OPOM_{<1.6}$ (density <1.6 g cm^{-3}) was only of minor importance in respect of carbon storage. The high maize-derived percentages in the FPOM fractions of Halle and Rotthalmünster and the lower maize-derived percentages in the OPOM fractions emphasized the importance of physical protection. For the Halle soils, the fraction $OPOM_{<1.6}$ was the pool with the slowest turnover that could be measured in the entire study. The mineral fraction with a density > 2.0 g cm^{-3} contained the largest fraction of C, its maize-derived percentages were intermediate.

For the determination of the extractable microbial biomass, various methods were compared in this study. The microbial biomass of the Halle soils was determined using 0.5 M K_2SO_4 as extraction agent after a chloroform-fumigation extraction (CFE). For the determination of the microbial biomass of Rotthalmünster, the CFE-method was compared to a freeze-drying method, using water as extraction agent in both cases. Both at Halle and Rotthalmünster, the microbial biomass was low due to the adverse conditions of the monoculture. At Halle, the microbial biomass and their maize-derived percentages was higher in the fertilized soils, due to their higher input of organic residues. At Rotthalmünster, the microbial biomass was

highest in the grassland soil, followed by the maize sites and the wheat site. On average, the extractable carbon was 3.3 times higher after freeze-drying than after fumigation. The freeze-drying method probably extracted carbon from the killed biomass, but additionally carbon that was released from other processes due to the freeze-drying. Maize-derived percentages were higher after freeze-drying (surface soils: 51-61%, subsoils: 31-34%) than after chloroform-fumigation (surface soils: 47-58%, subsoils: 24-25%), however, significant differences could only be found in the subsoils.

In the bare surface soils of Halle, the production of CO_2, DOC and DON was higher in the rye soils than in the maize soils and higher under fertilization than without. The production of CO_2 from soil columns with a maize-stalk was higher than from any bare soil, whereas DOC and DON production were less than at the rye soils. The maize-derived percentages after 40 years of continuous maize cropping were highest in CO_2 (42 to 79%), followed by C_{mic} (23 to 46%), DOC (5 to 30%) and SOC (5 to 14%). Young, C_4-derived carbon showed a higher turnover than older, C_3-derived, more recalcitrant carbon. Strong correlations were found between C_4-derived C_{mic} and C_4-derived SOC, DOC and CO_2 ($r \geq 0.90$), whereas the relationships between C_3-derived C_{mic} and C_3-derived SOC, DOC and CO_2 were not as pronounced ($r \leq 0.67$). A comparison of the results for surface soils and subsoils showed that the significance of DOC compared to CO_2 to export carbon from the soil was minor but increased with soil depth. When including soil columns with a standing stubble into the study to represent the inhomogeneity of maize residue distribution after harvest of maize for silage making, the results showed that the uneven distribution of maize residues resulted in a considerably increased heterotrophic activity within the maize rows as compared with soil between seed rows. However, there was no or only a marginal effect of maize stubble decomposition on leaching of DOC, dissolved organic nitrogen and NO_3^-. The results about CO_2 and DOC losses emphasized that the relative importance of DOC leaching for the loss of SOC increases with increasing age and stability of SOC.

The results of the ^{13}C natural abundance technique were successfully employed to model the SOC dynamics in the long-term maize cropping systems of Halle (NPK fertilization or unfertilized) without using adjustable parameters. The modeled size of the “inert organic matter” pool agreed well with published equations for its determination from soil texture (KÖRSCHENS, 1980; KÖRSCHENS ET AL., 1998). Furthermore, the total as well the maize-derived fraction 0–63 µm agreed well with the total and maize-derived sums of the model pools “inert organic matter”, “humified organic matter” and “microbial biomass”.

The study showed that newly incorporated carbon has a considerably higher turnover than older carbon in the soil, thus questioning the long-term mitigation potential of soils. The method of natural ^{13}C abundance that was applied to the study sites enabled valuable insights into the sequestration of carbon in total soil and in soil constituents that play an important role

in the carbon turnover in soils. The microcosm experiment showed the interaction of SOC, C_{mic}, DOC and CO_2 during the formation and export of soil organic matter. The results of the different soil carbon pools are a valuable source for the improvement of soil carbon models.

Zusammenfassung

Die organische Bodensubstanz beeinflußt alle Bodenfunktionen und ist ein entscheidender Faktor im globalen Kohlenstoffzyklus. Böden enhalten den größten aktiven terrestrischen Kohlenstoffpool der Erde und tragen durch die Bodenatmung einen jährlichen CO_2-Fluß zur Atmosphäre bei der 10 mal höher ist als jener durch die Verbrennung fossiler Energien. Andererseits bieten Wälder, landwirtschaftliche Flächen, und weitere terrestrische Ökosysteme ein signifikantes, aber oft nur temporäres, Verbessungspotential für den Treibhauseffekt an.

Die Stabilisierungsmechanismen der organischen Bodensubstanz sind nur schlecht verstanden. Ziel dieser Studie war es, die Dynamik der organischen Bodensubstanz aus Langzeit-Monokulturen mit einem Kulturwechsel von einer C_3-Pflanze (Roggen oder Weizen) zu einer C_4-Pflanze (Mais) mit Hilfe der natürlichen ^{13}C-Abundanz zu bestimmen. Zusätzlich wurde der Kohlenstoffumsatz unter unterschiedlichen statischen Düngungen verglichen. Die Beziehung zwischen der Bodenstruktur und der Fähigkeit der Böden, organische Bodensubstanz zu stabilisieren, ist ein Schlüsselelement für die C-Dynamik, daher war die Messung der Anreicherung maisbürtigen Kohlenstoffs in physikalischen Bodenfraktionen ein Ziel dieser Studie. Die mikrobielle Biomasse dient als Quelle und Senke für biologische Nährstoffe und ist verantwortlich für den Umsatz organischer Substanz und von Nährstoffen in Böden. Die Verfügbarkeit des organischen Kohlenstoff im Boden (SOC) für die mikrobielle Biomasse beeinflußt seinen Umbau und die Nährstoffverfügbarkeit für Pflanzen. Daher wurde der Aufbau der mikrobiellen Biomasse untersucht, indem ihre maisbürtigen Anteile bestimmt wurden. In Mikrokosmenexperimenten mit ungestörten Bodensäulen wurde die Bildung der gelösten organischen Substanz (DOC) und des CO_2 aus dem Boden quantifiziert. Da die Kohlenstoffdynamik des Bodens durch die Stickstoffdynamik des Bodens beeinflußt wird, wurde auch der Einfluß der Düngung auf die C Festlegung im Boden untersucht.

Zwei Untersuchungsflächen in Ost- und Süddeutschland mit unterschiedlichen Bodeneigenschaften und Kultivierungspraktiken wurden für diese Studie ausgewählt. Bei dem „Ewigen Roggen“ in Halle waren die untersuchten Flächen ein kontinuierliches Roggenfeld (seit 1878) und ein Maisfeld (seit 1961) mit und ohne mineralische Stickstoffdüngergabe. Da diese Fläche in der Nähe eines Bahnhofes und eines Industriegebietes liegt, was die anthropogene Umweltverschmutzung durch Kohle und Ruß sehr hoch. Bei der nicht verschmutzten Fläche in Rotthalmünster im Landkreis Passau wurden die folgenden Flächen ausgewählt: eine Weizenmonokultur mit NPK-Düngung (seit 1969), je eine Maismonokultur (seit 1979) mit NPK- oder organischer Düngung, ein Grünland mit NPK-Düngung (seit 1961) und ein Fichtenforst (~1920).

Die Methode der natürlichen ^{13}C Abundanz war sehr gut geeignet, um den Kohlenstoffumsatz im Boden zu bestimmen. Die Ergebnisse der Studie weisen darauf hin, daß sich junges C viel schneller als altes C im Boden umsetzt. In Halle war nach 40 Jahren Maismonokultur die Anreicherung des jungen C mit 14.1% unter NPK-Düngung und mit 9.5% ohne Düngen sehr gering. Die Prozentzahlen des maisbürtigen C waren in Rotthalmünster (35.1 – 35.8% maisbürtiges C) höher als in Halle, bedingt durch die höhere Biomasseproduktion, den höheren Pflanzeneintrag in den Boden nach der Ernte, die höhere NPK-Düngung und höhere Anteile an Schluff und Ton.

Die Stabilisierung von Kohlenstoff und Stickstoff war von ihrer Position im Boden abhängig: Die Ergebnisse der Größenfraktionierung für die Oberböden von Halle zeigen an, daß die C- und N-Anreicherung am höchsten in der Tonfraktion war, gefolgt von den Schlufffraktionen. Die C/N-Verhältnisse und die maisbürtigen Anteile zeigen an, daß die Feinsandfraktion und die Grobschlufffraktion die stabilsten Fraktionen waren.

In den Oberböden von Rotthalmünster wurden Aggregate > 1 mm durch das Pflügen zerstört: in den gepflügten Böden der Maisflächen waren die wichtigsten Fraktionen die Mikroaggregate (53-250 µm). Für Weizen (nur Grubbern seit 1998) waren die kleineren Makroaggregate (250-1000 µm) und für das Grünland und den Forst die Megaagregate (> 2000 µm) am wichtigsten. Unter Grünland und Forst wiesen die Oberböden eine höhere Aggregierung als die Unterböden auf. Aggregate schützen Kohlenstoff vor dem Abbau, daher war in allen Aggregatfraktionen > 53 µm der C-Gehalt höher als in der Schluff- und Tonfraktion (< 53 µm). Die Menge des C in den Mikroaggregaten plus Schluff und Ton war nahezu unabhängig von der Menge des SOC im Gesamtboden und, daraus folgend, der Kultivierung. Die Menge der Mega- und Makroaggregate war stark von dem SOC-Gehalt abhängig, diese Ergebnisse zeigen an, daß Kohlenstoff hauptsächlich aus Makroaggregaten freigesetzt wird, wenn eine Bodenbearbeitung beginnt. Mikroaggregate und die Ton- und Schlufffraktion der Maisflächen von Rotthalmünster wiesen geringere maisbürtige Anteile als die Mega- und Makroaggregate auf, damit wurde die höhere Konservierung des C in den Größenklassen < 250 µm nachgewiesen.

Die Dichtefraktionen aller Böden von Halle und Rotthalmünster (außer der Forstfläche) zeigten, daß von den leichten Fraktionen die in Aggregaten eingeschlossene partikuläre organische Substanz (occluded particulated organic matter, OPOM) mit einer Dichte von 1.6 to 2.0 g cm^{-3} ($OPOM_{1.6\text{-}2.0}$) daß für die C-Speicherung am wichtigsten war, gefolgt von der freien partikulären organischen Substanz ($FPOM_{<1.6}$, Dichte <1.6 g cm^{-3}), während die Fraktion $OPOM_{<1.6}$ (Dichte <1.6 g cm^{-3}) nur von geringer Bedeutung für die C-Speicherung war. Die hohen maisbürtigen Anteile in den FPOM-Fraktionen von Halle und Rotthalmünster und die geringen maisbürtigen Anteile in den OPOM-Fraktionen stellen die Bedeutung des physikalischen Schutzes vor Abbau heraus. Für die Halleböden war die Fraktion $OPOM_{<1.6}$ der Pool mit der geringsten Umsatzrate der in der gesamten Studie gemessen wurde. Die

mineralische Fraktion aller Böden wies die höchste C-Speicherung auf, ihre maisbürtigen Anteile waren intermediär.

Für die Bestimmung der extrahierbaren mikrobiellen Biomasse wurden verschiedenen Methoden verglichen. Die mikrobielle Biomasse der Halleböden wurde mit 0.5 M K_2SO_4 als Extraktionsmittel mit Hilfe der Chloroform-Extraktionsmethode bestimmt (CFE). Für die Bestimmung der mikrobiellen Biomasse in Rotthalmünster wurde die CFE-Methode mit einer Gefriertrocknungsmethode bestimmt, in beiden Fällen wurde Wasser als Extraktionsmittel eingesetzt. Sowohl in Halle als auch in Rotthalmünster war die mikrobielle Biomasse, bedingt durch die Monokultur, sehr gering. In Halle waren die mikrobielle Biomasse und ihre maisbürtigen Anteile in den gedüngten Böden höher, bedingt durch den höheren Eintrag an Maisresiduen. In Rotthalmünster wies der Grünlandboden die höchste mikrobielle Biomasse auf, gefolgt von der Mais- und Weizenfläche. Im Durchschnitt wurden durch die Gefriertrocknung 3.3-mal höhere extrahierbare C-Gehalte als bei der CFE-Methode gemessen. Die Gefriertrocknungsmethode extrahierte vermutlich nicht nur die abgetötete mikrobielle Biomasse, sondern auch zusätzliches, durch die Gefriertrocknung freigesetztes, C. Die maisbürtigen Anteile waren nach der Gefriertrocknung höher (Oberböden: 51-61%, Unterböden: 31-34%) als nach der CFE (Oberböden: 47-58%, Unterböden 24-25%), jedoch waren die Unterschiede zwischen den beiden Methoden nur in den Unterböden signifikant.

In den Bracheböden von Halle lag die Produktion von CO_2, DOC und DON in den Roggenböden höher als in den Maisböden und höher unter NPK-Düngung als ohne. Die Produktion des CO_2 aus Bodensäulen mit einem Maisstoppel lag höher als jene von allen andere Böden, während die DOC- und DON-Produktion unter jener der Roggenböden lag. Die maisbürtigen Anteile waren nach 40 Jahren Maismonokultur am höchsten im CO_2 (42 to 79%), gefolgt von C_{mic} (23 to 46%), DOC (5 to 30%) und SOC (5 to 14%). Junger, C_4-bürtiger C wies eine höhere Umsatzrate auf als älterer, C_3-bürtiger, rekalzitranterer C. Hohe Korrelation wurden zwischen C_4-bürtigem C_{mic} und C_4-bürtigem SOC, DOC und CO_2 ($r \geq 0.90$) gemessen, während die Beziehung zwischen C_3-bürtigem C_{mic} und C_3-bürtigem SOC, DOC und CO_2 weniger ausgeprägt war ($r \leq 0.67$). Ein Vergleich der Ergebnisse für Oberböden und Unterböden zeigte, daß die Bedeutung des DOC verglichen mit dem CO_2 gering war, aber mit der Bodentiefe zunahm. Die Bodensäulen mit den Maisstoppeln, die in die Studie eingeschlossen wurden, um die Heterogenität der Maisresiduen nach der Ernte zu repräsentieren, zeigten eine höhere heterotrophe Aktivität innerhalb der Maisreihen als zwischen den Maisreihen. Im Gegensatz dazu gab es keinen oder nur einen sehr geringen Effekt der Maisstoppelabbaus auf den Austrag von DOC, DON und NO_3^- aus dem Boden. Die Ergebnisse der CO_2- und DOC-Verluste zeigen, daß die relative Gewichtung der DOC-Auswaschung für den Verlust des SOC aus dem Boden mit zunehmendem Alter und Stabilität des SOC zunimmt.

Die Ergebnisse der natürlichen ^{13}C Abundanz wurden erfolgreich eingesetzt um die SOC-Dynamik in der Maismonokulturen in Halle ohne den Einsatz adjustierbarer Parameter zu modellieren. Die modellierte Größe des "inert organic matter" Pool zeigte eine gute Übereinstimmung mit publizierten Gleichungen für seine Bestimmung mit Hilfe der Bodentextur (KÖRSCHENS, 1980; KÖRSCHENS ET AL., 1998). Weiterhin stimmte die gesamte wie auch die maisbürtige Fraktion 0–63 µm gut mit der gesamten und maisbürtigen Summe der Modell-Pools "inert organic matter", "humified organic matter" und "microbial biomass" überein.

Die Studie zeigt, daß neu in den Boden eingebrachter Kohlenstoff einen weit höheren Umsatz als älterer Kohlenstoff im Boden zeigt, damit wird das Potential einer langfristigen Kohlenstoffspeicherung und eines positiven Beitrags der Böden zur Verringerung des Treibhauseffektes in Frage gestellt. Die Methode der natürlichen ^{13}C Abundanz, die in dieser Doktorarbeit angewendet wurde, ermöglichte Einsichten in die Prozesse der Kohlenstofffestlegung im Gesamtboden wie auch in Bodenbestandteilen, die eine wichtige Rolle für den Kohlenstoffumsatz in Böden spielen. Das Mikrokosmenexperiment zeigt die Interaktion von SOC, C_{mic}, DOC und CO_2 während der Bildung und des Exportes der organischen Bodensubstanz aus dem Boden. Die Ergebnisse für die einzelnen Kohlenstoffpools sind eine wertvolle Quelle für die Verbesserung von Boden-C-Modellen.

1 INTRODUCTION AND OUTLINE OF THE THESIS

Soil organic matter (SOM) influences all soil functions and is a crucial factor in the global carbon cycle. The understanding of organic carbon turnover and storage has for a long time been a major research area for soil- and geoscientists. Due to new analytical methods like the ^{13}C natural abundance technique or new methods describing the structure of SOM, knowledge in this field is rapidly growing. Since the Kyoto Protocol on climate change in 1992, the subject has also focused the attention of the public and policy makers (BACHELET ET AL., 2001).

The use of stable or radioactive isotopes is required to get an improved understanding of the SOC dynamics. Long-term field experiments, where a cultivation change from a C_3-plant to a C_4-plant was conducted, are especially useful to investigate carbon turnover by measuring $\delta^{13}C$-values and thus calculate percentages of young, C_4-derived, and older, C_3-derived C in the soil carbon constituents and CO_2 (Balesdent et al., 1987; Balesdent and Mariotti, 1996).

Understanding carbon dynamics in soil is the key to managing soil organic matter. The objective of this study was to quantify soil carbon dynamics in soils by using samples from long-term experiments under different static fertilization where a vegetation change from a C_3-plant to a C_4-plant took place. The major focus was on the specific turnover of young and old soil organic matter as they were expected to show different turnover rates.

Chapter 2 gives a review of the literature on the significance of soil carbon dynamics on the global carbon cycles and of the processes governing the soil organic matter turnover in total soils, physical soil fractions and the microbial biomass. Also, a brief overview concerning the modeling of soil carbon dynamics with a special consideration to inert organic matter is given.

The main objectives of the thesis are summarized in chapter 3. Chapter 4 provides an overview of the materials and methods used in this study.

The results and discussion section in chapter 5 gives the properties of the study sites and the enrichment of young carbon of the total soil (chapter 5.1). The relationship between the soil structure and the ability of soils to stabilize soil organic matter is a key element in soil C dynamics, thus the measurement of the enrichment of maize-derived carbon in size fractions, water stable aggregates and density fractions is described in chapter (chapter 5.2). The microbial biomass is a source and sink of biologically mediated nutrients and responsible for transforming organic matter and nutrients within soils. Thus, the formation of the microbial biomass was investigated by determining its maize-derived percentages (chapter 5.3). Carbon is exported from soils as dissolved organic carbon (DOC) and CO_2, thus their formation and

composition of young and old material was quantified (chapter 5.4). The results of the ^{13}C natural abundance technique were employed to model the SOC dynamics in the long-term maize cropping systems of Halle (chapter 5.5).

The conclusions from the experiments and modeling are summarized in chapter 6.

2 LITERATURE OVERVIEW

2.1 Carbon cycle and climate change

The main components of the natural global carbon cycle are the oceans (38,000 PgC; PgC=10^{15} g), the atmosphere (730 PgC) and carbon stored in terrestrial ecosystems: 1500 PgC in soils and 500 PgC in plants. Dissolved organic carbon is exported from the land to the ocean via the rivers at a rate of 0.4 PgC a^{-1}. A further 0.4 PgC a^{-1} flux of dissolved inorganic carbon (DIC) is derived from the weathering of $CaCO_3$, which takes up CO_2 from the atmosphere in a 1:1 ratio. The annual exchange of carbon from the land to the atmosphere is 120 PgC a^{-1}, it is 90 PgC a^{-1} between oceans and atmosphere (IPCC 2001a). The flux of 0.4 PgC a^{-1} from atmospheric CO_2 via plants to „inert" soil carbon is approximately balanced on a time-scale of several millenia by export of DOC in rivers (SCHLESINGER, 1990). Processes with even longer time-scales are the burial of organic matter (OM) as fossil organic carbon (including fossil fuels), and outgassing of CO_2 through tectonic processes (vulcanism). Disturbance of any of these carbon storage pools such as the oceans, the atmosphere or the terrestrial ecosystems has a direct effect on others because of the interlinkages among the pools. An increase in the atmospheric pool at the expense of soils, biotic, or oceanic pools can lead to global warming and climate change. Global warming can also shift the delicate balance among various pools (LAL ET AL., 1995).

The average temperature of the earth's surface, currently at about 15 °C, is controlled by the gaseous composition of the atmosphere. Radiatively-active gases in the atmosphere trap outgoing solar radiation which warms the earth. Important greenhouse gases in the atmosphere are water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), oxides of nitrogen (NO_x), tropospheric ozone (O_3), carbon monoxide (CO) and halocarbons (LAL ET AL., 1995). The atmospheric concentration of CO_2 has increased from 280 ppm in 1750 to 367 ppm in 1999 (31%) (IPCC, 2001a). Atmospheric methane (CH_4) concentrations have increased by about 150% (1,060 ppb) since 1750. The atmospheric concentration of nitrous oxide (N_2O) has steadily increased during the Industrial Era and is now 16% (46 ppb) larger than in 1750. Major natural sources of these gases are terrestrial ecosystems, including soils, biota, wetlands, and volcanic eruptions.

An increasing body of observations gives a collective picture of a warming world and other changes in the climate system (IPCC, 2001a). The global average surface temperature has increased over the 20th century by about 0.6°C. A doubling of preindustrial CO_2 concentrations by the end of the twenty-first century is expected to raise global mean surface temperature by about 2 °C and increase the frequency of severe weather events (MOSIER, 1998). Today's CO_2 concentration has not been exceeded during the past 420,000 years and likely not during the past 20 million years. Globally, it is very likely that the 1990s was the

warmest decade and 1998 the warmest year in the instrumental record, since 1861. Snow cover and ice extent have decreased. There has been a widespread retreat of mountain glaciers in non-polar regions during the 20th century. Global average sea level has risen and ocean heat content has increased (IPCC, 2001a).

Soils contain the largest "active" terrestrial carbon pool (as opposed to "passive" geological carbon reservoirs) on Earth, and through soil respiration, contribute an annual flux of CO_2 to the atmosphere that is 10 times greater than that from fossil fuel combustion (SCHLESINGER, 1997). On the other hand, forests, agricultural lands, and other terrestrial ecosystems offer significant, but often temporary, mitigation potential. Conservation and sequestration give time for other options to be further developed and implemented. By assuming that one-half to two-thirds of the estimated historic C loss from cultivated soils could be recovered in 50 years, the IPCC (2001b) proposed potential soil C increases of about 0.4 to 0.6 GtC a^{-1} from better management of existing agricultural soils. The current assessment of the potential of biological mitigation options is about 100GtC (cumulative) by 2050, equivalent to about 10% to 20% of expected fossil fuel emissions during that period. Increased carbon pools through the management of terrestrial ecosystems can only partially mitigate fossil fuel emissions. Moreover, larger C stocks may pose a risk for higher CO_2 emissions in the future, if the C-conserving practices are discontinued. C stocks stored in soils are not permanent and irreversible as they are often mineralized after changing land use or tillage practices (IPCC, 2001b). A drawback of the enhanced carbon sequestration by fertilization is that N_2O releases from soils can be enhanced and CH_4 uptake by soils can be decreased (FLESSA ET AL., 1996).

2.2 Soil organic matter turnover in soils

SOM can be defined as (i) the total of all biologically derived organic matter residing within the soil matrix and directly on the soil surface including thermally altered material (BALDOCK & SKJEMSTAD, 2000) or (ii) all dead material in or lying on the soil that contain organic C (SOLLINS ET AL., 1996). Next to its function as binding agent for carbon, SOM plays a crucial role in the development and maintenance of soil fertility, principally through the cycling, retention, and supply of plant nutrients, and in the creation and maintenance of soil structure (SWIFT, 2001).

The stabilization mechanisms of OM in soils are poorly understood. There are conceptual models but quantitative knowledge of such processes does not exist. A prognosis about the development of the C pool in soils under different management is not reliably possible. It is crucial to know more about the residence time of carbon in physical and chemical fractions of soils to predict and model the behavior of soil carbon with respect to climatic change (GLEIXNER ET AL, 2002). SOM is composed of different groups of constituents that vary in their chemical composition and turnover. For a quantitative analysis of soil organic carbon

(SOC) dynamics it is necessary to trace the origins of the soil organic compounds and the pathways of their transformations (FLESSA ET AL., 2000).

2.2.1 Carbon input, turnover and sequestration in soils

The amount of OM is a function of the amount and quality of plant residues returned to the soil and the rate at which those residues decompose (GREGORICH ET AL., 1996a). Major factors influencing the carbon turnover and sequestration in soils are the climate, soil relief, geological properties of a site, soil texture, pH, and anthropogenic influences (SCHEFFER & SCHACHTSCHABEL, 2002).

2.2.1.1 Below-ground biomass and rhizodeposition

A high proportion of the organic material becomes incorporated into the soil as below-ground input. Root-to-shoot ratios are very variable and range from 4-7 in tundra, grassland and cold deserts to 0.1-0.5 for forest ecosystems and croplands (KÖGEL-KNABNER, 2002).

Rhizodeposition, i.e. all organic carbon released by living roots, accounts for a substantial input of OM in soils. Most of the exudates are rapidly consumed by soil microorganisms (KÖGEL-KNABNER, 2002). With the use of different label techniques, KUZYAKOV & DOMANSKI (2000) found that cereals (wheat and barley) translocate 20%-30% of total assimilated C into the soil via root respiration, exudates, and roots. Half of this amount was subsequently found in the roots and about one-third in CO_2 evolved from the soil by root respiration and microbial utilization of rootborne organic substances. The remaining carbon of the below-ground translocated C was incorporated into the soil microorganisms and SOM.

2.2.1.2 Nitrogen fertilization

Nitrogen acts as a macronutrient for plants. Maximizing N delivery to plants and minimizing nitrate leaching are apparently conflicting objectives, and optimal management depends on an understanding of the dynamics of N transformation in soils. The addition of inorganic amendments on a regular basis may lead to an increase in SOM (GREGORICH ET AL., 1996a). However, it is difficult to predict general changes in total C input into the soil by intensification of crop production: Mineral fertilization changes the amounts of C allocated beneath the ground as well as C individual soil pools (KUZYAKOV & DOMANSKI, 2000). In studies of wheat (LILJEROTH ET AL., 1990), maize (GEISLER & KRÜTZFELD, 1984; MERCKX ET AL., 1987; ANDERSON, 1988) and horticultural plants (KUZYAKOV ET AL., 2002b) it was observed that the relative amount of belowground assimilated C decreased due to N fertilization. This indicates that measures to optimize above-ground plant growth and total fixed C (total dry mass production) result in a decrease of below-ground translocated portion

of assimilated C although the amount of assimilated C increases (KUZYAKOV & DOMANSKI, 2000).

2.2.1.3 Soil fauna

Quantitatively, the relative amount of residues of the soil fauna in the C turnover and therefore also as parent material for humification in soils is small (KÖGEL-KNABNER, 2002). Nevertheless, soil animals, particularly invertebrates, play an essential role in controlling litter decomposition in soils (WOLTERS, 2000). Soil animals contribute to the stabilization and destabilization of SOM by simultaneously affecting chemical, physical, and microbial processes over several orders of magnitude. Invertebrates have been shown to influence almost every level of the decomposition cascade by internal (ingestion and associated transformations) and external (defecation, constructions) control mechanisms. Basal respiration and microbial biomass were significantly increased in formicaries of *Lasius flavus* as compared to the surrounding grassland soil, and chemical and microbial analyses showed the higher availability of phosphate, nitrate and ammonium for microorganisms (PLATNER ET AL., 2001). Using microcosm experiments, THEENHAUS ET AL. (1999) found that the effects of the collembola species *Onychiurus fucifer* (Börner) and *Heteromurus nitidus* (Templeton) on microbial activity and nitrogen mobilization indicate that they equalize carbon and nutrient fluxes in space and time. Thus, they increase microbial activity in patches of low activity but reduce it in patches of high activity. In grasslands, soil invertebrate fauna enhances grassland succession and diversity, it also influenced the root and shoot biomass distributions of various plant species, mainly due to root herbivory (DE DEYN ET AL., 2003).

2.2.2 Origin and composition of SOM

Modern analytical techniques to characterize the chemical composition of SOC and its precursors include, among others, solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy (KÖGEL-KNABNER, 2002), direct pyrolysis-mass spectrometry (Py-MS; SCHULTEN, 1996), Curie-point pyrolysis coupled on-line with a gas chromatography/mass spectrometry (Py-GC/MS) and GC-C-IRMS (gas chromatography-combustion-isotope ratio mass spectrometry), fourier-transform infrared spectroscopy (FTIR), and UV/VIS (SCHULTEN, 1996).

The composition of the organic substances in SOM and its precursors is very complex. Plant litter materials provide the primary resources for OM formation in soil (KÖGEL-KNABNER, 2002; GLEIXNER ET AL., 2002). The amount of plant litter, its composition and its properties are essential controlling factors for the formation of SOM and humification processes in terrestrial ecosystems. The microbial biomass also represents a significant compartment of the terrestrial biomass and microbial residues in soil are an important parent material for humus formation (HAIDER, 1992). The major organic materials of plants are easily degradable and

thus provide carbon and energy sources for microorganisms. Important components of maize leaves are carbohydrates, lignin monomers, n-fatty acids, n-alkanes, and sterols (GREGORICH ET AL., 1996b). Fungi consist mainly of homo- and herteropolysaccharides, lipids and melanins are quantitatively minor components of fungal cell walls. Bacterial cell walls are composed of a peptidoglucan (murein), which contains carbohydrate as well as amino acid elements, additionally bacteria produce structural components as lipopolysaccharides and aliphatic biomacromolecules which might serve as precursors for aliphatic components of the soil organic matter (KÖGEL-KNABNER, 2002).

SOC is traditionally divided into humic acids that are soluble in dilute alkali but are coagulated by acidification of the alkaline extract, fulvic acids that remain in the alkaline extract after acidification and humins, which cannot be extracted from the soil by either dilute base or acid (SCHEFFER & SCHACHTSCHABEL, 2002; SCHNITZER, 1978). Using pyrolysis-soft ionization mass spectrometry, SCHNITZER & SCHULTEN (1992) demonstrated that carbohydrates, phenols, lignin monomers, lignin dimers, lipids (alkanes, alkenes, fatty acids, and n-alkyl esters), alkyl aromatics, and N-containing compounds are the major components of humic acids. The influence of more than 100 years of fertilization with farmyard manure on SOM in comparison to unfertilized soil was studied at the „Ewiger Roggen“ in Halle using elemental (C and N) analyses and pyrolysis-field ionization mass spectrometry. A higher relative abundance of N compounds, carbohydrates, phenols, lignin monomers, alkanes, and alkenes were observed in the unfertilized variant. Lignin dimers and fatty acids were more abundant in the farmyard manure treatment (SCHULTEN & LEINWEBER, 1991).

When performing Py-GC/MS-C-IRMS on maize leaves and two soils cultivated with maize and wheat at Boigneville, France, GLEIXNER ET AL. (2002) found that most of the pyrolysis products present in maize leaves were not detected in soil pyrolysates. In addition, highly specific lignin biomarkers were not found in soils, proving that lignin was severely biodegraded and not present anymore in soils in its initial form. In agreement with the low stability of the input material, the same 18 pyrolysis products were identified in both cultivated soils with nearly identical peak areas. Most of them were related to polysaccharides, proteins or compounds from multiple sources. Using ^{13}C isotopic analysis, they showed that the majority of pyrolysis products in the maize soil originated from a slowly degrading C pool (aged 10 to 100 years). Pyrolysis products stemming from N-containing precursors, such as proteins, amino acid moieties or chitin, and polysaccharides had high residence times of about 50 years, proving their high importance for the stabilization of carbon and nitrogen in soils. Except for the aliphatic compounds, pyrolysis products obtained from the maize soil and the wheat soil showed high similarities with products identified in humin or insoluble organic matter of several soils (e.g. GREGORICH ET AL., 1996a; SAIZ-JIMENEZ & DE LEEUW, 1986), suggesting a common „formation“ process independent from

input material, probably related to soil organisms and their extracellular polymeric substances.

2.3 Application of ^{13}C and ^{14}C to trace the origin and turnover of carbon in the soil

Carbon has two naturally occurring stable isotopes, ^{13}C and ^{12}C, approximately 98.89% of all carbon in nature is ^{12}C, and 1.11% is ^{13}C. The natural ^{13}C:^{12}C ratio is denoted as $\delta^{13}C$ in per mil PDB [‰]:

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{reference}} - 1 \right) * 1000 \quad \textbf{Equation 2.1}$$

The usual reference is the Pee Dee Belemnite (PDB), which is obtained from the carbonate skeleton of a crustacean mollusc, *Belemnitella americana*, from the Creataceous Pee Dee formation in South Carolina. The original material no longer exists. It has been replaced by assigning exact $\delta^{13}C$ values to another carbonate (NBS-19 or VPDB) relative to PDB (GOLCHIN ET AL., 1995; WERNER & BRAND, 2001).

As a result of the biochemical properties of the primary carbon-fixing enzymes and limitations to CO_2 diffusion into the leaf, all plants discriminate against $^{13}CO_2$ during photosynthesis (BOUTTON, 1996). The extent of the discrimination is variable due to the existence of three different photosynthetic pathway types (C_3, C_4 and Crassulacean acid metabolism) among terrestrial plants. Further consideration will only be given to C_3- and C_4-plants as they were used for this study.

2.3.1 ^{13}C-Fractionation by C_3-Plants

Plants with the C_3 pathway of photosynthesis reduce CO_2 to phosphoglycerate, a 3-carbon compound, via the enzyme RuBisCO. Approximately 85% of all plant species use the C_3 pathway of photosynthesis (EHLERINGER ET AL., 1991). Plants possessing the C_3 pathway have $\delta^{13}C$ values ranging from approximately –32‰ PDB to –22‰ PDB, with a mean of -27‰ PDB (BOUTTON, 1991; O'LEARY, 1988). The stable isotope composition δ_{plant} of C_3 plants can be predicted by the quantitative model of FARQUHAR ET AL. (1982):

$$\delta_{plant} = \delta_{atm} - a - (b-a) * (p_i/p_a) \quad \textbf{Equation 2.2}$$

where δ_{atm} is the $\delta^{13}C$ value of atmospheric CO_2 (about –8‰ PDB), a is the isotopic fractionation resulting from differences in the diffusion rates of $^{13}CO_2$ and $^{12}CO_2$ in air (4.4‰

PDB), b is the isotopic fractionation due to the primary carbon fixing enzyme RuBisCo (30‰ PDB), p_i is the intercellular CO_2 concentration in the leaf, and p_a is the partial pressure of atmospheric CO_2. The major source of variability in the isotopic composition of C_3 plants is the term (p_i/p_a). As this (p_i/p_a) ratio reflects the rate at which CO_2 diffuses into the leaf relative to the rate at which it is consumed by photosynthesis, any factor influencing diffusion influences the $\delta^{13}C$ of plant carbon too. Factors influencing the term (p_i/p_a) are, for example, irradiance, vapor pressure deficit, soil moisture availability, soil fertility, atmospheric CO_2 concentration, developmental status and the genetic variation of the plant (BOUTTON, 1996; ZHAO ET AL., 2001).

2.3.2 ^{13}C-Fractionation by C_4-Plants

C_4 species comprise only about 5% of all plant species (EHLERINGER ET AL., 1991). C_4 plants evolved from those with C_3 photosynthesis and may represent an adaptation to lower atmospheric CO_2 concentrations (BOUTTON, 1996). C_4 plants reduce CO_2 to aspartic or malic acid, both 4-carbon compounds, via the enzyme phosphoenolpryruvate (PEP) carboxylase. Plant with C_4 photosynthesis discriminate less against $^{13}CO_2$ during photosynthesis, thus they have greater $\delta^{13}C$ values than C_3 plants. C_4 plants have $\delta^{13}C$ values ranging from approximately –17‰ PDB to –9‰ PDB, with a mean of –13‰ PDB (Boutton, 1991).

The $\delta^{13}C$ value of C_4 plants can be predicted by (FARQUHAR, 1983)

$$\delta_{plant} = \delta_{atm} - a - (c - b\phi - a) * (p_i/p_a) \qquad \textbf{Equation 2.3}$$

where c is the fractionation from gaseous CO_2 through PEP carboxylase (-5.7‰) and ϕ is the proportion of carbon fixed by PEP carboxylase that subsequently leaks out of the bundle sheath; the other terms are the same as above. The (p_i/p_a) ratio can be influenced by the same factors as for C_3 plants, but changes in the term (p_i/p_a) have the opposite, though lower, effect as in C_3 plants.

2.3.3 Trends in atmospheric CO_2 and $^{13}C/^{12}C$ ratios

The CO_2 isotopic composition and the observed decrease in O_2 demonstrates that the observed increase in CO_2 is predominately due to the oxidation of organic carbon by fossil-fuel combustion and deforestation. Associated with the increasing concentration of atmospheric CO_2 is a decreasing trend of its $^{13}C/^{12}C$ ratio which has decreased from about -6.5‰ PDB to -8.0‰ PDB over the last 150 years (KEELING ET AL., 1989). A long-term decline in $\delta^{13}C$ has been reported in herbarium and tree ring samples (FENG ET AL., 1998; TANG ET AL., 1999). MARINO & ELROY (1991) demonstrated that the $\delta^{13}C$ of C_4 plants can be used as a proxy for the $\delta^{13}C$ of the atmospheric CO_2, because their $\delta^{13}C$ varies little with

environmental conditions. They showed a clear decreasing trend in the $\delta^{13}C$ for kernels of maize grown at the same location from 1948 to 1986. For C_3 plants like wheat or rye, $\delta^{13}C$ varies more widely as a result of environmental variations. Both grain and straw $\delta^{13}C$ of wheat plants from Rothamsted, England, have decreased by 2.5 - 2.8‰ PDB from 1845 until 1997, and since the 1960s the decrease has been more rapid than the decrease of atmospheric CO_2 (ZHAO ET AL., 2001).

2.3.4 Use of ^{13}C natural abundance to measure SOM dynamics

The natural isotopic differences of plants derived from each photosynthetic pathway type make it possible that the origin of carbon can be traced in the SOM pool. The use of stable or radioactive isotopes is required to get an improved understanding of the SOC dynamics. Because there is little change in the $\delta^{13}C$ of plant material as it decomposes, the $\delta^{13}C$ of soil organic carbon integrates the relative contributions of the different photosynthetic pathway types to the soil organic carbon pool (BOUTTON, 1996). Long-term field experiments, where a cultivation change from a C_3-plant to a C_4-plant was conducted, are useful to investigate carbon turnover by measuring $\delta^{13}C$ values and thus calculate percentages of C_4- and C_3-derived C in the soil carbon constituents and CO_2 (BALESDENT ET AL., 1987; BALESDENT & MARIOTTI, 1996).

The changes of maize-derived carbon in soil with continuous maize cultivation were described in a number of studies (e.g., GREGORICH ET AL., 1996a, b; HUGGINS ET AL., 1998; COLLINS ET AL., 1999; GREGORICH ET AL., 2000; LUDWIG ET AL., 2003). For instance, GREGORICH ET AL. (2000) found that after seven years of maize cultivation on loamy sand with former grassland, 15% of SOC, 34% of water soluble organic matter and 60% of the C_{mic} were maize-derived. The sequestration of maize in different fractions of SOC is affected by several factors such as climate, soil properties and C inputs. Under similar climatic and soil conditions, this sequestration is primarily controlled by the amount and quality of plant residues.

2.3.5 Bomb ^{14}C as a tracer for soil organic matter dynamics

Radiocarbon dating of soils is based on the decay of ^{14}C in plant material which had a $^{14}C/^{12}C$ ratio similar to that of atmospheric CO_2 at the time of its death and incorporation into the soil. The degree to which the $^{14}C/^{12}C$ ratio in soil organic matter differs from the plant matter from which it is derived reflects the mean age of carbon in soils, often used to calculate mean residence times (TRUMBORE, 1993). Detonation of thermonuclear devices in the 1950s and 1960s resulted in the enrichment of the atmosphere with ^{14}C. This spike input of bomb ^{14}C to the stratosphere subsequently entered the terrestrial ecosystem through plants and then recycled through soil animals, microorganisms, and SOM (GOH, 1991). The bomb peak can be used as ^{14}C-tracer to evaluate mean residence times of carbon pools (RETHEMEYER ET AL.,

2001) if historic samples of the time before the bomb peak are available. Measurement of ^{14}C by accelerator mass spectrometry (AMS) has greatly improved ^{14}C measurements as compared to conventional methods that measure the ^{14}C decay.

2.4 Carbon turnover in physical soil fractions

The relationship between soil structure and the ability of soils to stabilize soil organic matter is a key element in soil C dynamics (SIX ET AL., 2002). A stable structure is essential for a fertile soil (PUGET ET AL., 2000). Aggregate structure influences many soil properties including aeration, water infiltration, drainage, bulk density, and resistance to erosion. A decrease in aggregate stability can have detrimental effects on the physical properties of soils and may lead to a reduction in crop productions (LYNCH & BRAGG, 1985). Physical fractionation of soils emphasizes the role of soil minerals in SOM stabilization and turnover. The physical fractionation techniques are considered chemically less destructive, and the results obtained from physical soil fractions are anticipated to relate more directly to the structure and function of SOM in situ (CHRISTENSEN, 1992). CHRISTENSEN (2001) suggested three levels of structural and functional complexity in the turnover of SOM in the soil. Primary organomineral complexes are isolated from fully dispersed soils as clay-, silt- and sand-sized complexes, where surface reactions between substrates, organisms and minerals are the main regulatory mechanisms. Additionally, uncomplexed SOM belongs to the primary level of complexity. CHRISTENSEN (2001) defined uncomplexed SOM as the fraction of SOM that is neither present as readily recognizable litter components (<2 mm) nor incorporated into primary organomineral complexes, thus it is composed of free SOM and SOM which is included in aggregates. Functional features of this primary structure are the chemical stabilization of SOM, its surface reactivity and the adhesion of microbes. The secondary structure in the soil are aggregated organomineral complexes (i.e. aggregates). The physical protection of uncomplexed SOM and soil organism and the creation of gas and moisture gradients are features regulating the turnover of substances at this level of complexity. The structurally intact soil in situ constitutes the third level of complexity, its features are related to the transport and exchange of solutes and gases, the spatial distribution of litter crop, and productivity.

2.4.1 Carbon turnover in size fractions

Particle size fractionation has allowed to identify pools with different turnover rates. By measuring ^{13}C values in size separates from a temperate Hapludalf planted with maize for 23 years after pine forest clearing, BALESDENT ET AL. (1987) found that SOM in silt (2-20 μm) contained the lowest proportion of maize-derived SOM (12%), thus, it had the slowest turnover. Coarse sand (200–2000 μm) had the highest turnover with 61% originating from maize, the turnover of the finer sand separates (200–50 μm and 20-50 μm) was slower.

Turnover rates were higher with 18% and 26% maize-derived carbon in the coarse clay (2-0.2 µm) and fine clay (<0.2 µm) fractions. The influence of particle sizes on chemical properties of the SOM in size fractions was shown by measurements using Py-FIMS and Py-GC/MS. The proportions of phenols plus lignin monomers, carbohydrates and N-containing compounds decreased from clay to medium silt. The proportions of lignin dimers and lipids increased with increasing particle size. Sand fractions were characterized by large proportions of phenols plus lignin monomers, lignin dimers and carbohydrates. The spectra of SOM compositions in sand fractions were very similar to that of grass roots, rye roots and straw, indicating the predominance of less decomposed plant residues in sand fractions, which was in line with observations made under the microscope. Alkylaromatics are relatively uniformly distributed in all of the particle size fractions. (LEINWEBER & SCHULTEN, 1993 and 1995; SCHULTEN & LEINWEBER, 2000).

2.4.2 Carbon turnover in aggregate fractions

An understanding of the factors that determine aggregate stability may help efforts to develop management practices that promote the formation of stable aggregate soil structure (GALE ET AL., 2000). Individual grains or organic materials may remain as discrete structural units or be held together by various aggregating agents in aggregates, separated from one another by planes of weakness. This planes of weakness can either exist as pores of variable diameter or as weaknesses within the soil matrix along which preferential fracturing occurs when stresses are applied. Various researchers have proposed models of soil aggregation which show that soils are not homogenous, but are made up of aggregates of different size classes held together by various organic and inorganic materials.

EDWARDS & BREMNER (1967) proposed that soils consist of microaggregates (<250 µm diameter) bound into macroaggregates (>250 µm) and that bonds within microaggregates are stronger than those between macroaggregates. This model has been further developed by many authors. Macroaggregation is very sensitive to changes in land use and cultivation practice, whereas microaggregation is much less so. Stable macroaggregates are richer in total C and in young C than unstable ones (PUGET ET AL., 1995). SIX ET AL. (2002) proposed that SOM can be (1) physically stabilized, or protected from decomposition, through microaggregation, or (2) in intimate association with silt and clay particles, and (3) biochemically stabilized through the formation of recalcitrant SOM compounds. GOLCHIN ET AL. (1997) proposed that humified and biologically processed organic material are involved in the binding of clay packets and silt particles <20 µm into aggregates <53 µm. Particulate organic materials (POM) form a core around which clay packets and small microaggregates are bound into larger microaggregates 53-250 µm and small macroaggregates 250-2000 µm. The size of stabilized macroaggregates is a function of the size, geometry and mode of deposition of POM. For example, long pieces of debris are derived from roots and fungal

hyphae from associations with soil particles during their growth and have the potential to span across groups of microaggregates and pores to form macroaggregates through processes of physical entanglement and the production of metabolic binding agents. Observations of macroaggregates using optical microscopy and scanning electron microscopy have shown that the action of hyphae and root enmeshing soil particles and microaggregates is important in stabilizing macroaggregates. In contrast, POM mixed into the soil matrix by processes such as cultivation are probably less homogeneously distributed than root-derived POM and have little prior association with soil particles. As a result, cropping systems which include the production of species with extensive fibrous root systems (e.g., grass pastures) would produce the highest levels of macroaggregation (GOLCHIN ET AL., 1997; TISDALL & OADES, 1982).

2.4.3 Carbon turnover in density fractions

GOLCHIN ET AL. (1997) proposed a model linking POM decomposition and aggregate dynamics which is cited in this chapter. They suggested that free particulate organic matter (FPOM) <1.6 g cm^{-3} is located between aggregates or that the level of association between the FPOM and the soil mineral matrix is low and limited to the adsorption of individual primary particles on POM surfaces. Thus the FPOM can be floated out of the soil with gentle shaking using dense solutions.

With time, the microbial colonization of FPOM increases, resulting in the further production of metabolic binding agents which strengthen the interaction between POM and the surrounding mineral colloid. This process can be proven by electron micrographs that show the encrustation of organic material with inorganic soil particles (OADES & WATERS, 1991). As the encrustation of POM with soil mineral particles increases due to the continued decomposition of POM and the production of various soil binding agents, POM forms centers of intense biological activity around which aggregations of mineral particles are stabilized. Macroaggregate stabilization by POM is a transient process, and maintenance of a given level of macroaggregation is dependent upon the continual addition of POM to the soil. Although the initial phase of POM decomposition is viewed as having a beneficial effect on macroaggregation through the production of metabolic soil binding agents, as POM decomposition continues, the organic cores holding macroaggregates together are broken down into smaller pieces. Fragmentation of POM is thought to result from the action of soil fauna and the selective microbial oxidation of portions of the POM which are exposed in large pores where oxygen and nutrient movement are not limiting. A point is reached where the POM is no longer of a size sufficient to maintain the integrity of macroaggregates against applied disruptive forces. As a result, the macroaggregate fracture will be a function of the size of the residual POM and the content of soil binding agents. However, with continued decomposition of the POM, the stability of small macroaggregates will also decrease such that only microaggregates will remain. Microaggregates released due to the fracturing of

macroaggregates are thought to consist of small fragments of partially degraded plant debris bound in a matrix of mucilages and mineral particles. GOLCHIN ET AL. (1997) thus proposed a progressive decrease in the contribution of microaggregate-POM to the stabilization of microaggregates as the density of occluded particulate organic matter (OPOM), released by ultrasonic treatment, decreases from 1.8-2.0 g/cm³ to 1.6-1.8 g/cm³ and then to <1.6 g/cm³. They also suggested that OPOM of the fraction 1.8-2.0 could be derived from macroaggregates in which decomposition of the OPOM has progressed to the point that a significant interaction with soil mineral particles has occurred, but the POM has not yet been fragmented.

2.5 Influence of the microbial biomass on carbon turnover in soils

The microbial biomass (C_{mic}) is a source and sink of biologically mediated nutrients and responsible for transforming OM and nutrients within soils (GREGORICH ET AL., 2000). The availability of SOC to the C_{mic} influences its degradation and the nutrient availability for plants. An understanding of the cycling of organic carbon through the C_{mic} is of particular interest in SOM cycling for numerous reasons: 1) the C_{mic} is a transformation station for all SOM processes, where materials are taken up, converted into new compounds and actively or passively released to various other carbon pools, 2) the C_{mic} is a functionally relevant carbon pool (as opposed to those defined by various operational methods of separations), 3) an understanding of carbon turnover in the C_{mic} provides a rigorous test of model data and concepts, and suggests where further research might be focused, and 4) the C_{mic} is sensitive to changes in soil management, and provides an indicator of long term effects on SOM as a whole (RYAN ET AL., 1995). Despite the vast amount of SOC present in soil, microbial activity is often energy-limited, presumably because most of the soil C is chemically recalcitrant or physically inaccesible to microorganisms (WAGAI & SOLLINS, 2002).

RYAN ET AL. (1994, 1995) suggested a method to investigate the carbon dynamics of the C_{mic} using the chloroform-fumigation-extraction method (CFE) and natural ^{13}C abundance. Other researchers determined $\delta^{13}C$ values of the soil C_{mic} by the CFE method after addition of ^{13}C-labeled C-substrates (GAILLARD ET AL., 1999; TRINSOUTROT ET AL., 2000).

Besides the standard CFE method for the killing of the C_{mic} in the soil, a freeze-drying method has been suggested (ISLAM ET AL., 1997). To date, no standard procedure exists for the extraction of soil samples and preparation of the extracts for $^{13}C/^{12}C$ analysis, and a vast variety of methods has been described. The major differences among the methods are the type and concentration of the extractant as well as the following on-line or off-line preparation procedure for the oxidation of the extracted organic C and the purification of the produced CO_2 (POTTHOFF ET AL., 2003).

2.6 Production of dissolved organic matter and CO_2 from soils and fresh organic matter

In contrast to SOC dynamics, less information is available about the origin of gaseous and dissolved C compounds (DELPRAT ET AL., 1997; FLESSA ET AL., 2000; LIANG ET AL., 2002). DOC exports carbon from the soil (chapter 1), additionally, DOC in seepage water can combine with Al and heavy metal ions and organic pollutants and transport them through the soil profile with a potential to contaminate groundwater (LUDWIG ET AL., 2000a). A summary of the factors controlling dissolved organic matter (DOM) concentrations and fluxes in soils established from laboratory and field observations is given by KALBITZ ET AL. (2000): Critical solid phase properties include the amount of litter, the SOM content, the C/N ratio, the microbial activity, the portion of fungi, Fe- and Al- oxides and hydroxides and the clay content. Solution phase properties are pH, ionic strength and the species of solute ions, decisive environmental conditions include the temperature, wet-dry cycles, water saturation, water fluxes, freeze/thaw cycles, N-deposition, liming and organic fertilization. DELPRAT ET AL. (1997) reported that the maize C accounted for 12 to 19% of the dissolved organic carbon (DOC, water extraction on fresh soil) after 22 years of continuous maize cropping.

Leaching of dissolved organic nitrogen (DON) following cultivation could make a significant contribution to the nitrate leaching if mineralized and nitrified in surface waters or groundwaters. Alternatively, mineralisation of DON within the soil profile could contribute to the crop N supply (BHOGAL ET AL., 2000). Nevertheless, measurement of the soluble organic N content of soils has largely been overlooked (BHOGAL ET AL., 2000), thus information on DON are scarce. DON can arise in soils by several processes: substrate fragmentation, depolymerisation and solubilisation, microbial lysis, faunal grazing of soil microbes and freeze/thawing cycles (WANG & BETTANY, 1994).

Factor controlling the production of CO_2 include addition of easily decomposable material (PAUL ET AL., 1999; LUDWIG ET AL., 2000b), soil temperature (ROCHETTE & GREGORICH, 1998), microbial activity (RAUBUCH ET AL., 2002), moisture and rewetting of the soil (FRANZLUEBBERS ET AL., 2000; RAUBUCH ET AL., 2002), mineral and manure amendments (SALINAS-GARCIA ET AL., 1997; ROCHETTE & GREGORICH, 1998), crop (PAUL ET AL, 1999) cutting plants (KUZYAKOV ET AL., 2002a), photosynthesis (KUZYAKOV & CHENG, 2001), and tillage (SALINAS-GARCIA ET AL., 1997; PAUL ET AL., 1999).

FLESSA ET AL. (2000) measured in a microcosm study with soils from the maize and rye plots with NPK fertilization from the „Ewiger Roggen“ that 15% of the C in the SOC, 30% of the C in the DOC and 58% of the C in the CO_2 was maize-derived. LIANG ET AL. (2002) observed in a greenhouse study with a loamy sand previously managed with C_3-plants, that after growing maize for 110 days, the percentage of maize-derived C was 12% for SOC, 23% for

water soluble organic C and 48% for C_{mic}. However, no study could be found that integrated the stocks of SOC and C_{mic} with the production of CO_2, DOC and DON.

The determination of degradation rates of plant residues is necessary for the modeling of the turnover and sequestration of carbon in the soil. After the harvest of silage maize, maize roots are an important source for SOM. BALESDENT & BALABANE (1996) found for maize that the contribution of root-derived C to soil organic matter was 1.5 times that of stalks and leaves. This was attributed to a relatively slow biodegradation of root-derived material. Studies have shown that crop residue decomposition can be increased (ROCHETTE ET AL., 1999) by tillage, however, considerable mineralization of crop residues can also occur without chopping and incorporation into soil (FRYE & BLEVINS, 1997). Since maize is usually sown in rows of 65 to 75 cm, degradation of standing maize stubble may result in a distinct variability of mineralization and losses of C and N within the field (e.g. in and between the rows with maize stubble). An efficient tool to trace the degradation of maize residues in soil is the analysis of the carbon stable isotope composition. Various studies showed the decomposition of chopped or milled plant material in soils and its subsequent mineralization, transformation or incorporation into the SOM (LIANG ET AL., 1999; ROCHETTE ET AL., 1999; POTTHOFF ET AL., 2001). For instance, during the course of a 35-day incubation, 19.7% of the maize residues were mineralized after a thorough mixing of ground maize residues with a sandy clay loam soil (LIANG ET AL., 1999). However, these studies are not suitable to depict mineralization processes induced by decomposition of standing maize stubble.

When easily decomposable carbon is added to a soil, a priming effect may occur (KUZYAKOV ET AL., 2000). In the course of priming effects C, N and other nutrients can be released or immobilized in soil in a very short time. The natural ^{13}C abundance method was shown to be a useful tool to determine the degree of priming effects in soils amended with maize residues. LIANG ET AL. (1999) found in an incubation study with chopped (<2 mm) above-ground maize residues that mineralization of indigenous soil organic C was considerably increased after the addition of maize residues.

2.7 Modeling of carbon turnover in soils

Long-term SOC dynamics can often be described using simple models in which pools of different turnover rates are included and it is assumed that the soil is homogenous and first order decomposition kinetics prevail (JENKINSON & RAYNER, 1977; PARTON ET AL., 1987; PAUSTIAN ET AL., 1992; SMITH ET AL., 1997). This approach has been criticized recently and there is a need for a new generation of models which focus more on soil structural and microbial kinetic parameters (ARAH & GAUNT, 2001). However, the simple models with only a small number of adjustable parameters might be useful for long-term predictions. In a comparison of nine soil organic matter models using 12 datasets from seven long-term experiments, the widely used Rothamsted Soil Carbon Model (RothC) belonged to one group

of models (RothC, CANDY, DNDC, CENTURY, DAISY) where the model errors did not differ significantly from each other. RothC produced low errors for all datasets with three minor exceptions (SMITH ET AL., 1997).

Various physical, chemical and biological SOC fractionation procedures have already been developed to obtain SOC pools with different turnover rates (chapters 2.4, 2.5), but their usefulness to constitute distinct pools of different characteristic properties and turnover rates has rarely been investigated by using radioactive or stable isotopes or by modeling (BALESDENT, 1996; COLLINS ET AL., 2000). Using the natural ^{13}C labeling technique, BALESDENT (1996) studied the turnover of C in various separates from long-term maize field experiments. Primary particle-size fractions coarser than 50 µm had short lives, and could be associated with the plant structural compartment of models. However, none of the chemical separates obtained by acid hydrolysis, wet oxidation, thermic oxidation, pyrolysis or alkaline extraction were enriched either in young or old C (BALESDENT, 1996). COLLINS ET AL. (2000) also used the natural ^{13}C abundance technique for soils under maize cultivation and found laboratory incubations and acid hydrolysis useful to identify a fast and slow SOC pool (using a bi-exponential equation for the CO_2 evolved) and a resistant SOC pool.

2.7.1 Inert and refractory soil organic matter

Most models for the turnover of soil organic matter include a compartment that is either considered inert organic matter (IOM) or has a very slow turnover time, for example refractory soil organic matter (RSOM) or the passive SOC pool of the CENTURY model (SMITH ET AL., 1997). IOM has been defined as not biologically decomposable organic matter without a decomposition rate (FALLOON & SMITH, 2000). On contrary, KÖRSCHENS (1997) defined the inert organic matter as the minimum carbon content under field conditions if no fertilizer is given and humus-consuming crops or no plants at all (i.e., black fallow) are grown. In RothC, IOM is uncoupled from the other soil organic matter pools, and is effectively a constant. However, JENKINSON ET AL. (1992) admit, that the IOM is one of the least satisfactory features of the model as in all probability there is a continuum of resistant C, from virtually indestructible charcoal fragments to material that is little more resistant than that in the humified organic matter (HUM) compartment of the RothC. By contrast, RSOM interacts with the rest of SOM and the ecosystem, and may be a very long-term CO_2 sink of considerable importance for C sequestration (BATJES, 1998).

A wide range of compounds (e.g. acid-hydrolysis residues, humin, humic acids, and interlayer organic complexes) have been identified as „highly resistant“ compounds of SOM, but model passive or stable pools are not defined with respect to chemical composition (FALLOON & SMITH, 2000). The processes of RSOM formation and protection are not clearly understood. Airborne particles such as coal dust, coke and other residues from fossil fuel combustion

stemming from industrial activity were found in long-term agroecosystem experiments in Thyrow, Bad Lauchstädt and in Skierniewice (Poland) (KIEM ET AL., 2002). Black carbon (BC), produced by incomplete combustion of fossil fuels and vegetation, occurs ubiquitously in soils and sediments. Finely divided charcoal appears to be a major constituent of many Australian soils and probably contributes significantly to the inert or passive organic carbon pool recognized in carbon turnover models (SKJEMSTAD ET AL., 1996). BC exists as a continuum from partly charred material to highly graphitisized soot particles, with no general agreement on clear-cut boundaries of definition or analysis (SCHMIDT ET AL., 2001). SCHMIDT ET AL. (2002) thus characterized the nanomorphology and chemical structure of SOC from European Chernozems, and identified submicron remnants of burned biomass (15-45 percent of SOC), coexisting as amorphous char, BC derived from pyrolized cellulose or soot-BC. The BC was several millenia in age (1160-5040 carbon-14 years) and up to 3990 radiocarbon years older than bulk SOC, indicating significant residence times for BC in soils.

The amount of IOM is an important component in many SOC models, because this amount and the annual amount coming from plant residue input contribute to the total SOC stock. Thus, uncertainties in the amount of IOM might lead to wrong estimates of C input into the soil (for a review see FALLOON & SMITH, 2000). FALLOON ET AL. (1998) used a model approach and ^{14}C data to determine the IOM amounts for different long-term experimental sites and suggested that IOM can be estimated from the total SOC stock (IOM (in t C ha^{-1}) = 0.049 $SOC^{1.139}$). However, they admitted that their equation cannot provide precise prediction. RÜHLMANN (1999) suggested a simple equation to calculate the amount of SOC in long-term bare fallow soils using the percentage of soil particles <20 µm. A similar approach using the percentage of soil particles <6.3 µm was suggested by KÖRSCHENS (1980). Their equations give considerable different results. Summarizing the results of the above IOM estimates it has to be concluded that when modeling SOC dynamics it is essential that the size of any inert or passive SOC pool is accurately specified (SKJEMSTAD ET AL., 1996). It is clear, too, that there is much uncertainty which approach should be applied to a specific site.

3 OBJECTIVE OF THIS THESIS

To study the carbon turnover in soils, fwo study sites in East and South Germany with differing soil properties and cultivation practices were chosen for this thesis. At the „Ewiger Roggen“ in Halle, the investigated plots were continuous maize and rye plots with and without mineral N fertilization. At the Höhere Landbauschule at Rotthalmünster in the rural district of Passau, the following sites were chosen: a continuous wheat plot with NPK-fertilization on former grassland, continuous maize plots with NPK-fertilization with or without organic fertilization, continuous grassland with NPK-fertilization, and a spruce forest.

The objectives of this thesis were subdivided as follows:

1. *To determine the dynamics of stabilization of fresh residues in the soil*

   Carbon content and $\delta^{13}C$ values were determined for the surface soils and subsoils of all sites from Halle and Rotthalmünster up to a depth of about 60 cm and maize-derived percentages (BALESDENT & MARIOTTI, 1996) calculated for the maize fields. By analyzing historic samples, the dynamics of the stabilization of maize residues were reconstructed for the Halle site.

2. *To analyze the influence of fertilization on carbon sequestration in soils.*

   The influence of organic and inorganic nutrient addition on the turnover and stabilization rates of corn residues was determined. The carbon and the nitrogen cycles in soils interact, thus, C/N ratios were quantified.

3. *To analyze the role of primary soil particles on the stabilization of SOC in the soil.*

   Carbon and nitrogen content and maize-derived percentages were measured in size fractions from the surface soils of Halle.

4. *To show the effect of aggregation on the carbon stabilization of SOC in the soil.*

   In water-stable aggregates from Rotthalmünster and in density fractions from Halle and Rotthalmünster, the carbon content and the maize-derived percentages were determined.

5. *To determine the importance of old and young SOC as substrate for microbial biomass formation.*

   The microbial biomass was determined in the surface soils and subsoils of all experimental plots excluding the forest site by using the CFE method (JÖRGENSEN, 1996) for Halle and Rotthalmünster and by comparing the CFE method to a freeze-drying method for Rotthalmünster (ISLAM ET AL., 1997). The comparison of the methods for the

(i) killing and extraction of the microbial biomass as well as (ii) the determination of maize-derived percentages in the extracts was an important aspect of this investigation.

6. *To quantify the specific production rates of CO_2 and DOC from younger, maize-derived and older, C_3-derived SOC.*

   In incubation studies (FLESSA ET AL., 2000) with surface soils and subsoils from Halle the effect of long-term static fertilization on the total and maize-derived amounts of DOC and CO_2 was identified in microcosm experiments with surface soils and subsoils from rye and maize plots. Subsequently, the specific production rates of DOC, CO_2 and C_{mic} from the maize-derived and rye-derived SOC were determined. In addition to the carbon export, nitrogen export as nitrate and dissolved organic nitrogen was quantified.

7. *To determine the decomposition of fresh plant material in soils thus resembling the unevenly distributed plant residues after harvest.*

   The production of DOC, DON, nitrate and CO_2 from soil columns from the NPK-fertilized maize site including a standing maize stubble was determined.

8. *To model changes in SOC the Rothamsted Carbon Model using the ^{13}C data and to compare the modeled pools to measured soil fractions.*

   To keep the number of adjustable parameters as low as possible, additionally ^{13}C data were used for the modeling. The results for IOM were compared with the approaches suggested by FALLOON ET AL. (1998), KÖRSCHENS (1980) and RÜHLMANN (1999). The modeled SOC pools were compared with measured SOC pools.

4 MATERIALS AND METHODS

4.1 Study sites

4.1.1 Halle

The experimental site at Halle/Saale was the long-term field experiment "Ewiger Roggen", the world's second oldest field experiment (Figure 4.1). The field experiment was established in 1878 as a continuous rye cropping (*Secale cereale L.*). In 1961, after harvest, a continuous maize (*Zea mays L.*) cropping was started on a plot of the continuous rye field. The following five treatments were used for our study: (i) soil from the continuous maize plot since 1961 with mineral NPK fertilization (Ha-M_{NPK}); (ii) soil with one cut maize stalk (length <5 cm) of the continuous maize plot since 1961 with mineral NPK fertilization (Ha-M_{stalk}); (iii) soil from the continuous maize since 1961 without fertilization (Ha-M_0); (iv) soil from the continuous rye since 1878 with mineral NPK fertilization (Ha-R_{NPK}); and (v) soil from the continuous rye since 1878 without fertilization (Ha-R_0). Nitrogen fertilization was 40 kg ha^{-1} a^{-1} until 1991 and 60 kg ha^{-1} a^{-1} afterwards. The field trial is located 110 m above sea level. The mean annual precipitation was 465 mm and the mean annual temperature was 9.2 °C. The experimental site belongs to the central German arid region. The soil (Figure 4.1) was a moderately degraded black earth (Parabraunerde-Tschernosem; FAO: Haplic Phaeozem) on sandy loess (~80 cm) over glacial till (STUMPE ET AL., 2000). The texture of the soil consists of 70% sand, 20% silt, and 10% clay (GARZ ET AL., 1996). A detailed description of the experimental site and the field management was given by MERBACH ET AL. (1999). The rye was threshed and the straw was removed from the field. The maize was used for silage-making and only the short maize stubble was ploughed in. The depth of the plough horizon was 20 cm until 1969. From 1970 onwards, the horse plough was replaced by a tractor plough and the depth of the plough horizon increased to 25 cm. From the mid-nineties onwards, the depth of the plough horizon increased further to 30 cm in 2000. The homogenous $\delta^{13}C$ values of the plough layer (Table 5.1) were a result of the homogenization of the surface soil caused by ploughing (FLESSA ET AL., 2000). Liming was done every few years to avoid acidification of the soil, the last liming was done in 1985 (SCHLIEPHAKE ET AL., 2000).

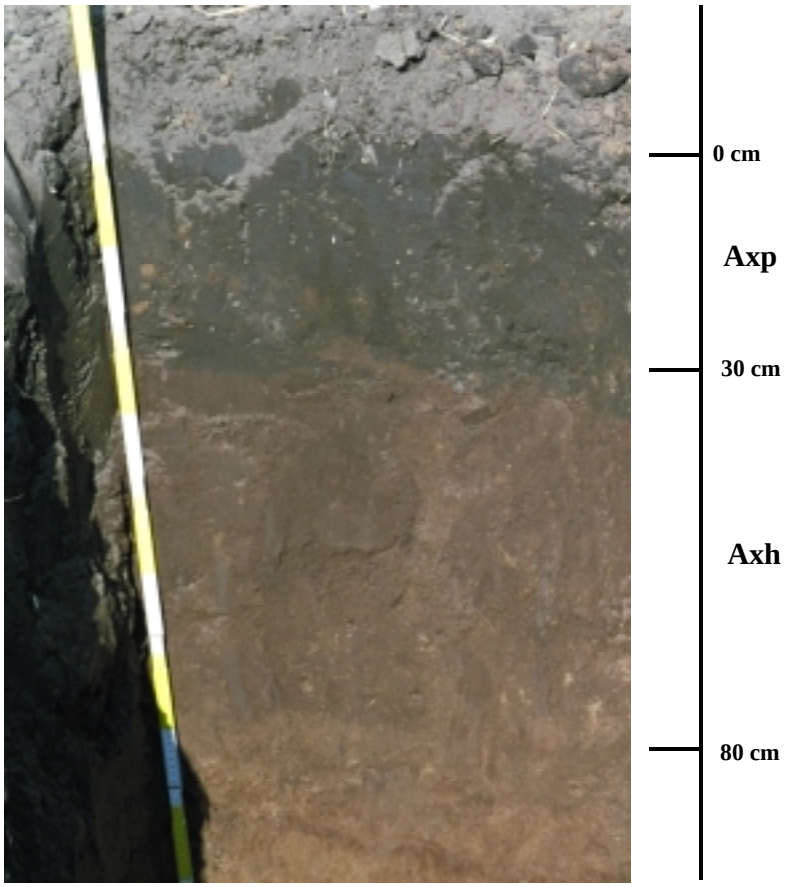

Figure 4.1: Soil profile of Halle (Haplic Phaeozem), Photo: H. Flessa.

4.1.2 Rotthalmünster

The long-term experiment at Rotthalmünster was run by the "Höhere Landbauschule" in Rotthalmünster, a comprehensive description was given by SCHNELLHAMMER & SIRCH, 2002. The following sites were chosen: (i) continuous wheat plot (*Triticum aestivum* L., since 1969) with NPK-fertilization on former grassland (Ro-W_{NPK}), in the most years *Sinapis alba* L. was used as an intercrop (J. Sirch, Höhere Landbauschule Rotthalmünster, personal communication). Since 1998, cultivation was done as conservation tillage experiment; only grubbing was used after harvest. (ii) continuous maize plot (since 1979) with NPK-fertilization (Ro-M_{NPK}). (iii) continuous maize plot (since 1979) with NPK-fertilization and whey (1979-1982), cattle slurry (1983) and pig slurry (since 1984) application (Ro-M_{org}). Previous cultivation on the maize plots was probably grassland until 1970, subsequently spring wheat and winter wheat were planted (J. Sirch, personal communication). As additional sites (iv) continuous grassland (since 1961) with NPK-fertilization (Ro-Grass) and (v) a spruce forest (*Picea abies* L.; ~ 1920) on a former forest site (Ro-Forest; Obermeier, Höhere Landbauschule Rotthalmünster, personal communication) were chosen.

The field trial is located 360 m above sea level. The mean annual precipitation over a period of 50 years was 886 mm and the mean annual temperature was 8.7 °C. Rotthalmünster is

located in a rural area, thus pollution from anthropogenic sources was low. The field site was located in the „tertiäres Hügelland“ of the lower Rottal. It was of dilluvial origin. The soil profile of an adjacent field is shown in Figure 4.2a. This soil was classified as a “Pseudogley-Kolluvisol aus Kolluviallöß über Löß“, deriving from loess (KLEBER, 2003). Soil cores taken directly from the plot Ro-M_{NPK} were classified as “Pseudogley-Parabraunerde” (Figure 4.2b). The soil was composed of 11% sand, 72% silt and 17% clay. At the wheat and maize fields, the plough horizon was 30 cm deep, the straw was returned to the field after harvest. At Ro-W_{NPK}, the mean N-fertilization (1971-2001) was 171 kg N ha^{-1} (data provided by R. Obermeier), at Ro-M_{NPK}, the standard N-fertilization was 180 kg N ha^{-1} (SCHNELLHAMMER & SIRCH, 2001). At Ro-M_{org}, from 1979 until 1982, whey was applied as organic fertilizer, following 1983, pig slurry was applied every spring. The applied slurry was equivalent to 1260 kg C ha^{-1} and 163 kg N ha^{-1}, additionally, 30-40 kg mineral N was applied each year. Liming was done every few years, the last time in 2001.

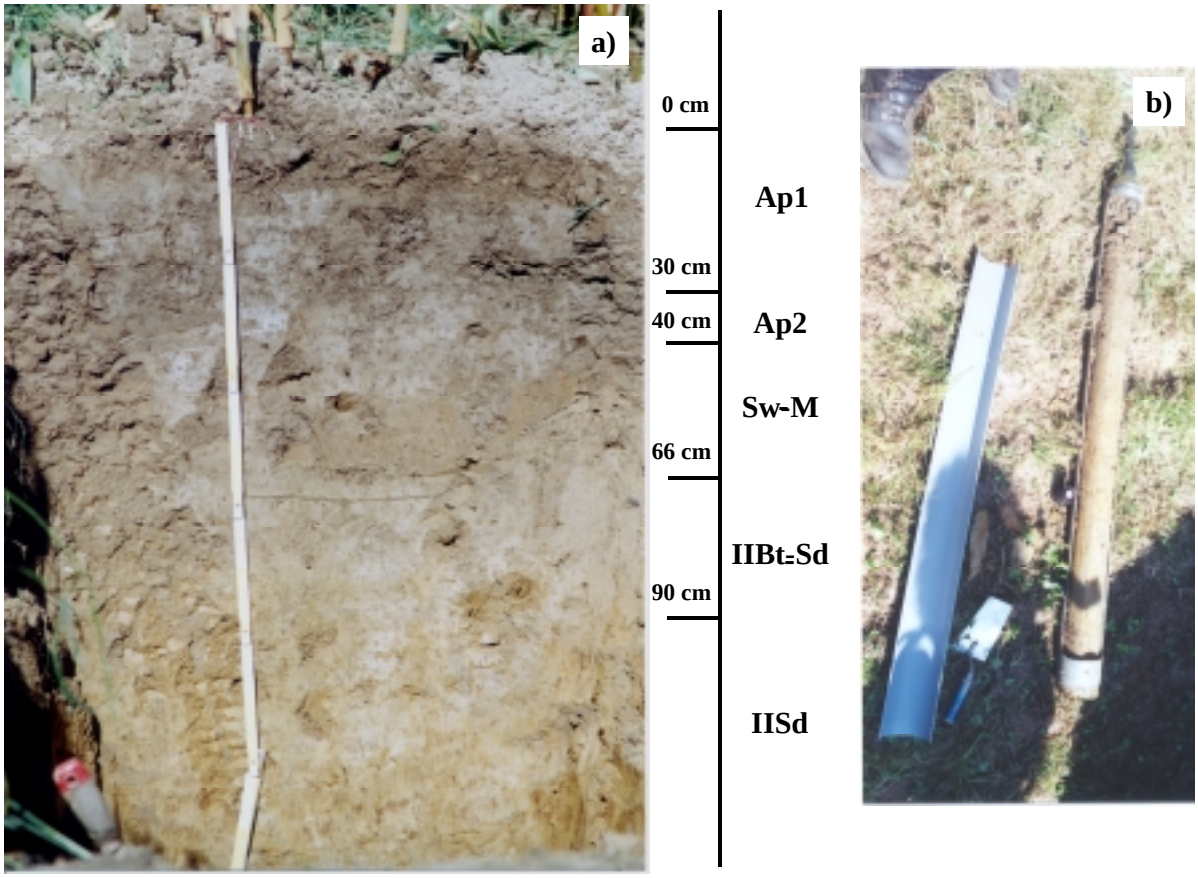

Figure 4.2: Rotthalmünster: a) Soil profile of “Pseudogley-Kolluvisol aus Kolluviallöß über Löß“ at nearby maize site and b) drilling core of “Pseudogley-Parabraunerde” at Ro-M_{NPK}. Photos: T. Yamashita.

At the grassland, cropping for hay was done four times a year, nitrogen fertilization was done using physiologically alkaline fertilizers (160 kg N ha^{-1}). The original aim of the experiment

was to show how fertilizers affect the botanical composition and yield of a mixed population of grasses, clovers and other herbs. The floral composition before the first harvesting was changing over time due to the continued alkaline fertilization (Table 4.1). Liming was done regularly, the last liming was carried out in 1991.

Table 4.1: Major species before the first harvest of the year at Ro-Grass in the years 1994 and 2001.

Species	Plant coverage [%]	
	1994	2001
Achillea millefolium	3	6
Agrostis alba	6	
Alopecurus pratensis	15	28
Dactylis glomerata	3	4
Gallium mollugo	6	
Holtus lanatus	5	
Lolium perenne		3
Plantago lanceolata	2	4
Poa pratensis	8	
Poa trivialis	2	
Ranunculus acris	1	
Ranunculus repens	2	
Taraxacum officinale		5
Trifolium pratense	8	
Trifolium repens	4	
Trisetum flavescens	15	34

4.2 Soil sampling

At Halle, soil samples were collected on September 21, 2000, after the harvest and tillage of the rye and after harvest but before the tillage of the maize fields. To determine SOC, N_t and C_{mic}, disturbed soil samples from the depth 0-10, 10-20, 20-30, 30-40, 40-50 and 50-60 cm in five replicates were taken. For the incubation experiments, undisturbed soil columns (diameter 14.4 cm) from the surface soil (0–25 cm) and subsoil (25–50 cm) were sampled with five replicates, respectively. Additionally, from the site Ha-M_{NPK}, four columns with maize stalks (<5 cm length) were taken. For the size fractionation of Halle soils with size fractionation method II (chapter 4.7.1), soil samples were collected in October 1998 after harvest (FLESSA ET AL., 2000).

For the Rotthalmünster site, sampling was done on September 4 (field sites) and September 5 (forest site), 2002, after the harvest of the wheat field and before the harvest of the maize fields. Soil was taken from the depth steps 0-30, 30-45, and 45-60 cm at Ro-W_{NPK}, Ro-M_{NPK}, and Ro-M_{org} (0-30 cm). Ro-Grass was sampled at the depth steps 0-10, 10-20, 20-30, 30-45 and 45-65 cm, Ro-Forest at 0-7, 7-25, 25-40 and 40-65 cm plus the organic layers. Soil samples were collected of at least four locations per variant, combined, homogenized and divided into four subsamples per variant. Sampling of the forest needles and of the pig slurry was done on March 24, 2003.

4.3 ^{13}C Measurements and calculation of maize-derived percentages

The measurement of the solid samples was performed with two continuous flow isotope ratio mass spectrometers (IRMS, DELTA^{plus}, Finnigan Mat, Bremen, Germany) coupled to two different elemental analyzers (EA 1108 and NA 2500, both from Fisons, Milan, Italy). For on-line measurements of the stable isotope ratios, the samples were weighed into tin capsules. By flash combustion (1800°C) all carbon in the samples was completely oxidized to CO_2 using chromium oxide as catalyst. For CO_2 separation, the gases were first led through a water trap containing $Mg(ClO_4)_2$, subsequently through a GC-column (Porapak PQS). Then the gas was flowing through a thermal conductivity detector to measure CO_2 and N_2 concentrations (elemental analysor). Afterwards, an open split interface was used to transport the reaction product CO_2 into the ion source and to introduce a reference gas under identical conditions. It also allowed the dilution of the reaction product CO_2 with He to keep signal intensities in the range of the operation of the IRMS. For the analysis of the isotope ratios of carbon in a sample, 50 µg C to 500 µg C were used, the open-split interface was adjusted accordingly. The $\delta^{13}C$ values were normalized using NBS-21 (-28.1‰ PDB), a graphite, or IAEA CO-8 (-5.75‰ PDB), a calcite, as references. In addition, Acetanilid (-33.7‰ PDB) was used as the internal laboratory standard.

The measurement of the gaseous samples was performed with a GC-IRMS (DELTA C or DELTA^{plus}, Finnigan Mat), the GC-Interface contained a Poraplot Q column. As reference gas for the $\delta^{13}C$ values the CO_2-Standard ISO-TOP (-25.3‰ PDB, Messer-Griesheim) was applied.

The accuracy of the measurements was 0.1‰ PDB (absolute) for all IRMS. All $\delta^{13}C$ values in this thesis are given relative to the standard PDB (chapter 2.3).

For the determination of $\delta^{13}C$ values not the carbon directly, but CO_2 is measured, which contains a number of species with different masses. All combinations of stable isotopes of C and O are present. The list of isotopomers includes the major species $^{12}C^{16}O^{16}O$ (m/z = 44), $^{13}C^{16}O^{16}O$ and $^{12}C^{17}O^{16}O$ (m/z = 45), $^{12}C^{16}O^{18}O$ (m/z = 46) as well as the minor species

$^{13}C^{17}O^{16}O$ and $^{12}C^{17}O^{17}O$ (m/z = 46), $^{13}C^{17}O^{17}O$, $^{13}C^{18}O^{16}O$ and $^{12}C^{17}O^{18}O$ (m/z = 47), $^{12}C^{18}O^{18}O$ and $^{13}C^{17}O^{18}O$ (m/z = 48) and $^{13}C^{18}O^{18}O$ (m/z = 49). When working in the natural abundance range of the isotopes, as was the case during this thesis, the contributions of the minor species are small enough to be neglected. The ^{17}O moiety at m/z = 45 has a ~7% contribution to the mass 45 ion current and must always be corrected for when determining $\delta^{13}C$ values (CRAIG, 1957; BRAND, 1996). This correction was done using the software program ISODAT (Finnigan Mat).

The proportion of C derived from maize in a sample was calculated according to BALESDENT & MARIOTTI (1996):

$$f = (\delta_{sam} - \delta_{ref}) / (\delta_{maize} - \delta_{ref\text{-}plant}) \qquad \textbf{Equation 4.1}$$

where *f* stands for the proportion of maize-derived C in the sample, δ_{sam} for the measured $\delta^{13}C$ of the sample, δ_{ref} for the $\delta^{13}C$ of the corresponding sample from the C_3 reference soil, and δ_{maize} and $\delta_{ref\text{-}plant}$ for the $\delta^{13}C$ values of the maize and reference plant (rye or wheat) residues (stubble and root) collected on the experimental plots. At Halle, the $\delta^{13}C$ value (mean ± standard deviation) was –28.4 ± 0.1‰ PDB for rye and –11.6 ± 0.1‰ PDB for maize, giving a difference of 16.8‰ PDB. At Rotthalmünster, the $\delta^{13}C$ value (mean ± standard deviation) was –26.8 ± 0.1‰ PDB for wheat and –12.7 ± 0.2‰ PDB for maize, resulting in a difference of 14.1‰ PDB. The standard deviation s_f of maize-derived DOC and CO_2 was calculated from the standard deviations of δ_{ref} ($s_{\delta ref}$) and δ_{sam} ($s_{\delta sam}$) and on the assumption that the contributions of the uncertainties in δ_{maize} and $\delta_{ref\text{-}plant}$ were negligible (Ludwig et al., 2003):

$$s_f = ((s_{\delta ref}/(\delta_{maize}-\delta_{ref\text{-}plant}))^2 + (s_{\delta sam}/(\delta_{maize}-\delta_{ref\text{-}plant}))^2)^{0.5}. \qquad \textbf{Equation 4.2}$$

4.4 ^{14}C Measurements

^{14}C measurements of size and density fractions were carried out by J. Rethemeyer (Leibniz-Labor, Kiel; unpublished data) with an Accelerator Mass Spectrometer (AMS). Prior to analysis, from the coarse sand and middle sand fraction, visible plant and root as well as coal particles were sorted out under the microscope, all other size and density fraction were not treated prior to analysis. The routine acid-alkali-acid extraction was not used as preliminary experiments showed that no carbonates were present.

Carbon in each sample was completely oxidized at 900 °C with copper oxide and silver wool, subsequently, it was reduced to graphite with H_2 at 600 °C over an iron catalyst. The iron/carbon mixture was pressed as a pellet into a target holder for AMS measurements in a 3 MV Tandetron from High Voltage Engineering Europa (HVEE) with a single caesium sputter ion source and a separator/recombinator for simultaneous injection of the three

isotopic carbon beams, thus imparting high energies to the carbon ions. This technique enables positive identification of the carbon ions and discriminates against other ions of similar masses. The ^{14}C concentration of the sample was measured with the mass spectrometer by comparing the simultaneously collected ^{14}C, ^{13}C, and ^{12}C beams of each sample with those of a standard CO_2 sample (GOH, 1991, NADEAU ET AL., 2001).

^{14}C-contents are reported either as „percent modern carbon" (pMC) or with their conventional ^{14}C-age (time in years before present, BP) (STUIVER & POLACH, 1977). pMC was calculated as

$$pMC = 100 * \frac{specific\ activity\ of\ the\ sample}{specific\ activity\ of\ the\ standard}.$$ **Equation 4.3**

4.5 Soil analysis

4.5.1 General soil and plant analysis

Soil samples and soil fractions were oven-dried at 40°C and ball-milled, and SOC and N_t contents of the samples were determined by an automated C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany) if enough sample material was available. For the light fractions of the density fractions (chapter 4.7.3) and the freeze-dried extractable microbial carbon of Rotthalmünster soils (chapter 4.6), C values were determined with the elemental analyzer coupled to the IRMS (chapter 4.3). Prior to ^{13}C measurements (chapter 4.3), samples from the surface soils of Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org}, and Ro-Grass were acidified with 10% HCl to remove carbonates.

For the Halle soil, soil bulk density at several depths of the Ap horizon was determined on undisturbed soil cores with a diameter of 14.4 cm (FLESSA ET AL, 2000). Data for the bulk density of the subsoil were taken from SCHLIEPHAKE ET AL. (2000). For the measurement of the bulk densities of Rotthalmünster, soil samples with a defined volume were collected with four replicates, dried at 105 °C and weighed. The measured bulk densities of the depth 45-60 cm of Ro-M_{NPK} were assumed to be the same for Ro-M_{org}, where no extra samples were collected.

For all soils, pH was determined in a 10^{-2} M $CaCl_2$ solution (soil:solution ratio 1:2.5), for the forest soils (Ro-Forest), additionally, pH was determined in 10^{-2} M KCl solution (soil:solution ratio 1:2.5).

Collected plants, root biomass and the slurry of Rotthalmünster were oven-dried at 60°C and either ball-milled or consecutively milled by a ultra-centrifugal mill and a ball-mill. C and N contents were determined by an automated elemental analyzer (Heraeus Elementar Vario EL).

4.6 Microbial biomass

To obtain the microbial biomass carbon, soil was either fumigated with $CHCl_3$ or freeze-dried to kill the microbial biomass, then the soil was extracted. The microbial biomass C in the soil can be calculated as the difference between the C in the extract from the treated soil and the C in an extract from a control and applying a k_{EC} factor that represents the extraction efficiency.

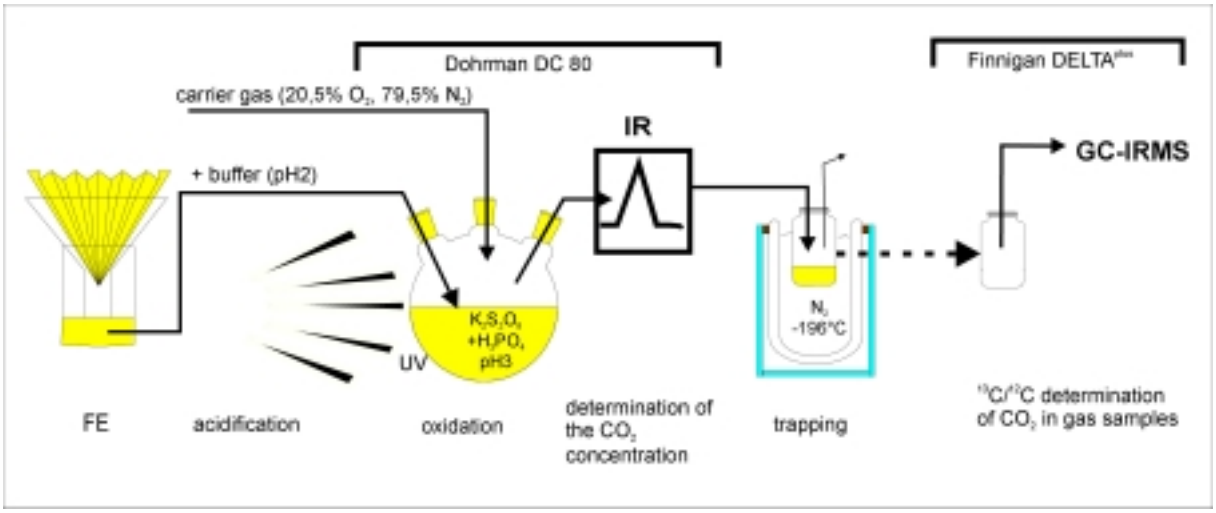

Figure 4.3: Scheme of the method to determine $\delta^{13}C$ in soil microbial C by liquid oxidation of organic C in extracts derived from the FE-method. Oxidation and infra-red CO_2 detection was combined with freeze-trapping of the CO_2 released and subsequent determination of $\delta^{13}C$ by GC-IRMS (Potthoff et al., 2003).

For the Halle soils, C_{mic} was determined by the fumigation extraction technique described by JÖRGENSEN (1996). Soil samples were adjusted to a water content of 40% maximum water holding capacity and divided into two portions equivalent to 20 g of oven-dry soil. One portion was fumigated for 24 h at room temperature with ethanol-free $CHCl_3$. Following the fumigant removal, the soil was extracted with 80 ml of 0.5 M K_2SO_4 by shaking for 1 h at a frequency of 160 rotations per minute and filtering the sample afterwards. The non-fumigated control was extracted in the same way. The organic C in the extract was measured using a DOC-Analyzer (Dohrman DC 80, Rosemount Analytical Division, Santa Clara, CA). The extractable microbial carbon C_{extr_fum} was calculated as

$$C_{extr\_fum} = C_{fum} - C_c \qquad \textbf{Equation 4.4}$$

and the microbial biomass C was computed as

$$C_{mic} = C_{extr\_fum}/k_{EC}, \qquad \textbf{Equation 4.5}$$

where k_{EC} = 0.45, C_{fum} = organic C extracted from fumigated soil, and C_c = organic C extracted from the control.

^{13}C-content of the extracts was measured after liquid oxidation and freeze-trapping of CO_2 (Figure 4.3; WU ET AL., 1990; POTTHOFF ET AL., 2003): The solutions were acidified with sodiumhexametaphosphate and H_3PO_4 to pH 2. Aliquots of 1 to 3 ml were digested with UV and potassium peroxodisulphate + H_3PO_4 (pH 3) in an automatic C analyzer (Dohrmann DC 80). The released CO_2 passed the IR detector of the C analyzer using synthetic air as carrier gas and was trapped in 2 ml glass vials at the gas outlet of the analyzer by liquid nitrogen. Vials were kept gas tight using semi-permeable rubber lids. The vials were placed in the autosampler of a GC-IRMS system (DELTA^{plus}, Bremen, Germany) for on line $^{13}C/^{12}C$ analysis.

For the Rotthalmünster soils, two different extraction methods for the measurement of microbial biomass C were applied.

Firstly, I changed the CFE method applied for the Halle soil (JÖRGENSEN, 1996) by using distilled water as the extraction agent (HANEY ET AL., 2001). The organic C in the extracts was measured using a total organic carbon analyzer (TOC 5050, Shimadzu Corp., Tokyo, Japan). C_{extr_fum} was calculated as described above.

Secondly, the freeze-drying method as described by ISLAM ET AL. (1997) was utilized, but instead of 0.5 M K_2SO_4 distilled water was used as extraction agent. The proposed maximum water holding capacity of 100% (ISLAM ET AL., 1997) was changed to 40%. Soil samples equivalent to 15 g of oven-dry soil were freeze dried (-60 °C), afterwards they were extracted with 60 ml distilled water as described above. The control sample for the fumigation and freeze-drying method was extracted with distilled water as described above. The organic C in the extracts was measured using the TOC-analyzer. C_{extr_freeze} was calculated as

$$C_{extr\_freeze} = C_{freeze} - C_c \qquad \textbf{Equation 4.6}$$

with C_{freeze} organic C extracted from freeze-dried soil, but C_{mic} could not be calculated as a conversion factor as the k_{EC} of JÖRGENSEN (1995) does not exist yet and would need further research (chapter 5.3.1.2). All extracts were freeze dried at –60°C before measuring the $\delta^{13}C$ values.

Accordingly, the $\delta^{13}C$ of FE extracts was determined by

$$\delta^{13}C_{extr\_fum} \times C_{extr\_fum} = \delta^{13}C_{fum} \times C_{fum} + \delta^{13}C_c \times C_c \qquad \textbf{Equation 4.7}$$

(Ryan et al., 1995) and

$$\delta^{13}C_{extr\_freeze} \times C_{extr\_freeze} = \delta^{13}C_{freeze} \times C_{freeze} + \delta^{13}C_c \times C_c, \qquad \textbf{Equation 4.8}$$

respectively.

4.7 Fractionation schemes

4.7.1 Size fractionation of dispersed soil from Halle

For the Halle soil, two size fractionation schemes were applied for the determination of carbon, nitrogen and ^{13}C in the size fractions. Additionally, a texture analysis was carried out. Prior to all size fractionations, the soil was dried at 40 °C and sieved (<2 mm).

For the first size fractionation scheme (Method I), distilled water (150 ml) was mixed with 30 g of soil and the suspension was sonicated at 60 J ml^{-1} as outlined by NORTH ET AL. (1976) and AMELUNG ET AL. (1998). The sonitrode was calibrated as described by SCHMIDT ET AL. (1999). The coarse (630-2000 µm) and medium (200-630 µm) sand fractions were obtained by wet sieving. The remaining fraction was sonicated at 440 J ml^{-1}. Subsequently, the fractions fine sand (63-200 µm) and coarse silt (20-63 µm) were gained by wet sieving. Centrifugation was applied to separate the clay (<2 µm) from the remaining middle and fine silt (2-20 µm) fraction using a temperature-controlled centrifuge (Sigma 6 K 15, Osterode am Harz). Each sample was divided in four subsamples as the centrifugation vials (50 ml) could not carry the whole dispersion. By assumin44g a zero diffusion and a spherical shape of the solid particles, the following formula was applied to calculate correct centrifugation times:

$$t = \frac{9\eta \ln\left(\frac{x_t}{x_0}\right)}{2(\rho_{solid} - \rho_{water})\omega^2 r^2}$$

Equation 4.9

The calculation of the centrifugation times was derived by applying Stokes' Law to centrifugation. A detailed derivation of the calculation of centrifugation times was given by SVEDBERG & PEDERSEN (1940). t [s] was the centrifugation time required for the clay particles to settle down, η [kg m^{-1} s^{-1}] the temperature-dependent viscosity of the water, x_t [m] the distance of the solid particles at the beginning of the centrifugation to the center of the rotor, x_0 [m] the distance of the solid particles at the end of the centrifugation to the center of the rotor, ρ_{solid} [kg m^{-3}] the density of the solid particles, ρ_{water} [kg m^{-3}] the density of the water, ω the angular frequency [s^{-1}] and r the radius of the clay particles [m]. ω was calculated using its definition as $\omega = 2\pi f$ with f [s^{-1}] being the frequency of the rotor. The following values were applied to calculate centrifugation times: η at 20 °C: 1.0019 kg m^{-1} s^{-1}, η at 25 °C: 0.89035 kg m^{-1} s^{-1}, x_t = 0.204 m, x_0 = 0.105 m, ρ_{solid} = 2.5 kg m^{-3}, ρ_{water} = 0.99821 kg m^{-3} (20 °C) and ρ_{water} = 0.99705 kg m^{-3} (25 °C), and r = 10^{-6} m. The frequency of the rotor was 1000 rotations per minute (rpm), so $\omega = 2 * \pi * (1000/60s) = 104.7$ s^{-1}.

When applying equation 4.9, it had to be assumed, that at the beginning of the centrifugation all particles were located at the upper boundary of the centrifugation tube, at x_t. Naturally, this was never the case, as the greater particles were already fallen down and clay particles were dispersed in the whole solution. Thus, to achieve the separation of the clay and silt particles, for the first four to five repetitions longer centrifugation times were applied to reach a quantitative precipitation of the silt particles. Whensoever the supernatant was clear, the repetitions of centrifugation were stopped. Centrifugation had to be repeated circa ten times to reach a nearly complete separation of the size classes. The supernatants of every centrifugation rerun were sampled in a beaker, the pellet was stirred up before the subsequent centrifugation run. After the centrifugation, the clay fraction in the beaker was precipitated using 0.5 M $AlCl_3$ and the supernatant was discarded (amount of discarded C was not determined). All fractions were dried at 50 °C and finely ground.

The second size fractionation scheme (Method II) was only applied for Ha-M_{NPK} and Ha-R_{NPK} with samples of September 1998. Distilled water (150 ml) was mixed with 25 g of soil and the suspension was sonicated at 60 J ml^{-1}. The sand fractions (coarse, medium and fine sand) including the particulate organic matter fractions were obtained by wet sieving followed by dry sieving. The remaining fraction was sonificated at 440 J ml^{-1}. The fractions coarse plus medium silt (6.3-63 µm) and fine silt plus coarse and medium clay (0.2-6.3 µm) were obtained by sedimentation. The fine clay fraction was precipitated using $AlCl_3$ and HCl and the supernatant was discarded (amount of discarded C was not determined). All fractions were dried at 50 ^oC and finely ground.

For all size fractions of methods I and II, enrichment factors E_C (mass C per mass separate / mass C per mass soil) and E_N (mass N per mass separate / mass N per mass soil) (CHRISTENSEN, 1992) were calculated.

For the soil texture analysis, the distribution of particle sizes was determined using a modified pipette method (MOSCHREFI, 1983). No previous treatment with H_2O_2 was necessary due to the low carbon content of the soil.

4.7.2 Fractionation of water stable aggregates of soils from Rotthalmünster

For the fractionation of water-stable aggregates, the methods of PUGET ET AL. (2000) and SIX ET AL. (1998) were combined (Figure 4.4). One hundred gram soil (dried at 40 °C) was immersed in distilled water for 10 minutes to allow slaking. After slaking, aggregates were separated by moving the sieve up and down by about 3 cm with 50 repetitions. The >2000 µm aggregates were collected and sieving was repeated for the <2000 µm fraction with the next smaller sieve (1000 µm). This procedure was repeated for the 250 µm and 53 µm sieves. The supernatant water of all fractions of a sample was siphoned off and combined. Then it was precipitated with 0.5 M $AlCl_3$, the supernatant after precipitation was discarded. All aggregate

size classes and the precipitate were oven-dried at 40 °C and aliquots were ball-milled for further analysis.

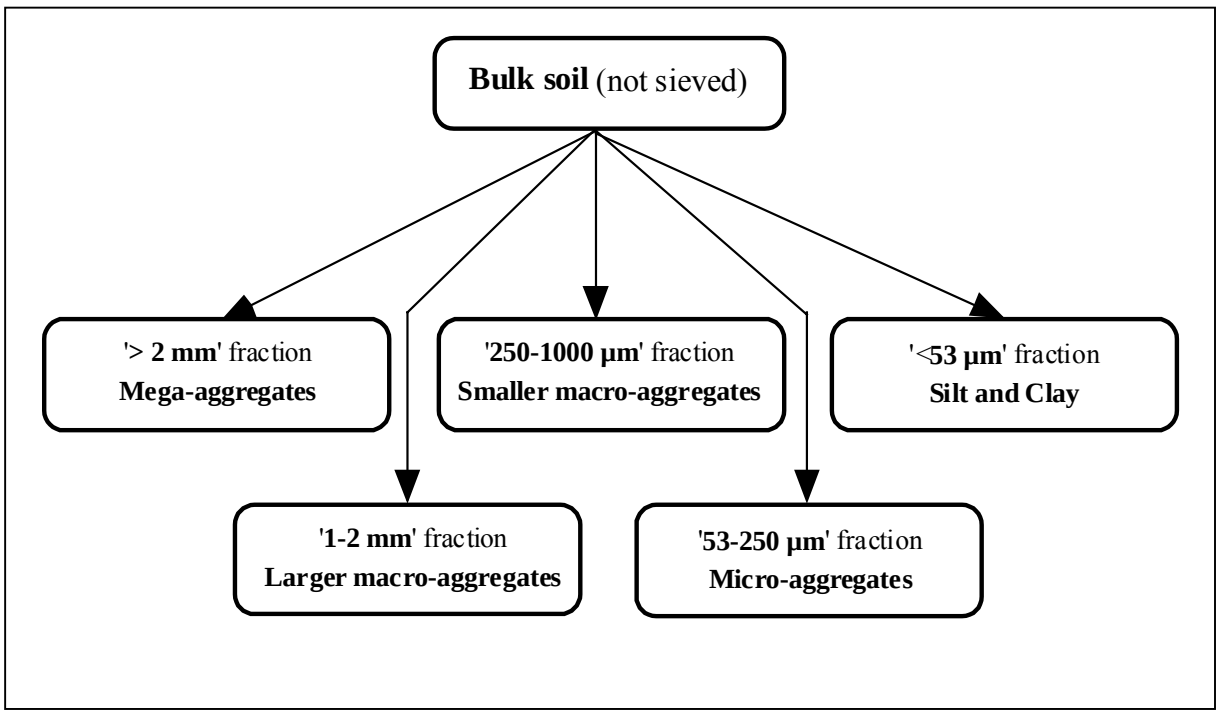

Figure 4.4: Size fractionation of water-stable aggregates. Figure drawn by T. Yamashita.

4.7.3 Density fractionation of soils from Halle and Rotthalmünster

For the thesis, the density fractionation method of GOLCHIN ET AL. (1994b) was adopted (Figure 4.5). Air dried soil (10 g, <2 mm) was placed in a centrifugation tube, 40 ml of sodium polytungstate solution (Sometu, Berlin, Germany) of a density of 1.6 g cm^{-3} was added. The tube was inverted gently by hand five times. After standing for 30 minutes, the solution was centrifuged with 4700 rpm (5085 g) for 1 hour. The supernatant with floating particles was filtered (0.45 µm) under vacuum and washed with distilled water. To do so, screw filters with filtering discs carrying the filter (0.45 µm) were plugged in six filtering flasks and connected to a vacuum pump via a vacuum distributor. After the filtering, the samples (free particulate organic matter <1.6 g cm^{-3}, $FPOM_{<1.6}$) were washed into evaporating dishes, dried, scraped out of the dish and mortared. To gain the fraction of occluded particulate organic matter with a density <1.6 g cm^{-3} ($OPOM_{<1.6}$), the soil was brought into solution with 40 ml of sodiumpolytungstate solution (1.6 g cm^{-3}) with a test tube shaker, then 10 glass beads with a diameter of 5 mm were added and the solution was shaken for 16 hours with orbital motion at a frequency of 60 rotations per minute (BALESDENT ET AL., 1991). After disaggregation, the soil suspension was centrifuged for 1 h at 4700 rpm. The supernatant with floating particles was filtered under vacuum (0.45 µm) and washed with distilled water. After drying, $OPOM_{<1.6}$ was mortared. The pellet was brought into solution with 40 ml of sodiumpolytungstate solution (2.0 g cm^{-3}) with a test tube shaker and shaken for 10 min with

orbital motion at a frequency of 100 rotations per minute. The supernatant (OPOM 1.6 – 2.0 g cm^{-3}, $OPOM_{1.6\text{-}2.0}$) with floating particles was filtered under vacuum (0.45 µm) and washed with distilled water. After drying, the particles were mortared. To remove the salt, the remaining mineral fraction (>2.0 g cm^{-3}, $Mineral_{>2.0}$) was washed by bringing it into solution with distilled water using a test tube shaker. Afterwards, the sample was centrifuged for 20 min at 4700 rpm and the supernatant was discarded. This procedure was repeated three times, then the pellet was dried and ball-milled for further analysis.

Before the ball-milling of the density fractions, pictures were taken using an Olympus SZ-PT Stereo Microscope.

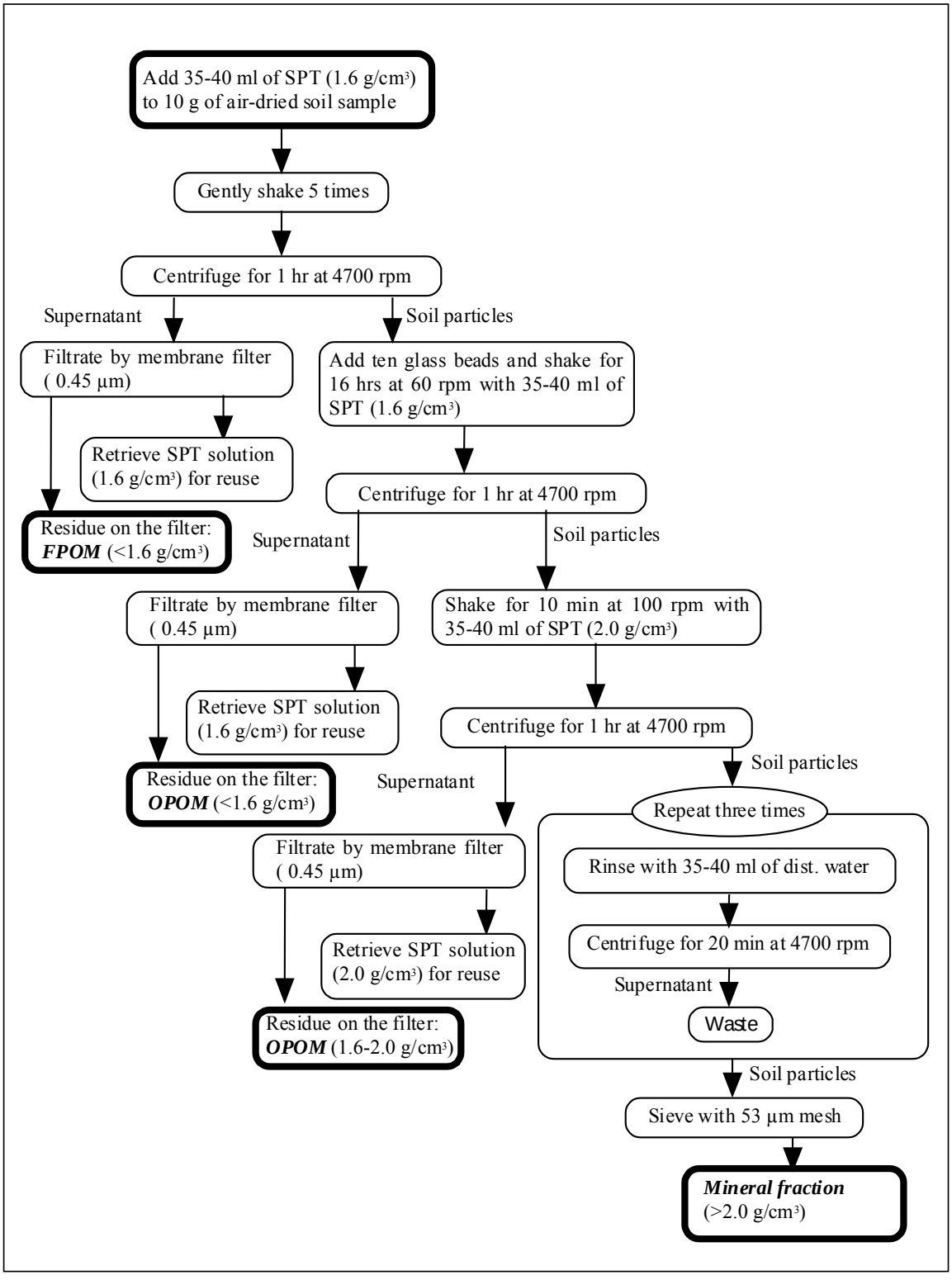

Figure 4.5: Density fractionation scheme. Figure drawn by T. Yamashita.

4.8 Microcosm Experiments

After preincubation without irrigation at 8 °C over 140 days, the soil columns were incubated for 230 days at 8°C using an automatic microcosm system (Figure 4.6). The system consisted of the soil columns, an automated irrigation system (2 mm 10^{-2} M $CaCl_2$ per day), a suction unit with a 0.45 µm filter for leachate sampling and an automated gas chromatographic (GC) system for CO_2 analysis (FLESSA & BEESE, 1995) of input air, exhaust air and calibration gases consisting of a ^{63}Ni-Electron Capture Detector (GC-ECD, Shimadzu). The headspace of each soil column was continuously flushed with a controlled flow (15 ml min^{-1}) of fresh air. Gas samples were collected in 2 ml vials at the outlet of the soil columns to determine $\delta^{13}C$ values of the CO_2 produced. If the difference between the CO_2 concentrations of the fresh air input and the exhaust air of the microcosms was too low for the calculation of the maize-derived C in the respired CO_2 (this was the case especially for the subsoil), columns were closed for at least 24 h before sampling with an air-tight syringe (50 ml) from the headspace. From the 50 ml syringe, a subsample was injected into a 2 ml gas sample vial. The $\delta^{13}C$ values of the collected air sample (δ_{outlet}) vials were measured in a GC-IRMS (Finnigan MAT, Delta C). Additionally, the $\delta^{13}C$ values of the input air (δ_{inlet}) were measured with 5 replicates.

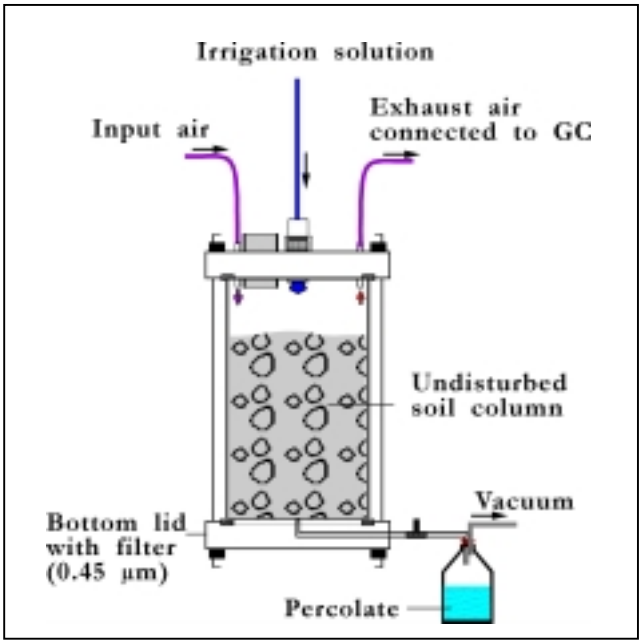

Figure 4.6: Microcosm incubation system in a climate chamber at 8 °C and with automatic irrigation [2 mm 10^{-2} M $CaCl_2$ d^{-1}] (from FLESSA & BEESE, 1995).

The $\delta^{13}C$ values of the CO_2 originating from the soil columns (δ_{resp}) were calculated as:

$$\delta_{resp} = \frac{\left(\delta_{outlet} - \delta_{inlet}\frac{[CO_{2inlet}]}{[CO_{2outlet}]}\right)[CO_{2outlet}]}{[CO_{2outlet}]-[CO_{2inlet}]} \qquad \textbf{Equation 4.10}$$

where $[CO_{2inlet}]$ was the CO_2-concentration of the fresh air input and $[CO_{2outlet}]$ the CO_2-concentration of the sample.

The leachate samples were obtained fortnightly. DOC was determined using a DOC-analyzer where a Pt-catalyzed, high-temperature combustion was followed by infrared detection of CO_2. Before the measurement, inorganic C was removed by adjusting the pH of the solution to a value of 2 with concentrated H_3PO_4 and purging with CO_2 free synthetic air.

Total dissolved nitrogen (TDN), NH_4^+-N, and NO_3^--N were determined by a continuous flow system (SAN^{plus} Segmented Flow Analyzer, Skalar, Erkelenz, Germany) with photometrical detection. Prior to the photometrical detection, TDN was treated with alkaline persulfate digestion and UV digestion to convert both NH_4^+-N and dissolved organic nitrogen to NO_3^--N, afterwards all nitrate was reduced to nitrite by passing a column containing a cadmium-copper granulate. Similarly, NO_3^--N was measured after its reduction to nitrite. DON was computed as

$$[DON] = [TDN]- [NH_4^+\text{-N}] – [NO_3^-\text{-N}]. \qquad \textbf{Equation 4.11}$$

$\delta^{13}C$ values of the DOC were determined after liquid oxidation and freeze-trapping of the CO_2 (Figure 4.3).

4.8.1 Analysis of soil, root biomass and stalks after the incubation of a maize stubble

Maize stubble and root being left at the end of incubation of Ha-M_{stalk} were manually removed and washed. Root biomass was gained by repeated sedimentation, decanting and wet sieving (<0.5 mm) in distilled water (LIVESLEY ET AL., 1999). Roots and stubble were dried at 60 °C and milled by an ultra-centrifugal mill and a ball-mill, then coal particles were sorted out with forceps from the root biomass. C and N contents were determined by an automated C and N analyzer (Heraeus Elementar Vario EL). The initial amount of carbon in maize roots and stubble was calculated from the remaining residues at the end of the incubation and the losses of CO_2-C and DOC originating from these residues during incubation.

Mineralization of recent maize residues (stubble and roots) in Ha-M_{stalk} was calculated by the total amount of CO_2-C produced and the ^{13}C abundance of the respired CO_2 (method 1) (LIANG ET AL. 1999). Additionally, I calculated the difference of the total amount of respired CO_2-C between Ha-M_{stalk} and Ha-M_{NPK} (method 2). Priming effects (i.e. increased

mineralization of indigenous soil organic C resulting from decomposition of fresh maize residues) were determined by comparing the results of method 1 and 2. This approach was also used to determine priming effects with respect to DOC production.

4.9 Modeling of carbon dynamics using the Rothamsted Soil Carbon Model

The Rothamsted Carbon Model (ROTHC26-3) (JENKINSON & RAYNER, 1977; COLEMAN & JENKINSON, 1999) which included the pools "decomposable plant material" (DPM), "resistant plant material" (RPM), "microbial biomass", "humified organic matter" and "IOM" was used to calculate the amount of maize-derived C in different SOM pools. This version of the model has been tested before (SMITH ET AL., 1997). The structure of the model is shown in Figure 4.7.

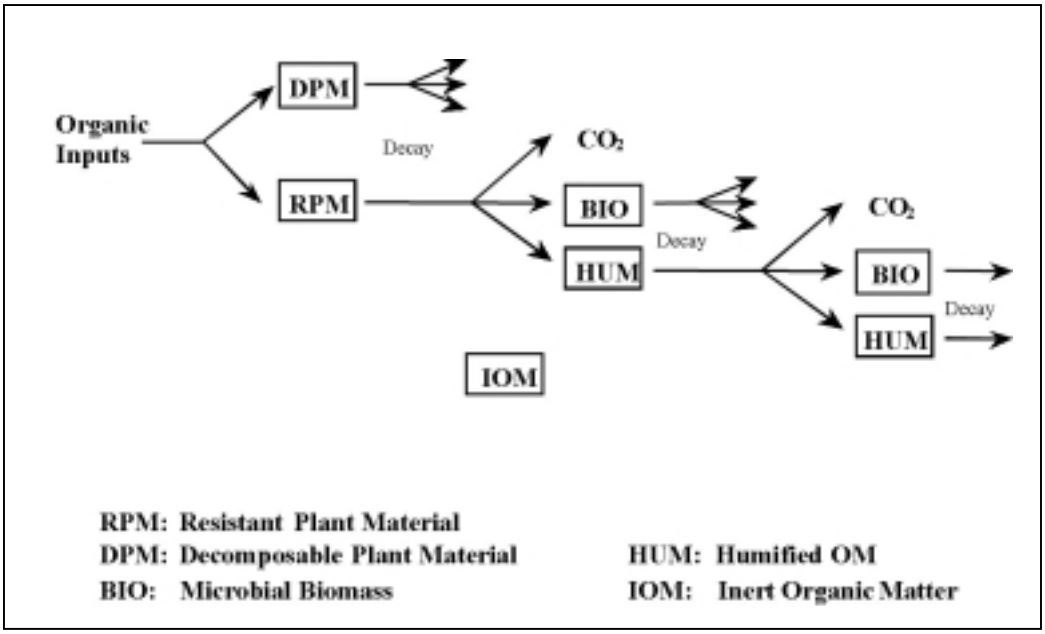

Figure 4.7: Structure of the Rohamsted Carbon Model (from COLEMAN & JENKINSON, 1999).

The decay of the pools DPM, RPM, microbial biomass and humified OM follows a first order kinetic:

$$Y_t = Y_0 (1 - e^{-abckt}) \qquad \textbf{Equation 4.12}$$

where Y_t is the amount of pool Y at time t, Y_0 is the initial amount of pool Y, a is the rate modifying factor for temperature, b is the rate modifying factor for moisture, c is the soil cover rate modifying factor, k is the decomposition rate constant for that compartment and t is the time. The decomposition rate constants (in $year^{-1}$) were set to 10.0 (DPM), 0.3 (RPM),

0.66 (microbial biomass) and 0.02 (humified OM) as suggested by COLEMAN & JENKINSON (1999).

At Halle, the model was run for the 0-25 cm depth for Ha-M_{NPK} and Ha-M_0. The data requirements are given in Table 4.2. Unknown parameters were the monthly input of plant residues and the amount of IOM. The following two model cases I and II were calculated to obtain these parameters:

a) Model case I (suggested by COLEMAN & JENKINSON (1999) for those sites where no additional information on the size of IOM is available, e.g., by radiocarbon measurements):

The amount of IOM was estimated using the equation given by FALLOON ET AL. (1998) (IOM (in t C ha^{-1}) = 0.049 $SOC^{1.139}$). The values for the amount of IOM were (in kg C m^{-2}): 0.31 (Ha-R_0, Ha-M_0) and 0.42 (Ha-R_{NPK}, Ha-M_{NPK}).

Then, the model was used to calculate the annual rye-C-input required to obtain a storage of 3.83 (Ha-R_0) or 4.94 (Ha-R_{NPK}) kg C_3-derived C m^{-2} in 0-25 cm (which are the measured SOC values for the rye-plots) in 1961 (assuming a steady state) using the land management for rye. The model calculated that the annual rye-C-inputs (in kg C m^{-2}) were 0.13 (Ha-R_0, Ha-M_0 until 1961), and 0.20 (Ha-R_{NPK}, Ha-M_{NPK} until 1961).

Finally, the model was used to calculate the annual maize-C-input required (from 1962 onwards) to obtain a storage of 3.65 (Ha-M_0) or 4.79 (Ha-M_{NPK}) kg C m^{-2} in 0-25 cm (which are the measured SOC values for the maize-plots) in 2000 using the land management for maize. The model calculated that the annual maize-C-inputs (in kg C m^{-2}) were 0.14 (Ha-M_0) and 0.22 (Ha-M_{NPK}).

b) Model case II (using the additional information from the ^{13}C analysis):

1. The model was used to calculate the annual maize-C-input (from 1962 onwards) required to obtain a storage of 0.35 (Ha-M_0) or 0.71 (Ha-M_{NPK}) kg maize-derived C m^{-2} in 0-25 cm (which are the measured values of maize-derived C for the maize plots) in 2000 using the land management for maize. The model calculated that the annual maize-C-inputs (in kg C m^{-2}) were 0.044 (Ha-M_0) and 0.089 (Ha-M_{NPK}).

2. Then, the model was used to calculate the annual rye-C-input required and the amount of inert organic matter (IOM) (i) to obtain a storage of 3.83 (Ha-R_0) or 4.94 (Ha-R_{NPK}) kg C_3-derived C m^{-2} in 0-25 cm (which are the measured SOC values for the rye-plots in 1961 (assuming a steady state) using the land management for rye and (ii) to obtain a storage of 3.30 (Ha-M_0) or 4.08 (Ha-M_{NPK}) kg C_3-derived C m^{-2} in 2000 (which are the measured values of C_3-derived C for the maize plots) using the land management for maize. The model calculated that the annual rye-C inputs were 0.055 (Ha-R_0, Ha-M_0 until

1961) or 0.09 kg m^{-2} (Ha-R_{NPK}, Ha-M_{NPK} until 1961). The calculated amounts of IOM were 2.3 (Ha-R_0, Ha-M_0) or 2.5 kg C m^{-2} (Ha-R_{NPK}, Ha-M_{NPK}).

Model case I was used to test how accurately the C dynamics can be modeled for a site where no additional information (^{13}C or ^{14}C data) is available. If model case I was useful then model case I and II would give the same results.

Table 4.2: Data requirements for the Rothamsted Carbon Model

Parameter	Values
Average monthly mean air temperature (°C)[a]	0.3 (J), 0.8 (F), 4.5 (M), 8.2 (A), 13.2 (M), 16.2 (J), 18.3 (J), 18.1 (A), 14.3 (S), 9.7 (O), 4.3 (N), 1.5 (D)
Monthly precipitation (mm)[a]	23.9 (J), 23 (F), 31.8 (M), 38.4 (A), 50 (M), 58.2 (J), 56.9 (J), 51.7 (A), 42.2 (S), 34.2 (O), 33.4 (N), 34 (D)
Monthly evaporation (mm)[a]	12 (J), 18.5 (F), 38.2 (M), 62.8 (A), 96.9 (M), 104.3 (J), 110.8 (J), 95.9 (A), 59.8 (S), 34.5 (O), 15.3 (N), 10.2 (D)
Soil depth (cm)	25
Clay content of the soil (%)	10
DPM/RPM ratio for rye and maize[b]	1.44
Soil cover	Rye crop production: covered from November till August. Maize crop production: covered from May till September.
Monthly input of plant residues	Unknown, obtained as described in model cases I and II
Amount of IOM	Unknown, obtained as described in model cases I and II

[a]Halle: The weather data were taken from a nearby station.
[b]The value suggested by COLEMAN & JENKINSON (1999) was used.

4.10 Statistical analysis

The data were evaluated using STATISTICA for Windows (StatSoft, Inc., 2001), Version 6. Data were tested for significance ($p<0.05$) by one-way analysis of variance (ANOVA), using the post-hoc Tukey test ("honestly significant difference test") or the two-tailed t-test if only two sample groups were compared. In the statistical analysis, a normal distribution of the data was presumed. For an examination of a normal distribution of the data notedly higher replicates would be necessary than they were feasible for this study (CLAUß & EBNER, 1985). Unless noted otherwise, results are given as means ± standard error (SE).

5 RESULTS AND DISCUSSION

5.1 Properties of the study sites

5.1.1 Carbon and nitrogen storage and pH at Halle and Rotthalmünster

At Halle, SOC contents were higher in the surface soils of Ha-R_{NPK}, Ha-M_{NPK}, Ha-R_0 and Ha-M_0 than in the subsoils and higher in the fertilized than in the unfertilized plots (Table 5.1, Table 5.4). The higher C-content of the NPK-plots compared to the unfertilized plots was probably caused by the higher input of biomass due to the higher production of stubble and root biomass through fertilization. The carbon contents in the subsoils as compared to the surface soils was significantly lower for all sites except Ha-M_0. As the soil at Halle is a degraded Chernozem, the subsoils exhibited high carbon contents.

For Rotthalmünster, C storage in the surface soils (30 cm) decreased as Ro-Grass > Ro-M_{org} ≈ Ro-M_{NPK} ≈ Ro-W_{NPK} > Ro-Forest. However, if the organic layers were included, C-storage was significantly highest at the forest site. No significant difference in C storage could be found at the depth 30-45 cm for all sites except Ro-Forest, where significantly less C was sequestered. At the lowest depth step (45-60 cm), the C storage showed no significant differences among the sites. Including the organic layers, cultivation resulted in a loss of carbon from Ro-Forest up to a depth of 60 cm when compared to the other sites, but no further significant C loss could be found from the grassland site as tillage commenced. The results show that surface soils and subsoils need to be accounted for when carbon storage under different degrees of cultivation is to be compared.

Fertilization influences the carbon level in soils: conventionally tilled continuous corn receiving low and high fertilization resulted in a 5% increase in SOC and 6% increase in total soil nitrogen after 6 years with a higher fertilization rate (400 kg N ha^{-1} vs. 170 kg N ha^{-1}; LIANG & MACKENZIE, 1992). Continuous long-term N fertilization resulted in a higher storage of SOC in a sandy clay loam in Texas (SALINAS-GARCIA ET AL., 1997). Findings in literature concerning the loss of carbon after cultivation are very variable. Most studies show a loss of carbon, sometimes as much as 40% of the carbon originally in the forest soil (HOUGHTON, 1995). Because pastures are not tilled, the loss of carbon from pasture soils is usually less than 25% of the initial carbon contained in the top 1 m (HOUGHTON, 1995). The C/N ratios were wider for the surface soils than for the subsoils due to the increasing humification of soil organic matter with soil depth at all sites of Halle and Rotthalmünster (Table 5.1, Table 5.2).

At the surface soils of the unfertilized plots of Halle, pH was lower than in the fertilized plots. It increased with soil depth at all Halle sites. At Rotthalmünster, no difference occurred

among the cropped soils, pH was lower at the grassland soil and lowest in the forest soil where pH was in the Al-buffer zone. At the limed soils of Rotthalmünster, pH was higher in the surface soils than in the subsoils. Conversely, at the forest soil, pH was lower at the surface soil than at the subsoils. As the soil pH was influenced by fertilization and liming, no further consideration is given to it.

5.1.2 $\delta^{13}C$ values of soils and plant material at Halle and Rotthalmünster

For surface soils (0-20 cm) under continuous rye, $\delta^{13}C$ remained approximately constant with time (Ha-R_0: $\delta^{13}C$ = -25.3 (1961) and –25.4‰ PDB (2000); Ha-R_{NPK}: $\delta^{13}C$ = -25.6 (1961) and –25.7‰ PDB (2000)), whereas for surface soils under continuous maize a considerable increase in $\delta^{13}C$ was observed (Ha-M_0: $\delta^{13}C$ = -25.3 (1961) and –23.8‰ PDB (2000); Ha-M_{NPK}: $\delta^{13}C$ = -25.4 (1961) and –23.4‰ PDB (2000) (LUDWIG ET AL., 2003). The difference of the $\delta^{13}C$ values in the subsoils was less pronounced. The differences in the $\delta^{13}C$ values of Ha-R_{NPK} and Ha-R_0 may be explained by the higher input of rye biomass (-28.4‰ PDB) caused by the higher production of biomass in the fertilized plot, since in 1961, the $\delta^{13}C$ values of the SOC had been more positive. Similarly, the more positive $\delta^{13}C$ value of Ha-M_{NPK} compared to Ha-M_0 in the year 2000 may be explained by the higher biomass production of the fertilized plot. Soil nitrogen availability influences carbon isotope discrimination of C_3-plants: plants with high nitrogen concentrations in their leaves usually have high levels of carbon-fixing enzymes and, therefore, an enhanced ability to capture CO_2 (BOUTTON, 1996). Enhanced photosynthetic capacity would increase consumption of intercellular CO_2 and decrease p_i/p_a (equation 2.2) thus resulting in a more positive $\delta^{13}C$–value in plants receiving high nitrogen supplements. Therefore, the plants and subsequently the SOC at the plot Ha-R_0 were expected to have a more negative $\delta^{13}C$–value than the plants and SOC at the plot Ha-R_{NPK}. This effect was probably outnumbered by the higher incorporation of plant material at Ha-R_{NPK} which was more ^{13}C-depleted than the original soil. Thus in spite of the higher N-availability at Ha-R_{NPK}, the SOC at Ha-R_{NPK} exhibited lower $\delta^{13}C$ values than Ha-R_0. Similar to the results at the Halle site, JENKINSON ET AL. (1992) found under C_3-plants at both Wilderness sites and Park Grass a small downward drift in $\delta^{13}C$ with time.

At Rotthalmünster, no historic soil samples were available. The most negative $\delta^{13}C$ value occurred at the surface soil (0-10 cm) of Ro-Grass (–28.0‰ PDB). $\delta^{13}C$ values were significantly increased from 10–30 cm and further increased down the depth profile with no significant differences in the isotopic composition from 20–65 cm (Table 5.2). $\delta^{13}C$ values of the above ground biomass (–28.9 ± 0.2‰ PDB) and below ground biomass (-29.2 ± 0.2‰ PDB) were not significantly different from each other and their mean value (-29.1‰ PDB) was applied for further analysis. Thirty-three years after its conversion from grassland to

wheat monoculture, the Ap-horizon (0-30 cm) at Ro-W_{NPK} (–26.5‰ PDB) was significantly less depleted in ^{13}C than the grassland, since the wheat plants had a more positive $\delta^{13}C$ value (-26.8‰ PDB) than the grassland plants. The subsoil at the wheat site exhibited significantly more negative values than the surface soils. After the conversion from C_3-plants (grassland and wheat, see chapter 4.1.2) to the C_4-plant maize, the $\delta^{13}C$ values of the Ap-horizon (0-30 cm) of Ro-M_{NPK} (–21.6‰ PDB) and Ro-M_{org} (-21.5‰ PDB) were significantly higher. ^{13}C-enrichment was lower in the subsoils due to the lower input of fresh maize biomass. The mean value (-12.7‰ PDB) of the above ground (–12.8 ± 0.0‰ PDB) and below ground maize biomass (-12.6 ± 0.1‰ PDB) was applied for further calculations, as no reliable data on root production were available. The isotopic composition of the corn cob (-11.5 ± 0.1‰ PDB) was not accounted for in further analyses since, unlike the maize straw and roots, it was not incorporated into the soil. No significant differences could be found in the isotopic composition of the maize sites, in spite of the organic amendments.

Similar to the field soils, $\delta^{13}C$ values of the forest soil were increasing with soil depth (-25.7 to -25.2‰ PDB), no significant difference existed for the isotopic composition of the organic layers (-25.8 to –26.0‰ PDB). The spruce needles (-28.3 ± 0.1‰ PDB), twigs (-26.6 ± 0.5‰ PDB) and cones (-25.9 ± 0.1‰ PDB) showed widely differing $\delta^{13}C$ values. The higher $\delta^{13}C$ values of the organic layers as compared to the needles, that constitute the major part of litter fall (ELLENBERG ET AL., 1986), was probably mainly due to the discrimination of ^{13}C by microbial decomposition (HEIL ET AL., 2000). Similarly, in 13 plots with healthy and declining Norway spruce plots, differing ^{13}C enrichments in needles (-27.3 to –29.1‰ PDB) and twigs (-25.3 to –27.8‰ PDB) were measured (GEBAUER & SCHULZE, 1991). At the surface of humus layers from beech and forest sites in Solling, Germany, the $\delta^{13}C$ values were 1‰ PDB to 4‰ PDB higher than in leaves and needles (HEIL ET AL., 2000). In Picea stands from an European North-South transect, NOVAK ET AL. (2003) found that mineralization in the soil profile left in situ residues that were enriched in the heavier isotopes ^{13}C, ^{15}N and ^{34}N.

Table 5.1: Halle: Bulk density (BD), pH (10^{-2} M $CaCl_2$), soil organic carbon (SOC), total nitrogen (N_t), C/N ratio and $\delta^{13}C$ values and maize-derived C [%] of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK}. Means and SE (n=5) of SOC, N_t, $\delta^{13}C$ values and maize-derived C.

Plot	Depth [cm]	BD [g cm^{-3}]	pH $CaCl_2$	SOC [g/m²]	N_t [g/m²]	C/N	$\delta^{13}C$ [‰ PDB]	Maize-derived C [%]
Ha-M_{NPK}	0 – 10	1.31	5.7	1634 (23)	106.1 (1.8)	15.4	-23.3 (0.0)	14.3 (0.3)
	10 – 20	1.58	5.8	2020 (51)	131.1 (1.1)	15.4	-23.4 (0.1)	13.7 (0.7)
	20 – 30	1.68	5.7	2115 (70)	133.9 (2.1)	15.8	-23.4 (0.1)	14.5 (0.7)
	30 – 40	1.76	6.6	1179 (81)	126.1 (6.5)	9.4	-24.6 (0.1)	6.0 (0.7)
	40 – 50	1.76	6.9	1333 (98)	136.8 (7.5)	9.7	-24.8 (0.1)	5.3 (0.5)
	50 – 60	1.76	7.1	1268 (55)	126.3 (3.7)	10.0	-24.9 (0.1)	3.6 (0.8)
Ha-M_0	0 – 10	1.31	5.3	1415 (34)	92.2 (2.6)	15.4	-23.9 (0.0)	9.3 (0.5)
	10 – 20	1.58	5.3	1569 (203)	103.7 (11.6)	15.1	-23.7 (0.1)	9.9 (0.6)
	20 – 30	1.68	5.4	1339 (140)	139.7 (24.7)	9.6	-24.0 (0.2)	9.0 (1.2)
	30 – 40	1.76	6.0	1427 (115)	134.4 (15.5)	10.6	-24.9 (0.1)	4.4 (0.4)
	40 – 50	1.76	6.3	1379 (156)	134.3 (15.0)	10.3	-25.0 (0.1)	4.2 (0.4)
	50 – 60	1.76	6.5	1107 (60)	111.6 (5.9)	9.9	-24.9 (0.1)	3.8 (0.7)
Ha-R_{NPK}	0 – 10	1.22	5.7	1414 (35)	96.3 (2.1)	14.7	-25.7 (0.0)	
	10 – 20	1.57	5.7	1976 (81)	131.1 (4.0)	15.1	-25.7 (0.1)	
	20 – 30	1.67	5.7	1955 (58)	130.8 (3.4)	14.9	-25.8 (0.0)	
	30 – 40	1.76	6.0	1083 (75)	103.0 (4.6)	10.5	-25.6 (0.0)	
	40 – 50	1.76	6.2	824 (30)	91.4 (3.4)	9.0	-25.7 (0.1)	
	50 – 60	1.76	6.3	661 (46)	73.8 (4.9)	9.0	-25.5 (0.1)	
Ha-R_0	0 – 10	1.22	5.5	1224 (35)	81.2 (1.6)	15.1	-25.5 (0.1)	
	10 – 20	1.57	5.5	1712 (52)	156.8 (19.2)	10.9	-25.4 (0.1)	
	20 – 30	1.67	5.5	1789 (47)	119.8 (3.2)	14.9	-25.5 (0.1)	
	30 – 40	1.76	6.0	910 (39)	97.5 (1.9)	9.3	-25.7 (0.0)	
	40 – 50	1.76	6.2	795 (32)	87.8 (2.6)	9.1	-25.7 (0.0)	
	50 – 60	1.76	6.4	630 (50)	72.0 (4.9)	8.7	-25.6 (0.1)	

Table 5.2: Rotthalmünster: Bulk density (BD), pH (10^{-2} M $CaCl_2$, Ro-Forest: additionally pH 10^{-2} M KCl), soil organic carbon (SOC), total nitrogen (N_t), C/N ratio, $\delta^{13}C$ values and maize-derived C [%] of Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org}, Ro-Grass, and Ro-Forest. Means and SE (n=4) of SOC, N_t, $\delta^{13}C$ values and maize-derived C.

Plot	Depth [cm]	BD [g cm^{-3}]	pH $CaCl_2$ (KCl)	SOC [g/m²]	N_t [g/m²]	C/N	$\delta^{13}C$ [‰ PDB]	Maize-derived C [%]
Ro-W_{NPK}	0-30	1.45	6.5	5197 (317)	551.8 (33.3)	9.4	-26.5 (0.1)	
	30-45	1.58	6.6	1075 (28)	138.0 (1.9)	7.8	-25.6 (0.1)	
	45-60	1.48	6.6	603 (6)	87.5 (0.7)	6.9	-25.1 (0.1)	
Ro-M_{NPK}	0-30	1.38	6.9	5361 (31)	560.7 (4.9)	9.6	-21.6 (0.2)	35.1 (1.5)
	30-45	1.53	6.5	1551 (37)	180.6 (5.0)	8.6	-23.4 (0.1)	15.4 (0.8)
	45-60	1.52	6.6	932 (27)	122.7 (3.7)	7.6	-23.7 (0.2)	10.1 (1.7)
Ro-M_{org}	0-30	1.44	6.8	5612 (36)	583.3 (3.9)	9.6	-21.5 (0.1)	35.8 (1.2)
	30-45	1.56	6.7	1514 (55)	180.4 (5.3)	8.4	-22.9 (0.2)	19.3 (1.2)
	45-60	1.52	6.2	801 (48)	105.2 (4.2)	7.6	-23.4 (0.1)	11.9 (0.9)
Ro-Grass	0-10	1.23	5.9	3023 (34)	294.4 (3.5)	10.3	-28.0 (0.1)	
	10-20	1.47	5.6	1683 (189)	182.6 (17.4)	9.2	-26.7 (0.2)	
	20-30	1.49	5.6	1160 (7)	136.9 (0.3)	8.5	-26.3 (0.0)	
	30-45	1.47	5.7	1159 (13)	146.2 (1.2)	7.9	-25.9 (0.1)	
	45-65	1.43	5.5	973 (50)	135.1 (5.5)	7.2	-25.7 (0.1)	
Ro-Forest	L (+12-+8)	0.20	3.4 (3.1)	6490 (599)	254.5 (12.6)	25.5	-26.0 (0.1)	
	Of (+8-+3)	0.23	3.0 (2.7)	6899 (60)	265.5 (1.7)	26.0	-25.8 (0.1)	
	Oh (+3-+0)	0.36	2.9 (2.6)	7506 (217)	297.9 (3.7)	25.2	-26.0 (0.0)	
	0-7	0.91	3.2 (2.9)	2568 (45)	117.4 (1.8)	21.9	-25.7 (0.0)	
	7-25	1.21	3.6 (3.3)	2078 (56)	111.8 (3.0)	18.6	-25.2 (0.1)	
	25-40	1.49	3.7 (3.3)	733 (17)	17.3 (17.3)	42.4	nd	
	40-60	1.59	4.0 (3.2)	619 (210)	nd	nd	nd	

5.1.3 Maize-derived carbon and ^{14}C age at Halle and Rotthalmünster

In the surface soils of Halle, the maize-derived SOC accounted for 9.5% of the total SOC at Ha-M_0 and 14.2% at Ha-M_{NPK} (Table 5.1). Maize-derived SOC was less in the subsoil with 5.2% of the total SOC at Ha-M_0 and 7.4% at Ha-M_{NPK}. In 1971 and 1972, the amount of maize-derived C (Ha-M_0: 3.8% and 4.4% of the SOC; Ha-M_{NPK}: 4.4%) was slightly less than in 1969 (Ha-M_0: 4.2%; Ha-M_{NPK}: 4.5%), presumably because of the deepening of the plough layer from 20 to 25 cm in 1970. From the mid-nineties onwards, a second deepening of the plough layer down to 30 cm resulted in approximately constant amounts of maize-derived C (Ha-M_{NPK}) or in a considerable decrease in maize-derived C (Ha-M_0) (Figure 5.1). From 1977 onwards, the amount of maize-derived C in the NPK treatment was greater than the amount in the treatment without fertilizer at all sampling times which was most likely caused by greater biomass production in the fertilized plots. Between 20 and 40 cm depth, the amounts of maize-derived C increased approximately linearly with time and the amounts were 6.7% (Ha-M_0) and 10.2% (Ha-M_{NPK}) of the SOC in 2000 (Figure 5.1). The large increase in maize-derived C in 1990 was probably derived from mixing with surface material because of the deepening of the plough layer rather than from C inputs from roots (root residues and rhizodeposition). In the subsoil (60-80 cm), amounts of maize-derived C were low (in 1990: Ha-M_0: 3.6%; Ha-M_{NPK}: 3.5%) (Figure 5.1). Similarly, BALESDENT ET AL. (1990) reported only small amounts of maize-derived C in the subsoil compared to the surface soil after 17 years of continuous maize cropping.

The percentage of maize-derived carbon was higher at Rotthalmünster than at Halle due to the higher production of biomass, higher input of plant residues after harvest, higher NPK-fertilization, and the high percentage of silt and clay. No significant difference was found between the maize-derived percentages of Ro-M_{org} (35.8%) and Ro-M_{NPK} (35.1%). Maize-derived percentages were significantly lower in the subsoils, but even at the depth step of 45-60 cm, 10.2% (Ro-M_{NPK}) and 11.9% (Ro-M_{org}) of the SOC were maize-derived (Table 5.2).

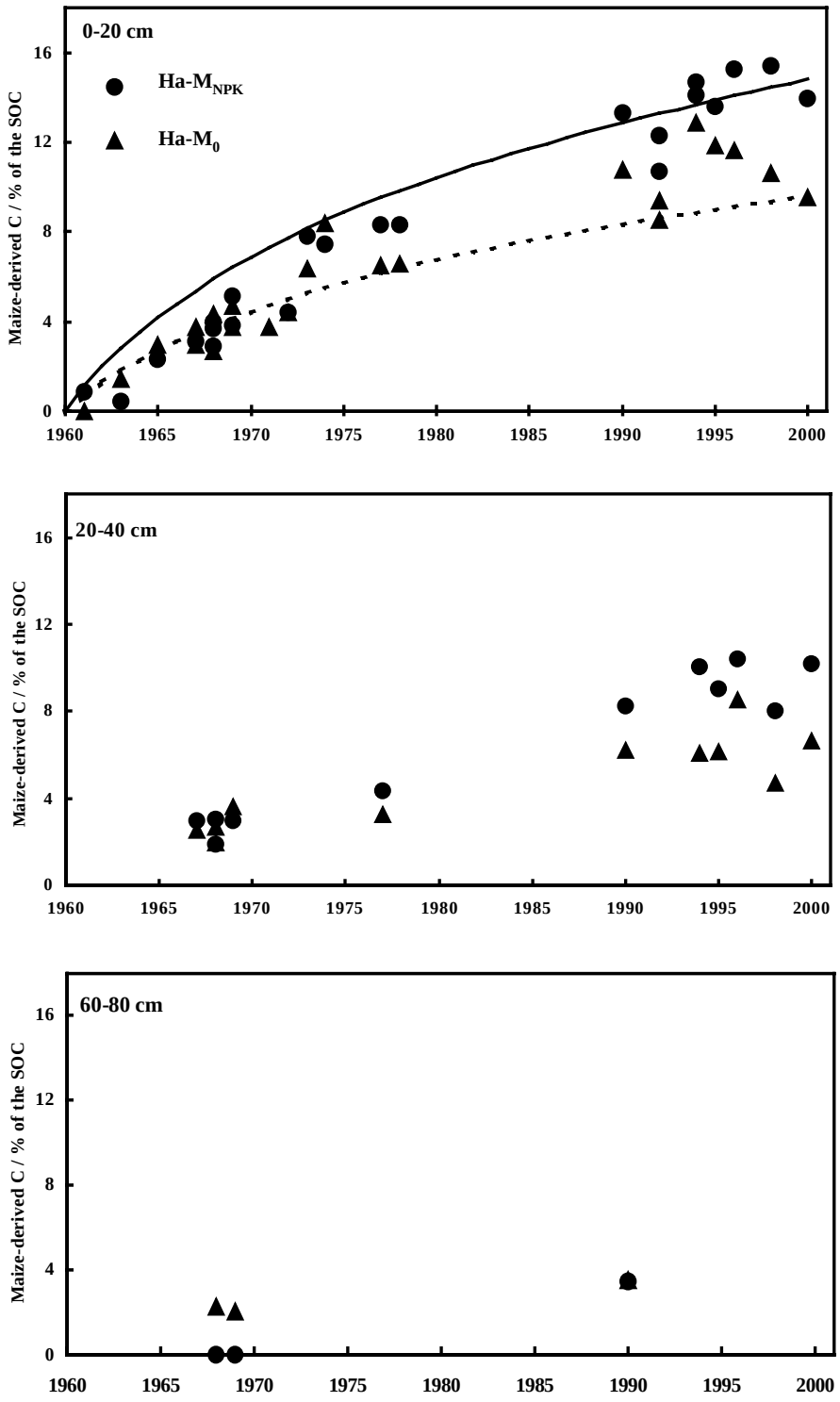

Figure 5.1: Measured (symbols) amounts of maize-derived SOC at different depths and modeled curves with amounts of maize-derived SOC (see chapter 5.5, model case II. Ha-M_{NPK}: solid lines, Ha-M_0: dashed lines).

At Rotthalmünster, the $\delta^{13}C$ values of the whey and slurry that was amended at Ro-M_{org} could not be reconstructed as historic samples do not exist, only one single $\delta^{13}C$ measurement of pig slurry (–24.3 ± 0.1‰ PDB) was possible. $\delta^{13}C$ values of the organic fertilizers are dependent on the isotopic composition of the forage of the livestock. Nevertheless, the organic amendments will have influenced the $\delta^{13}C$ values of the SOC, as they were incorporated in the SOM: In a long-term field experiment on a clay loam soil at Ultuna, Sweden, after 37 years of continuous input of animal manure, 27.3% of the total SOM were manure-derived as calculated from the change in the ^{13}C values. However, FTIR-measurements of extracts demonstrated that the characteristics of the extractable humic substances were not altered (GERZABEK ET AL., 1997). However, due to the limited data base concerning the isotopic composition of the organic fertilization over the last years, it was not taken into account when calculating maize-derived percentages.

At Halle, the enrichment of maize-derived C was low in comparison with similar studies (PUGET ET AL., 1995; BALESDENT ET AL., 1990; GREGORICH ET AL. 2000), where after shorter periods (23 to 35 years) more maize-derived C (22 to 44%) was stabilized. In contrast to this, the enrichment of carbon from maize in the soils at Rotthalmünster agreed well with literature values. GREGORICH ET AL. (1996) found that after 32 years of maize cultivation 22 to 30% of soil C was maize-derived under NPK treatment as compared to 15 to 20% under an unfertilized field. COLLINS ET AL. (1999) found that of eight soils in the maize belt of the US that have grown continuous maize for eight to 35 years, the C_4-derived C in the surface soils (0-20 cm) ranged from 23 to 60% and from 9 to 32% in the subsoils (25-50 cm). WANNIARACHCHI ET AL. (1999) measured 10% of maize-derived C in the SOC of a sandy loam in Ontario cropped to maize for six years with conventional tillage.

The yields and thus the below-ground biomass input through roots and rhizodeposition were reduced up to 30% at Halle (SCHMIDT ET AL., 2000) due to the long-term monoculture. At Rotthalmünster, the yield reduction was 24% at the wheat field when compared to the wheat in a crop rotation (SCHNELLHAMMER & SIRCH, 2001), thus, a reduction of the yields at the maize sites is likely. The main reason for the lower enrichment of maize-derived C in the SOC of Halle was the low C input, since the above-ground maize biomass was removed for silage-making. At Halle, excluding rhizodeposition, the yearly input from root and stubble biomass was estimated as 0.15 kg dry matter m^{-2} at Ha-M_{NPK} and 0.06 kg dry matter m^{-2} at Ha-M_0 by considering the mean dry matter yields and a (stubble and root biomass)/(aboveground yield) ratio of 0.20 according to the findings of BALESDENT & BALABANE (1992). Under the above assumptions concerning the relation of aboveground production to belowground production, the yearly input was 0.63 kg dry matter m^{-2} at Ro-M_{NPK}. It was 0.51 kg dry matter m^{-2} from plant material plus 0.13 kg dry matter m^{-2} from the organic amendments at Ro-M_{org}. At Halle, the maize residue input was considerably less than the residue input after the harvest of grain maize, e.g. GREGORICH ET AL. (1996a) estimated total amounts of 286 Mg ha^{-1} and 159 Mg ha^{-1} of corn residues returned to the soils of a NPK-

fertilized and non fertilized field in Ontario over a period of 32 years assuming a root:shoot ratio of 0.15, which was equivalent to 0.89 kg and 0.50 kg maize residues m^{-2} per year, respectively. The maize residue input to the soil at Rotthalmünster was comparable to the study site in Ontario.

The isotopic composition of atmospheric carbon has changed as a consequence of fossil fuel combustion (chapter 2.3), thus it influenced the $\delta^{13}C$ values of the crops planted at Halle and Rotthalmünster. Unfortunately, no historic samples of the cropped plants were stored and thus available for measurements. Nevertheless, the change in the isotopic composition of the plant material did not resemble the change in the isotopic composition of the soil organic matter, as only a part of the plant material was incorporated into the SOM. When taking the drift in $\delta^{13}C$ values into account for the Halle sites, it would be expected that $\delta^{13}C$ values would be increased by 0.1 to 0.2‰ PDB. However, this increase is in the range of the standard error of the measurements (Table 5.1) and was neglected in further analysis.

Halle is located in a heavily industrialized area, hence SOC and SON have been influenced by the anthropogenic immissions. Following 1949, a C-input from the nearby chemical industry, steam locomotives, thermal power station, coal loading, and domestic fuel took place (Schmidt et al., 2000), resulting in a monthly input of approximately 20 g m^{-2} of soot and coal dust (SCHARF, 1967; STUMPE, 1967; KOLBE & STUMPE, 1969).

Table 5.3 C-content and $\delta^{13}C$ [‰ PDB] in coal particles sorted out of Halle bulk soils.

Sample	C [%]	$\delta^{13}C$ [‰ PDB]
1	42.6	-25.9
2	43.8	-25.4
3	63.2	-24.1

Coal particles sorted out of the soil varied in respect of carbon content and $\delta^{13}C$ values, thus indicating variable sources (Table 5.3). Coal and lignite were formed from ancient C_3-plants, thus, their ^{13}C value resemble that of today's C_3-plants. Therefore, the coal input was in the range of the $\delta^{13}C$ values of the soils in this study. Nevertheless, the coal input influenced the $\delta^{13}C$ values of the soils, without it, the ^{13}C enrichment in the maize soils would have been higher, and the rye soils would possess more negative $\delta^{13}C$ values. Up to 28% of the SOC at Halle is pyrogen carbon at differing stages of degradation and charring of pedogenous and fossil origin (BRODOWSKI ET AL., 2003). However, to date, no valid quantification of the amount of carbon deriving from anthropogenic pollution was done.

The anthropogenic pollution strongly influenced the ^{14}C distribution in the soil, the surface soil exhibited a very steep heterogeneity in respect of the age of its carbon-containing components. Plant residues and roots had ^{14}C-contents in the range of the atmospheric CO_2

(approx. 108 pMC). In contrast to this, charred particles sorted out of the bulk soil ranged from 44 pMC (approx. 6655 BP) to 7 pMC (approx. 21360 BP), thus indicating a heterogeneous composition from younger charred plant residues and older coal or lignite (RETHEMEYER ET AL., 2001). With depth, ^{14}C-contents were increasing (RETHEMEYER ET AL., 2001) which was just opposite to the trend normally observed in soils (TRUMBORE, 1993). This indicated that the ^{14}C distribution was mainly a result of the degree of contamination with coal particles. ^{14}C contents of the historic samples before the bomb beak (1949) were equivalent to 51 pMC in the humins and 67 pMC in the humic acids (RETHEMEYER ET AL., 2001), even though humic acids normally show a higher turnover than humins. These measurements demonstrated that only ambiguous conclusions can be drawn when interpreting the ^{14}C data at this site.

^{13}C- and ^{14}C-measurements complement one another. To enable direct comparison between ^{13}C- and ^{14}C-data, as a second site Rotthalmünster was chosen. Rotthalmünster is located in a rural area, thus anthropogenic pollution was scarce and radiocarbon contents were close to the recent atmospheric ^{14}C content. ^{14}C values ranged from 106 pMC (humic acid) to 88.6 pMC (soil humin), indicating a low admixture of old material as compared to Halle (RETHEMEYER ET AL., 2003).

A comparison of the results from ^{13}C- and ^{14}C- measurements pinpoints their advantages and disadvantages: The method of natural ^{13}C abundance is mainly applicable to sites where a change from a C_3-plant to a C_4-plant or vice versa took place, additionally, a monoculture of the plants is advised for better results. This prerequisite is only valid for a very limited number of experiments. However, if these conditions were fulfilled, valid conclusions can be drawn considering the carbon dynamics and the origin of carbon in soils and soil fractions in recent times. Since the most long-term experiments with a vegetation change are relatively young, conclusions about carbon turnover typically cover only the periods from a few years to a few decades.

In contrast to ^{13}C-measurements, ^{14}C-measurements cover a range of about 40,000 years (GOH, 1991). By measuring ^{14}C-data by AMS and utilizing the bomb ^{14}C, the determination of the age of non-mixed materials (for example plants) can be determined with an accuracy of one to two years (P. Grootes, Leibniz Labor Kiel, personal communication). However, conclusions about the origin of mixed samples (for example soils) are not possible, as only mean residence times can be calculated from ^{14}C data. The applicability of the ^{14}C dating is questionable if anthropogenic pollution makes the results from ^{14}C dating unreliable, as was the case in Halle.

5.2 Carbon turnover in SOC fractions

5.2.1 Carbon turnover in size fractions from Halle

5.2.1.1 Methodical aspects

For the dispersion of soil samples prior to size fractionation, several methods have been proposed. Fractionation procedures include short-term stirring by hand, end-over-end shakers, high-speed mixers, and ball-assisted methods (CHRISTENSEN, 1992). The recommended and most widely used method for size fractions is ultrasonification (CHRISTENSEN, 1992). Care should be taken when interpreting results of size fractionations since ultrasonification may produce artefacts and a redistribution of C and N among size separates may occur (AMELUNG & ZECH, 1999; BALESDENT ET AL., 1991). To reduce the redistribution of coarse organic matter among finer size fractions, in this study a two-step disaggregation procedure was applied. In the first step of size fractionation method I, macroaggregates were destroyed by a low energy input of 60 J ml^{-1} and subsequent separation of coarse and middle sand. In the second step, a complete dissaggregation using 440 J ml^{-1} was performed prior to the remaining size fractionation (AMELUNG ET AL., 1998; chapter 4.7.1).

5.2.1.2 Distribution of the particle size fractions

For the size fractionation, two different methods (method I, II) were applied. Method II displayed similar results to method I, it was still included in this thesis as it provided additional information on the turnover of fine clay in the soil and an independent verification of the results of method I with a partly different fractionation procedure.

The yields of the particle size fractions showed that the texture was homogeneously distributed throughout the study area of Halle (

). After the size fractionation using method I, 4.2% of the total soil were located at the coarse sand, 32.2% at the medium sand and 31.1% at the fine sand. Less soil was located in the silt (12.6% at the coarse silt and 10.3% at the medium plus fine silt) and the clay fraction (8.1%). The mean recovery rate was 98.3 ± 0.2%. Method II showed comparable results to method I (

), and fine clay constituted 2.7% of the total soil. The texture analysis resulted in 4.8% at the coarse sand, 24.5% at the medium sand, 38.3% at the fine sand, 12.3% at the coarse silt, 10.8% at the medium plus fine silt and 10.8% at the clay fraction.

The boundary between the fine and medium sand revealed considerable variabilities among methods I and II to the standard texture analysis. This difference might be caused by the different breakup of the fractions due to the differences between wet sieving and dry sieving.

The results were comparable to former texture analyses at this study site, GARZ ET AL. (1996) measured 8% clay, 23% silt and 79% sand.

After the size fractionation with Method I, in the Ap horizon (0-10 cm) of Ha-M_{NPK}, Ha-M_0, Ha-R_{NPK}, and Ha-R_0, the C-content of the clay fraction ranged from 3.8 to 4.6% C (Table 10.1). C-content decreased with increasing particle size in all variants until the medium sand fraction where it ranged from 0.17 to 0.24% C and was heightened at the coarse sand fraction with carbon contents of 0.7 to 1%. Of the total C in the bulk soil, on average, 32% C were located in the clay fraction, 31% in medium plus fine silt fraction and 20% in the coarser fractions.

Method II yielded similar results to Method I, the fine clay fraction (0-0.2 µm) had C contents of 4.1% (Ha-M_{NPK}) and 4.9 (Ha-R_{NPK}; Table 10.2). C enrichment was higher at the fraction medium clay, coarse clay and fine silt with 5.1% C (Ha-M_{NPK}) and 5.9% C (Ha-R_{NPK}), subsequently, C content was decreasing with increasing particle size to the medium sand fractions with values of 0.26% C (Ha-M_{NPK}) and 0.32% C (Ha-R_{NPK}). Of the total SOC in the soil, 8% were located in the fine clay fraction and 48% in the coarse clay to medium silt fraction.

5.2.1.3 Distribution of carbon and nitrogen in particle size fractions

The carbon enrichment of clay and silt is inversely related to the proportion of these size separates in the soil (CHRISTENSEN, 1985; CHRISTENSEN 1996), whereas carbon enrichment of sand does not relate to sand yields. LEINWEBER (1995) proposed two power functions to calculate C enrichment factors E_C (chapter 2.4.1) using data from literature and from long-term experiments on pleistoceneous substrate:

$$E_{C1\_clay} = 18.86 * x_{clay}^{-0.73} \qquad \textbf{Equation 5.1}$$

$$E_{C1\_silt} = 32.36 * x_{silt}^{-1.04} \qquad \textbf{Equation 5.2}$$

with

E_{C1_clay} = C enrichment factor for clay (LEINWEBER,1995)
E_{C1_silt} = C enrichment factor for medium and fine silt (LEINWEBER, 1995)
x_{clay} = average clay content (8.1%)
x_{silt} = average medium and fine silt conten (22.9%).

By applying his equations for the clay fraction, a carbon enrichments of E_{C1_clay} = 4.1 and E_{C1_silt} = 2.7 would be expected. Similarly, using data from Danish arable soils, CHRISTENSEN (1996) proposed the power functions

$$E_{C2\_clay} = 39.7 * x_{clay}^{-0.84} \qquad \textbf{Equation 5.3}$$

$$E_{C2\_silt} = 59.0 * x_{silt}^{-1.30} \qquad \textbf{Equation 5.4}$$

with

E_{C2_clay} = C enrichment factor for clay (CHRISTENSEN, 1996)
E_{C2_silt} = C enrichment factor for medium and fine silt (CHRISTENSEN, 1996)

which resulted in expected $E_{C2\_clay} = 6.8$ and $E_{C2\_silt} = 2.6$. The results for the clay fraction of Halle (mean $E_C = 3.8$) and the smaller silt fractions (mean $E_C = 2$) agreed very well the power functions of LEINWEBER (1995), which were calibrated on sites that were comparable to the „Ewiger Roggen". They coincided satisfactorily with those of CHRISTENSEN (1996).

CHRISTENSEN (1996) cited several studies with arable soils low in macro-organic matter, where most of the carbon was found in the silt and clay fraction, and the clay fraction generally accounted for more than 50% of the whole carbon in the soil. On the contrary, LEINWEBER (1988) found in long-term experiments on pleistoceneous substrate, that clay contained 20-50% and silt 30–50% of the total carbon in the soil, which was comparable to the results of the Halle soil.

The C/N ratios of the size fractions of all sites peaked in the coarse silt fractions for all sites except for Ha-M_0, it was lowest in the clay fractions with values from 9.6 to 10.4, increased in the silt fractions (16.1 to 29.1) and was very variable in the coarse sand fractions with values ranging from 11.7 to 42.2. Due to the low N-content in the medium sand fraction, for only one single replicate of the medium sand fraction of Ha-M_{NPK} (Figure 5.2) a measurement was possible, thus the C/N ratio of 15.9 at this size fraction had to be interpreted cautiously. Method II showed again similar results to method I, for the fine clay fraction of Ha-M_{NPK} and Ha-R_{NPK}, C/N was 9.8 and 9.7, respectively. C/N was highest in the fraction of coarse and medium silt, then it was decreasing to the medium sand fraction.

The C/N ratio of the fine clay fraction in this study (9.8) compared well with the C/N ratio of the fine clay fraction in a Mollisol (7.5) and the microbial biomass in soil (8 – 12) (BALDOCK ET AL., 1992) which also indicated that substances derived from microbial biomass were accumulated in this fraction. The low C/N ratio of the coarse silt and fine sand fraction may be interpreted as a slower turnover of the SOM in this fraction. Similar to this study, AMELUNG ET AL. (1998) found in four size fractions <2 µm, 2-20 µm, 20-250 µm and >250 µm, that the finer the size fraction, the lower was its C/N ratio. The high C/N ratios of the coarse sand fractions suggested that the organic material in this fraction was fresh or little altered plant material, whereas more decomposed plant debris was located in the fine sand or finer fractions.

Similar to the C-content in the size fractions, the N content follows a power function that is dependent on the fraction of the particular size fractions in the soil. Average nitrogen

enrichment ratios were highest in the clay fraction (E_N = 5.7) and decreased with increasing particle size over the smaller silt fractions (E_N = 2.9), the coarse silt fraction (EN = 1.5) to the fine and medium sand fraction (E_N = 0.2, respectively), it increased at the coarse sand fraction (E_N = 0.5). These results agreed very well with the published power functions

$$E_{N1\_clay} = 25.34 * x_{clay}^{-0.74} \quad \textbf{Equation 5.5}$$

$$E_{N1\_silt} = 26.98 * x_{silt}^{-0.96} \quad \textbf{Equation 5.6}$$

$$E_{N2\_clay} = 36.6 * x_{clay}^{-0.76} \quad \textbf{Equation 5.7}$$

$$E_{N2\_silt} = 46.0 * x_{silt}^{-1.28} \quad \textbf{Equation 5.8,}$$

as for the clay fraction E_{N1_clay} = 5.4 (LEINWEBER, 1995) or E_{N2_clay} = 7.5 (CHRISTENSEN, 1996), for the smaller silt fractions, E_{N1_silt} = 2.7 (LEINWEBER, 1995) or E_{N2_silt} = 2.2 (CHRISTENSEN, 1996) were expected.

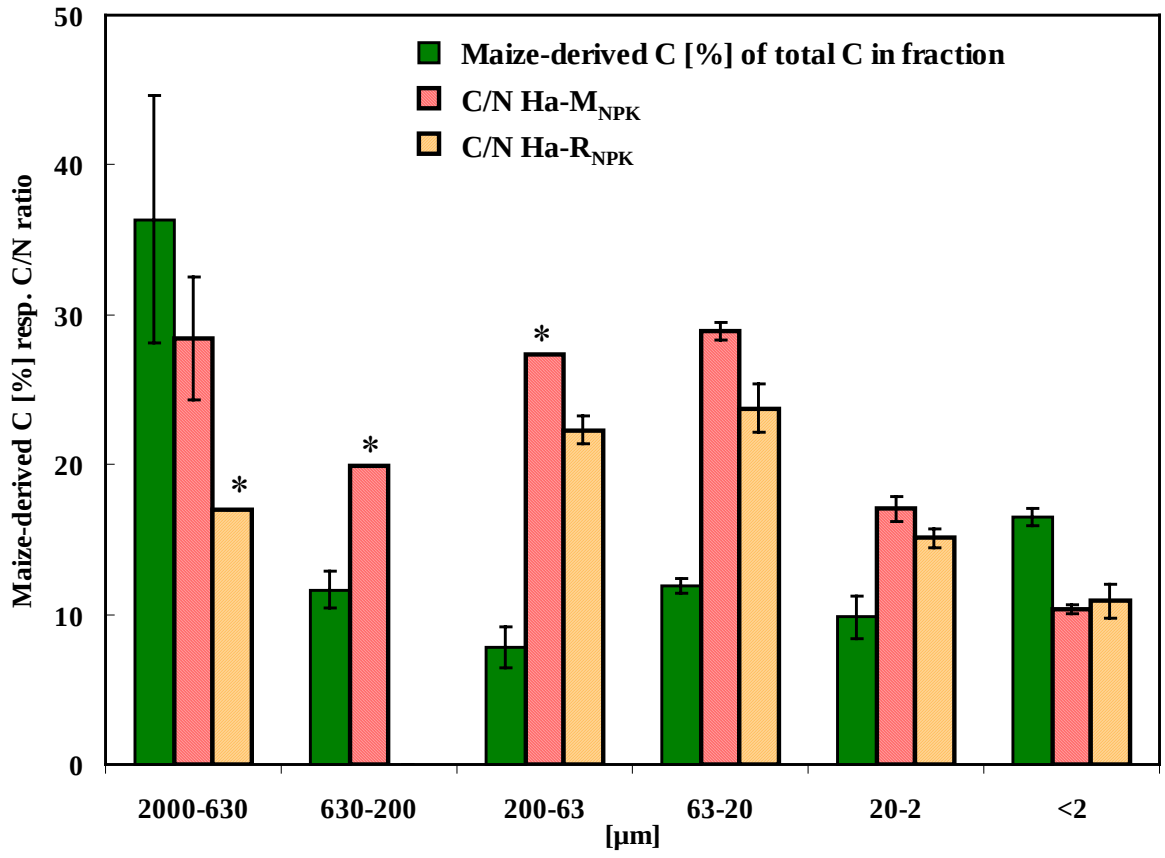

Figure 5.2: Distribution of C/N (Ha-M_{NPK} and Ha-R_{NPK}) and maize-derived C (Ha-M_{NPK}) among size fractions. Means and SE (n=4). *: only one measurement possible.

5.2.1.4 Distribution of maize-derived C and ^{14}C in size fractions

Maize-derived percentages of the carbon (Method I) were calculated for Ha-M_{NPK} and Ha-M_0. At Ha-M_{NPK}, coarse sand had a significantly higher maize-derived percentage (36.4%) than

all other size fractions (Figure 5.2). The maize-derived percentage of the fine silt to medium sand fractions ranged from 7.8 to 11.9% maize-derived C, thus it was depleted in younger carbon as compared to the bulk soil. The clay fraction (0-2 µm) had a slightly larger content of maize-derived C (16.5%) than the SOC. Maize-derived percentages in the fine sand fraction were significantly lower than in the clay fraction, the remaining fractions exhibited no significant differences. At Ha-M_0 (Figure 5.3), maize-derived percentages were significantly highest in the coarse sand fraction (24.7%). Maize-derived carbon was decreasing with particle size up to the fine sand fraction (5.3% maize-derived C), then it was increasing again with decreasing particle size to the clay fraction (10.9% maize-derived C). No significant differences could be found among the size fractions smaller than the coarse sand.

With method II, in the Ap horizon of M_{NPK}, the same trend as for method I was discernable: the fine clay fraction (0-0.2 µm) had a larger-than-average content of maize-derived C (18.5%), maize-derived percentages were decreasing to the fraction of coarse and medium silt (5.9%) and increasing up to 20.6% at the medium sand fraction.

The high maize-derived percentage of the fine clay fraction (0-0.2 µm) suggested that substances derived from microbial biomass or fresh substrates were accumulated in this fraction. Consistent with this, by applying ^{14}C-dating to Ap-horizons of three Borolls, ANDERSON & PAUL (1984) found that coarse clay (0.2 to 2 µm) and fine silt (2 to 5 µm) contained the oldest SOC, but for one soil the coarse silt (5-to 50 µm) appeared to encompass the oldest SOC. The SOC in fine clay (<0.2 µm) was invariably the most enriched in ^{14}C and was thus taken to have the fastest rate of turnover. Fine clay was won by freeze-drying the suspension left after removal of larger size particles, thus, SOC that came into solution during the fractionation procedure and accumulated in the fine clay fraction. This soluble substance might be dominated by contributions from recently added substrates and from cell contents of C_{mic} killed during soil dispersion and was likely very young. However, ROSCOE ET AL. (2000) hypothesized that sonification manufactured C from different sources in the clay fraction.

C/N measurements and $\delta^{13}C$ values of the size fractionation indicated that the fine sand fraction (Method I) and coarse and medium silt (Method II) fractions were the most stable fractions, however, differences were not significant. Similar to our study, BALESDENT ET AL. (1998) reported for the silt fraction of soil in a forest-cultivation sequence that it contained some very stable C. Also, CHRISTENSEN (1996) suggested that SOC in the silt fraction is the most stable SOC particle fraction in temperate soils. The relatively large ratio of maize-derived C (17.5%) in the coarse sand fractions (Method I) and medium sand fraction (method II) may be derived from fresh substrate. GREGORICH ET AL. (1996b) and LUDWIG ET AL. (1998) also reported that the sand fraction contained considerable higher amounts of maize-derived C than the silt fraction, however, they did not differentiate the sand fraction further

but drew their conclusions only for the whole sand fraction. The order of turnover rates in the particular separates agreed well with decomposition studies of CHRISTENSEN (1987) who found that degradability of SOM decreased in the order sand (2000 – 20 µm) > clay > silt (20 - 2 µm). Low O/C ratios indicate aromatic structures that are typical for pyrogen C. In size fractions from Halle, O/C ratios were highest (0.27 ± 0.02) in the medium and coarse sand (250-2000 µm), followed by the fine and medium sand (0.16 ± 0.04; 63 - 250 µm). There was no difference between the silt (2-63 µm) and clay (<2 µm) fraction (0.11 ± 0.02 and 0.12 ± 0.02), respectively (BRODOWSKI ET AL., 2003).

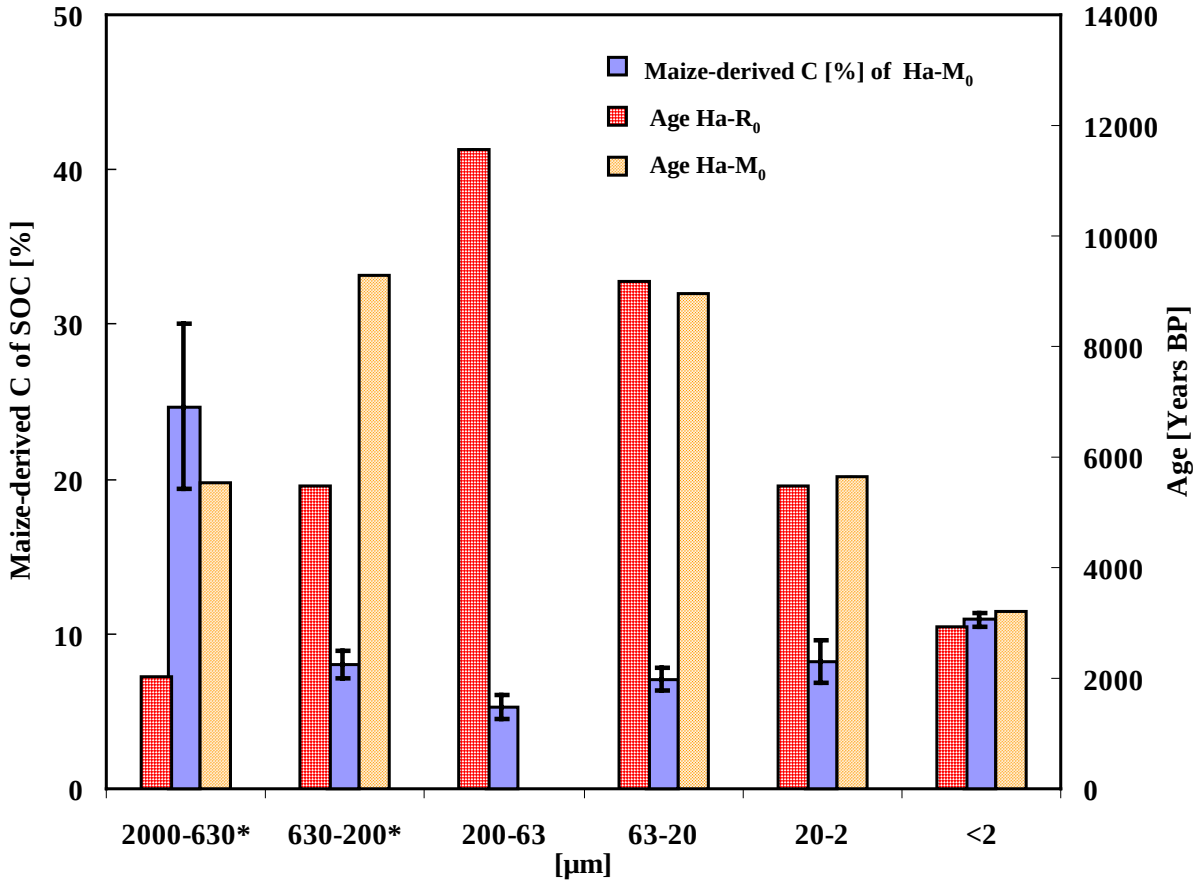

Figure 5.3: Distribution of maize-derived C (Ha-M_0, n=4) and ^{14}C-age (Ha-M_0 and Ha-R_0, combined samples) among size fractions. For the maize-derived C, means and SE (n=4) are given. * ^{14}C contents of the coarse sand (2000-630 µm) and medium sand (630-200 µm) were measured after the separation of coal particles and plant residues.

^{14}C-measurement at the particle size fractions of the unfertilized variants of the Halle soil indicated a decrease from the clay fractions to the fine sand fractions (Figure 5.3). The heterogeneity of the coarser sand fractions was demonstrated by ^{14}C measurements of subfractions: After the sorting of the medium sand of Ha-M_0, the mineral fraction had a pMC of 31.5 (9275 BP), the plant residues were recent with a pMC of 106.0, the coal particles were very old with 4.0 pMC (25775 BP). Similarly, in the total coarse sand, the mineral fraction

showed 50.2 pMC (5531 BP), the plant residues 107.7 pMC and the coal 0.85 pMC (38325 BP).

The relatively young age of the clay fraction might be caused by the relatively high enrichment of carbon from fresh residues or microbial biomass (see above). The partitioning of the ^{14}C values indicates the distribution of fossil carbon with a maximum in the fine sand fraction. Coal particles might be either charred plant residues or of anthropogenic i.e. fossil origin. The high ^{14}C content in the coarse sand (total fraction or mineral fraction) may be due to its high percentage of plant residues, which could not be removed from the mineral fraction quantitatively.

A comparison of ^{13}C- and ^{14}C-measurements showed a similar trend for these isotopes. However, since the soil at Halle is heavily polluted from anthropogenic immissions, care has to be taken when comparing ^{13}C- and ^{14}C-data.

5.2.2 Carbon turnover in water-stable aggregates from Rotthalmünster

5.2.2.1 Methodical aspects

Sieving methods and soil wetting pretreatments prior to sieving can have profound effects on the distribution of C among aggregate size fractions. A sudden wetting of dry soil causes considerable disruption (slaking) of the soil structure as a result of internal pressure that builds up when air is trapped within the pore spaces of macroaggregates. Only highly stable macroaggregates are able to withstand these forces. In contrast, slowly wetting (e.g. vapor or capillary wetting) a soil prior to wet sieving allows the air to escape with minimal disruption of existing aggregates in the soil. The macroaggregate size classes obtained by the latter approach contain relatively unstable macroaggregates in addition to those that are highly stable. Therefore, the stability of macroaggregates that survive capillary wetting is less than the stability of macroaggregates that survive slaking (CAMBARDELLA & ELLIOTT, 1993). Slaking-resistant macroaggregates had higher concentrations of new, root-derived C compared to relatively less stable macroaggregates in a capillary-wetted treatment. Conversely, microaggregates that were released from unstable macroagregates with slaking were less enriched in new, root-derived C compared to the microaggregates in the capillary-wetted treatment (GALE ET AL., 2000). As the fractionation by slaking produced more meaningful results on other soils, this method was also applied for this study.

5.2.2.2 Distribution of water-stable aggregates

In the topsoils, the distribution of aggregate size classes was influenced by land cultivation: the most important fractions were the microaggregates (53-250 µm) for maize, the smaller macroaggregates (250-1000 µm) for wheat (Table 10.3) and the megaaggregates (>2000 µm)

for the grassland and forest soils (Table 10.4). At the grassland and forest, surface soils were more aggregated than subsoils. The distribution of the dry matter maxima in the sites was probably due to different tillage regimes: While conventional tillage was applied to the maize culture, only conservation tillage was applied at the wheat field since 1998. No tillage took place at Ro-Grass and Ro-Forest, thus preserving their soil structure. Similarly, when comparing aggregate stability under different tillage systems, SIX ET AL. (2000) found that at three out of four sites, the fraction 53-250 µm was the most abundant under conventional tillage and the fraction 250-2000 µm the most abundant under no tillage. After wet sieving, from the loamy soil under continuous corn, 32% and 29% of the total dry weight were located in the fractions <50 µm and 50-250 µm. Contrary to this, under a meadow, only 7% of the total dry weight were located in the fraction <50 µm and the remaining soil was rather evenly distributed among the other size fractions that ranged up to >2000 µm (ANGERS & GIROUX, 1996). Seven years after its conversion from forest to maize, 28.6% of the total soil were located in the fraction >200 µm, 18% in the fraction 50-200 µm and 49.5% in the fraction <50 µm (BESNARD ET AL., 1996). Only a slight further degradation of the soil structure was measured on a nearby field after 35 year of maize cropping, 28.5% were located in the aggregates >2 mm, 17% in the size class 50 – 200 µm, and 52.5% in the size class <50 µm. Only the POM showed significant decreases with 0.71% (>200 µm) and 0.25% (50 – 200 µm), respectively. At the adjacent forest site, macroaggregates were most important with 52.4% (>200 µm), followed by 25.2% (50 – 200 µm) and 17.9% (<50 µm), respectively.

5.2.2.3 Carbon and nitrogen storage in water-stable aggregates

The carbon and nitrogen concentrations in aggregates were dependent on aggregate size (Table 10.3; Table 10.4). For all sites and depths, C-content was lowest in the fraction <53 µm. At the field soils Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org}, and Ro-Grass, C-content was second lowest in the fraction 53-250 µm, thus C content was lower in the microaggregates than in the macroaggregate fractions. No significant difference occurred for the C-content of same-sized aggregate fractions of Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org}.

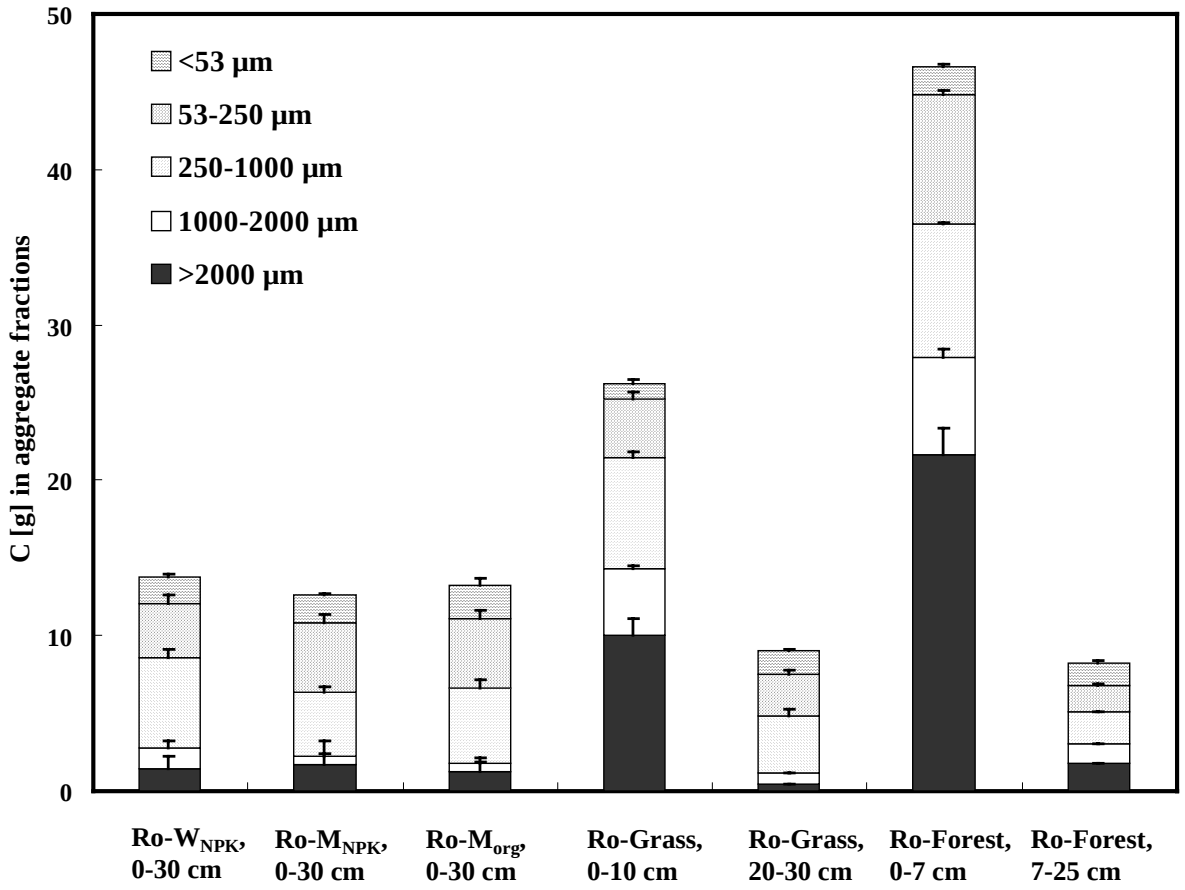

Figure 5.4: Distribution of C in 1 kg soil among aggregate fractions at Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org}, Ro-Grass, and Ro-Forest. Means and SE (n=4).

C-content in aggregate fractions from Ro-Grass was always higher than in its counterparts from the fields planted with maize or wheat, this difference was significant for all fractions >53 µm. Likewise, C-content in the aggregates of Ro-Forest was always significantly higher than in same-sized aggregates of any of the field soils. Of the total carbon in one kg soil, for Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org} the fraction 250-1000 µm stored the most carbon as compared to the other size fractions (Figure 5.4). In the surface soils of Ro-Grass and Ro-Forest, the aggregates >2 mm and in the subsoils the aggregates 250-1000 µm stored the most carbon as compared to the other fractions. When comparing the carbon storage in a meadow and a corn field, ANGERS & GIROUX (1996) found that for the meadow the fraction 1-2 mm was the most important as compared to a maize field where the fraction <50 µm stored the most C.

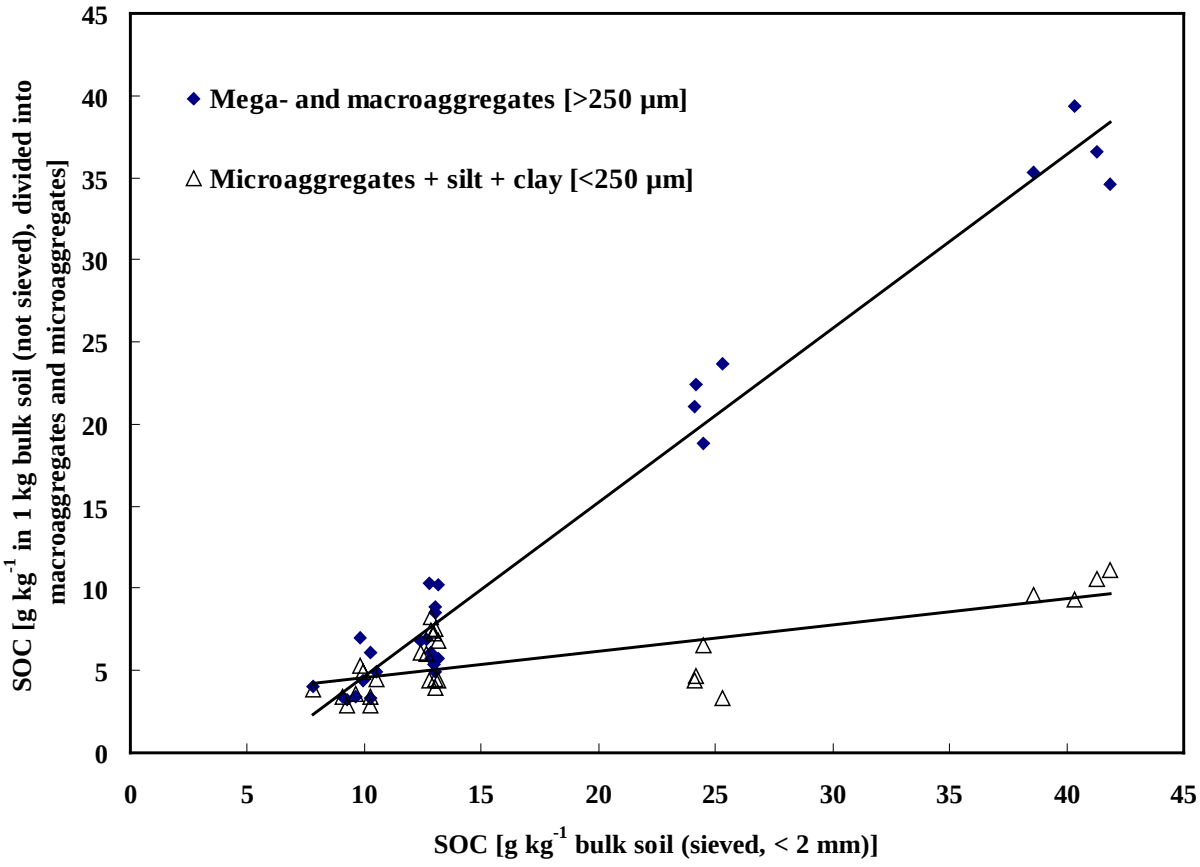

Figure 5.5: Correlation among the SOC in mega- and macroaggregates and microaggregates plus silt and clay, respectively, of 1 kg soil, to SOC in 1 kg bulk soil for Ro-W_{NPK} (0-30 cm), Ro-M_{NPK} (0-30 cm), Ro-M_{org} (0-30 cm), Ro-Grass (0-10, 10-30 cm), and Ro-Forest (0-7, 7-25 cm). All data points.

A higher slope and a higher correlation coefficient (r = 0.99) of the total C stored in the macroaggregates (>250 µm) in one kg soil to the total SOC in one kg soil as compared to the lower slope and lower correlation coefficient (r = 0.72) of the microaggregates (<250 µm) suggested that macroaggregates are more dependent on the SOC content of the soil than microaggregates (Figure 5.5). The results also proved that the amount of carbon stored in microaggregates is less influenced by cultivation than carbon in macroaggregates (chapter 2.4.2) and that carbon is mainly lost from macroaggregates if a cultivation change from forests to grasslands or further to ploughed soils takes place. The correlation coefficients between the carbon stored in aggregate fractions and the SOC in the bulk soil nevertheless indicate a higher correlation than the figure suggests as the distribution of the data is very patchy: At the narrow range from 12.4 to 13.2 g SOC kg^{-1} that belongs to the Ap-horizons of Ro-W_{NPK}, Ro-M_{NPK}, and Ro-M_{org} , the carbon stored in macroaggregates scatters from 4.9 to 10.3 g C due to the influence of cultivation and crop.

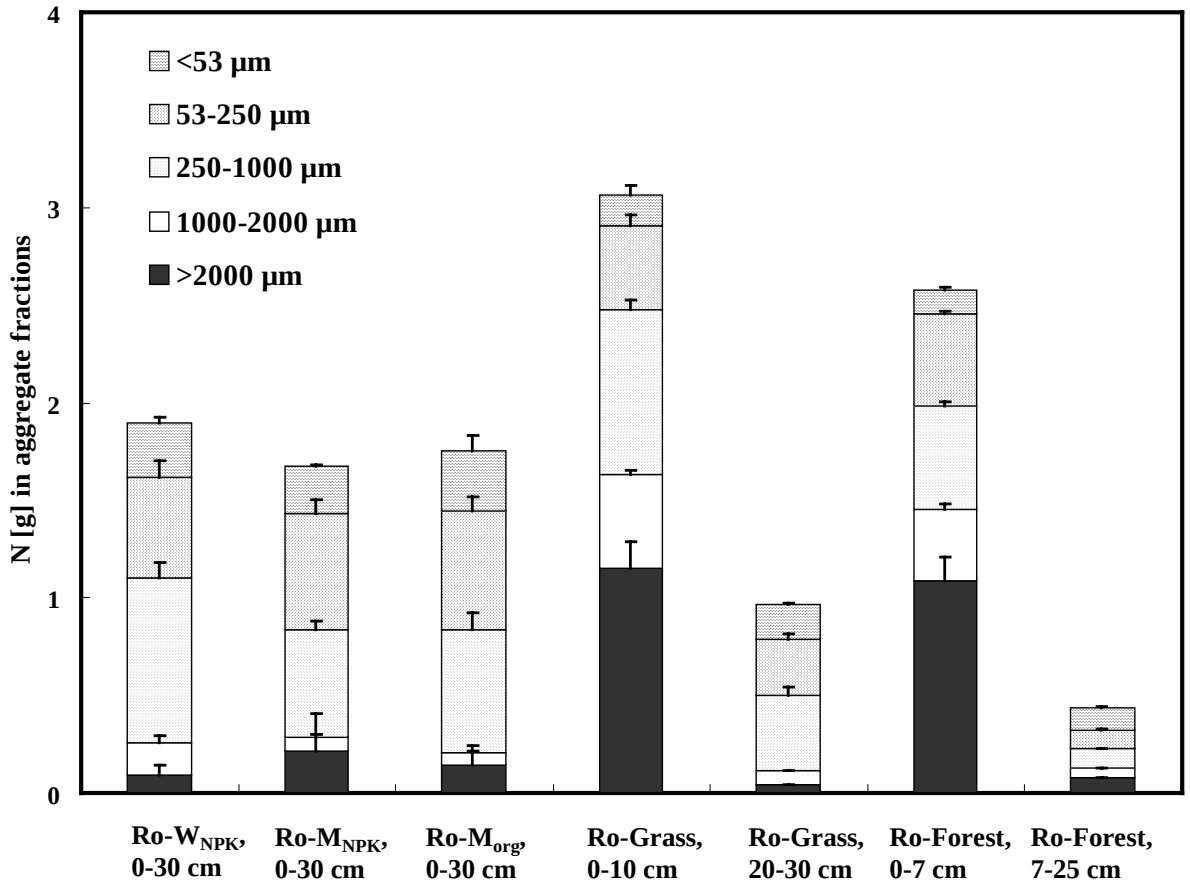

Figure 5.6: Distribution of N in 1 kg soil among aggregate fractions at Ro-W$_{NPK}$, Ro-M$_{NPK}$, Ro-M$_{org}$, Ro-Grass, and Ro-Forest. Means and SE (n=4).

For all non-forest sites, N content was smallest in the fraction <53 µm, for the other size classes of Ro-W$_{NPK}$, Ro-M$_{NPK}$, Ro-M$_{org}$, no significant differences could be found (Table 10.3; Figure 5.6). N-content in the grassland soils was always higher than at the sites cropped to wheat or maize (Table 10.4; Figure 5.6). N-content in the aggregates from the forest soil was the highest as compared to the other sites. Of the total nitrogen in one kg soil, for Ro-W$_{NPK}$ and Ro-M$_{org}$ the fraction 250-1000 µm and for Ro-M$_{NPK}$ the fraction 53-250 µm contained the most nitrogen as compared to the other size fractions. In the surface soils, for Ro-Grass and Ro-Forest, the aggregates >2000 µm and in the subsoils the aggregates 250-1000 µm stored the most nitrogen as compared to the other fractions. For all soils, C/N was lowest in the fraction <53 µm. For Ro-W$_{NPK}$, Ro-M$_{NPK}$, Ro-M$_{org}$ and Ro-Grass (0-10 cm and 10-30 cm) it was increasing with the aggregate size until the size fraction 1000-2000 µm and second highest at the fraction >2000 µm. For Ro-Forest, it was highest for the fraction >2000 µm. BALABANE (1997) showed that clay-associated organic N had slower turnover rates in microaggregates <100 µm than in larger soil aggregates.

5.2.2.4 $\delta^{13}C$ values and maize-derived carbon in water-stable aggregates

$\delta^{13}C$ values were dependent on the aggregate class (Figure 5.7). At Ro-Grass and Ro-W_{NPK}, ^{13}C content increased with particle size, indicating different turnover rates for the aggregates even for the C_3-soils, as younger material has a lower $\delta^{13}C$ values due to the decreasing trend of $^{13}C/^{12}C$ of the atmospheric CO_2 (chapter 2.3.3).

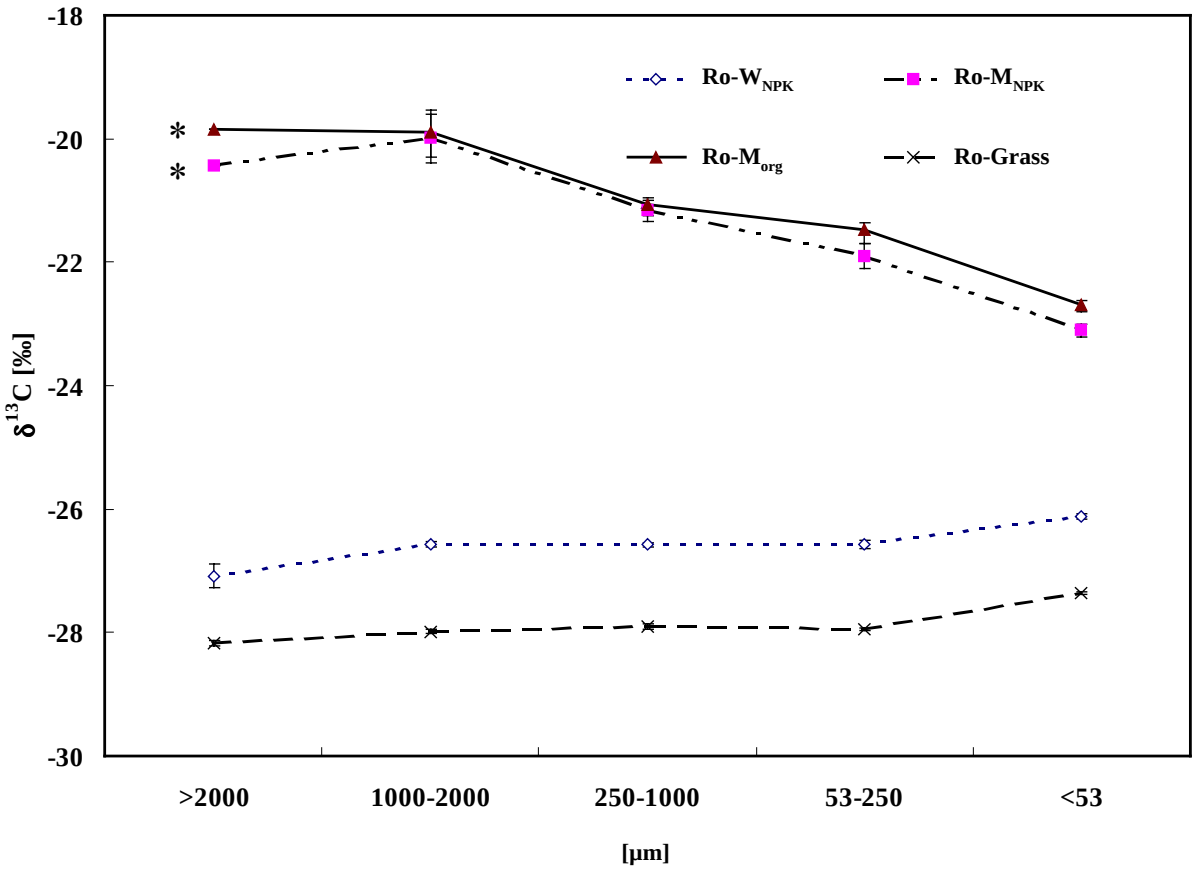

Figure 5.7: $\delta^{13}C$ values in aggregate fractions from Ro-W_{NPK} (0-30 cm), Ro-M_{NPK} (0-30 cm), Ro-M_{org} (0-30 cm), Ro-Grass (0-10 cm). Means and SE (n=4). *: only one measurement possible.

Similar to the results of this study, ANGERS & GIROUX (1996) found that ^{13}C contents were increasing with decreasing particle size under a meadow, they found $\delta^{13}C$ values of –26.8‰ PDB at the fraction <50 µm and –27.5‰ at the fraction >2 mm. Aggregates from the maize sites showed an increasing enrichment of ^{13}C with increasing particle size with one exception: the fraction >2000 µm of Ro-M_{NPK} was less ^{13}C enriched (0.4‰ PDB) than the next smaller fraction 1000-2000 µm, however, this difference was not significant.

No significant differences could be found between maize-derived percentages in aggregate classes from Ro-M_{NPK} and Ro-M_{org}. Maize-derived percentages were lowest in the fraction <53 µm with 21.1% (Ro-M_{NPK}) and 24.0% (Ro-M_{org}) maize-derived C, respectively (Figure 5.8). The percentage of young carbon was significantly higher in the fraction 53-250 µm with

32.7% (Ro-M_{NPK}) and 35.6% (Ro-M_{org}), and in the fraction 250-1000 µm with 38.1% (Ro-M_{NPK}) and 38.8% (Ro-M_{org}), no significant difference was found between those two size classes. Maize-derived percentages were significantly higher in the fraction 1000-2000 µm, with 46.9% (Ro-M_{NPK}) and 47.6% (Ro-M_{org}), respectively.

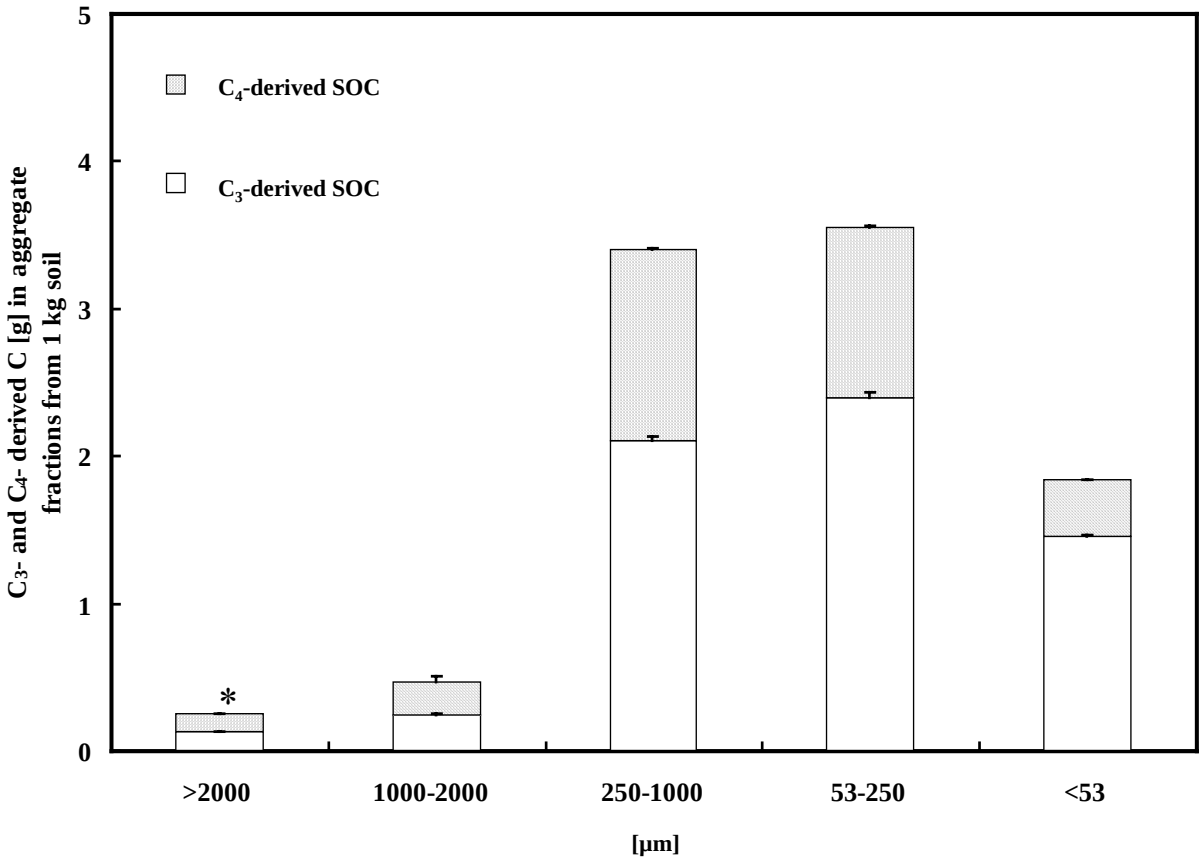

Figure 5.8: Distribution of C_3- and C_4-derived C in aggregate classes of Ro-M_{NPK}. Means and SE, n = 4. *: only one measurement possible.

The results were in line with the concept of aggregate hierarchy according to which primary mineral particles are bound together with bacterial, fungal, and plant debris to microaggregates. These microaggregates, in turn, are bound together into macroaggregates by transient binding agents (i.e., microbial- and plant-derived polysacchaarides) and temporary binding agents (roots and fungal hyphae) (TISDALL & OADES, 1982; SIX ET AL., 2000). The consequences of this aggregate hierarchy are an increase in C concentration with increasing aggregate-size class because large aggregate-size classes are composed of small aggregate-size classes plus organic binding agents (ELLIOTT, 1986). SOC that is contained in macroaggregates is younger and more labile than in microaggregates (ELLIOTT, 1986). JASTROW ET AL. (1998) evaluated that the lengths of fibrous roots and external mycorrhizal hyphae, the microbial biomass C, hot-water soluble carbohydrate C and soil organic C

explained 88% of the variation in macroaggregates >212 µm in a chronosequence of tallgrass prairie restorations.

PUGET ET AL. (2000) separated macroaggregates of 2-3 mm in diameter from two silty cultivated soils. They were slaked and seven aggregate classes (2-3 mm, 1-2 mm, 0.5-1 mm, 0.2-0.5 mm, 0.1-0.2 mm, 0.05-0.1 and <0.05 mm) were separated. When using the ^{13}C natural abundance after the conversion to maize, they found that the stable macroaggregates <200 µm were richer in total C and in young C than the unstable ones. The young C comprised 50% POM, 20% associated with silt and 30% with clay particles. They concluded that stable aggregates are formed by the binding of microaggregates by additional young SOC. Young SOC is preferentially incorporated and is responsible for aggregation, though it is eventually redistributed among aggregate classes through the destruction and re-formation of the aggregates. When calculating turnover times, they concluded that stable macroaggregates exist for a few years but that microaggregates may exist for decades. Using natural ^{13}C abundance after a vegetation change from a C_4-grassland to wheat at a loamy soil in Sidney, Nebraska, SIX ET AL. (2000) found that under conventional tillage 0.4%, 8%, and 39% were wheat-derived in the fractions <53 µm, 53-250 µm and 250-2000 µm, respectively. After 15 years of maize monoculture on a loamy silt in Québec, Canada, previously planted with C_3-meadow, ANGERS & GIROUX (1996) found for water-stable aggregates a decreasing percentage of maize-derived carbon with decreasing aggregate size: 20.5% (>2000 µm), 18.2% (1000-2000 µm), 11.6% (500-1000 µm), 8.2% (250-500 µm), 3.4% (50-250 µm) and 0.3% (<50 µm) were maize-derived.

5.2.3 Carbon turnover in density fractions from Halle and Rotthalmünster

5.2.3.1 Methodical aspects

GOLCHIN ET AL. (1994a, 1994b, 1995, 1997), who introduced the density fractionation procedure utilized in this study, applied ultrasonification to destroy aggregates. This method has the backdraw that it is known to redistribute organic material among fractions. BALESDENT ET AL. (1991) compared the soil dispersion by ultrasonification and by glass beads. They found that ultrasonification resulted in the splitting of more than half of the organic fraction >50 µm (by weight in C) into finer fractions. They also proved that the dispersion with glass beads completely dispersed a soil when they compared the weight of inorganic material in size fractions to size fractions of a soil gained by ultrasonification.

The sodium polytungstate solution that was used for the density fractionation was chosen because of its advantages over other high-density liquids. It is less toxic than solutions of $ZnBr_2$ or NaI, has a lower viscosity than other solutions at high concentrations and can be used to produce a wide range of densities (SIX ET AL., 1999).

For the recovery of the density fractions, the light fractions <2.0 g cm^{-3} were filtered (0.45 µm) and $Mineral_{>2.0}$ was washed three times to remove the salt (chapter 4.7.3). This preparation procedure resulted in a specific loss of carbon from the sample: on average, only 92.6% of the carbon, but 101.3% of the total soil were recovered. The analysis of the $\delta^{13}C$ values indicated that the loss of carbon was not specific for young or old carbon from the sample.

5.2.3.2 Photographs of density fractions

Typical photographs representing each of the density fractions <2.0 g cm^{-3} from Halle and Rotthalmünster appear in Figure 5.9. Under the microscope, no visual differences among density fractions from rye and maize (Halle) or wheat, grassland and maize (Rotthalmünster) were found. At Halle and Rotthalmünster, $FPOM_{<1.6}$ consisted mainly of recognizable plant debris with a beginning mineral encrustration. OPOM fractions of Halle apparently contained a considerable proportion of gray particles which might be charcoal or charred particles, no particles of recognizable floral or faunal origin were found. Contrary to this, OPOM fractions of Rotthalmünster contained no recognizable charred material. $OPOM_{1.6\text{-}2.0}$ of Rotthalmünster showed some plant debris with a high degree of humification, while $OPOM_{<1.6}$ appeared to contain mostly humified material and mineral-organic associated particles. Overall, the microscopic examination of the density fractions $FPOM_{<1.6}$, $OPOM_{1.6\text{-}2.0}$ to $OPOM_{<1.6}$ suggested a progressive degree of decomposition combined with an increasing degree of mineral-organic association. This is consistent with an interpretation of similar fractions (GOLCHIN ET AL., 1995; BAISDEN ET AL., 2002).

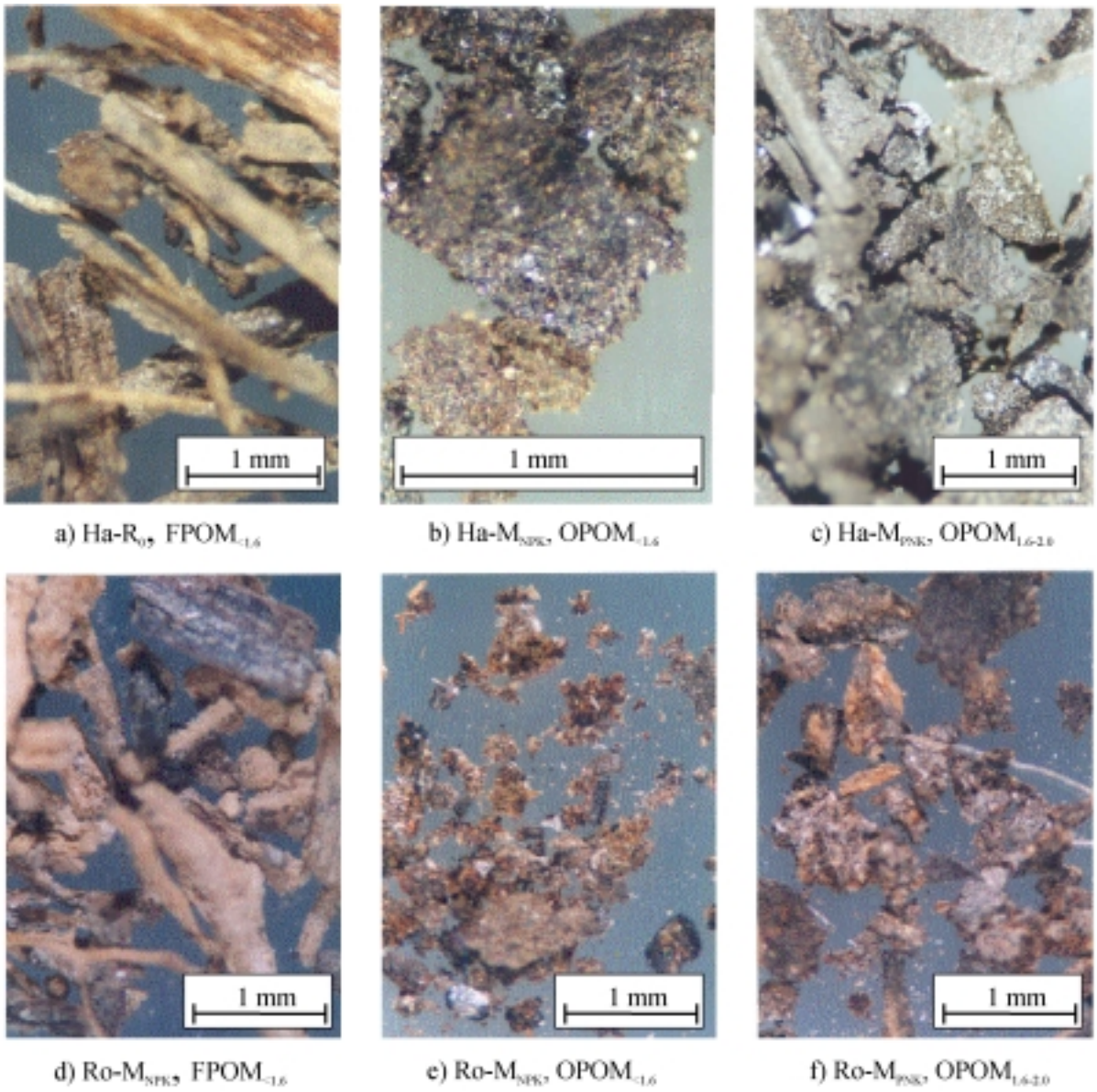

Figure 5.9: Density fractions of surface soils from Halle (0-10 cm; a-c) and Rotthalmünster (0-30 cm; d-f).

5.2.3.3 Distribution of the carbon and nitrogen in density fractions and ^{13}C in density fractions from Halle and Rotthalmünster

In respect of the C-storage, of the light fractions $OPOM_{1.6\text{-}2.0}$ was most important, followed by the $FPOM_{<1.6}$, whereas the $OPOM_{<1.6}$ was only of minor importance for carbon storage. The major part, however, was located in the mineral fraction $Mineral_{>2.0}$. At Halle, of the total SOC in the soil, 6.3 – 9.6% were located in the $FPOM_{<1.6}$, 2.0 – 4.5% in the $OPOM_{<1.6}$ and 11.2 – 20.7% in the $OPOM_{1.6\text{-}2.0}$. The remaining C was in the mineral fraction $Mineral_{>2.0}$. The percentage of C of the total SOC was lower in the mineral fractions of soils under NPK-fertilization with 60.0% at $Ha\text{-}R_{NPK}$ and 63.6% at $Ha\text{-}M_{NPK}$ than in the unfertilized soils with 67.6% under $Ha\text{-}R_0$ and 66.6% under $Ha\text{-}M_0$. These results showed that fertilization favored aggregation and the protection of carbon against degradation as the relative contribution of

carbon in FPOM and OPOM to the total carbon in the soil was higher under NPK-application. This is in line with the concept of aggregate hierarchy as OPOM acts as a binding agent for aggregates (chapter 2.4.3).

At the wheat and maize sites of Rotthalmünster, the distribution of total carbon and maize-derived carbon in the density fractions exhibited a similar pattern when compared to Halle, but it was significantly different at the grassland soil. Of the total carbon in the surface soils (0-30 cm) of Ro-W_{NPK}, Ro-M_{NPK} and Ro-M_{org}, 5.7 to 6.4% were located at the $FPOM_{<1.6}$, 1.0 to 2.2% at the $OPOM_{<1.6}$ and 15.9 to 18.1% at the $OPOM_{1.6\text{-}2.0}$. The C storage of the light fractions was higher at Ro-Grassland (0-10 cm) where 10.7% of the total carbon of the bulk soil were located at the $FPOM_{<1.6}$, 3.6% at $OPOM_{<1.6}$ and 25.9% at $OPOM_{1.6\text{-}2.0}$. C storage was highest for all soils at the mineral fraction with 75 – 77% at Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org} and 60% at Ro-Grass. An overview of the distribution of the carbon in 1 kg of soil of the respective plots is given in Figure 5.10.

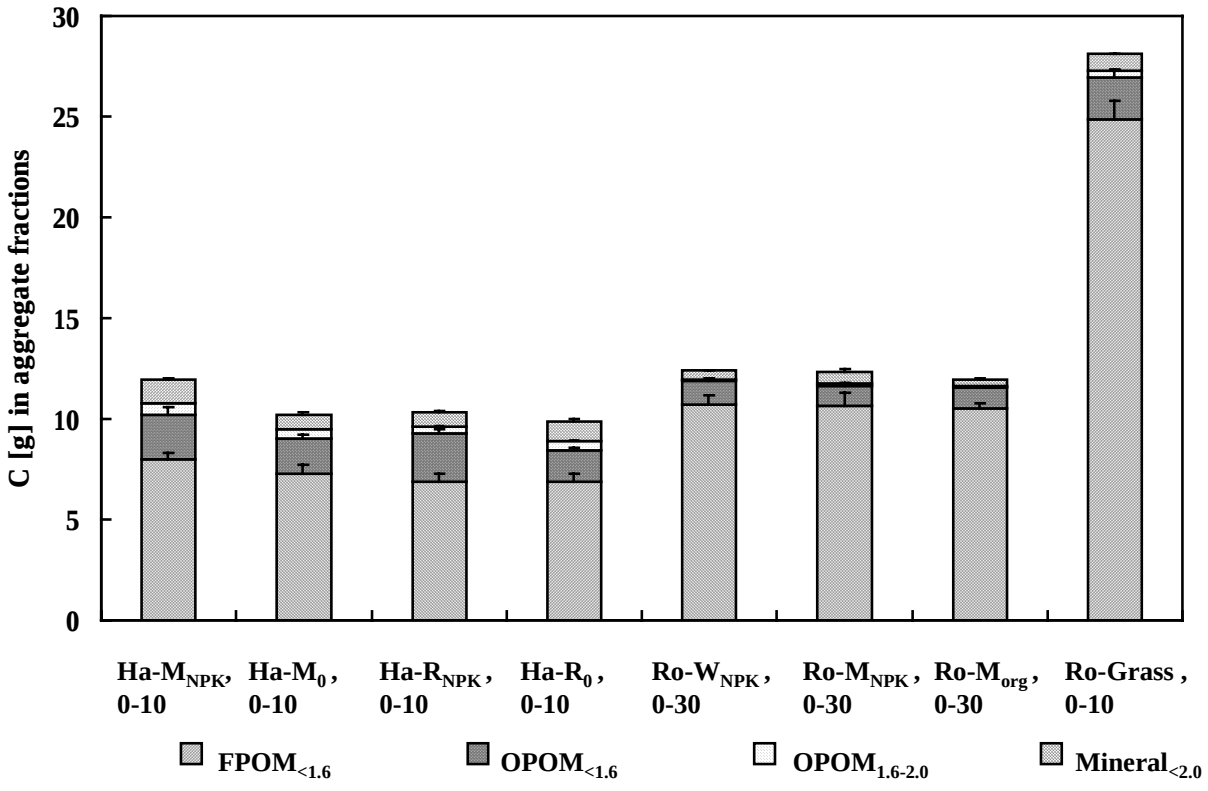

Figure 5.10: Distribution of C in 1 kg soil among density fractions from Halle and Rotthalmünster. Means and SE (n=4).

In a soil under forest vegetation and in soils under pasture for 35 years and 83 years, GOLCHIN ET AL. (1995) found the same pattern of carbon distribution with 5 – 7% in the $FPOM_{<1.6}$, 1 - 4% in the $OPOM_{<1.6}$, 11 – 20% in the fraction $OPOM_{1.6\text{-}2.0}$ and the remaining C located in the mineral fraction. GOLCHIN ET AL. (1994 a) found for a Red-brown earth (Rhodoxeralf) under old pasture (>60 years) with 17% clay, a pH of 5.5 and a SOC-content of 2.82 that 7.7% of the total C in the soil were in the $FPOM_{<1.6}$ and 9.7% in the $OPOM_{<1.6}$. For a black earth (Pellustert) under native grassland with a clay content of 72%, a pH of 8.0 and a SOC-content of 2.8% they found that 6.9% of the total C in the soil were in $FPOM_{<1.6}$ and 15.6% in the $OPOM_{<1.6}$. Contrary to these results, BAISDEN ET AL. (2002) did not find a clear pattern concerning the C storage in density fractions (occluded particulate organic matter gained by ultrasonification) from annual grassland surface soils. In three out of five Australian soils, the C-storage in the $FPOM_{<1.6}$ was higher than in the $OPOM_{<1.6}$ (GOLCHIN ET AL., 1995). GOLCHIN ET AL. (1997) did not make size fractions first to determine whether the separated OPOM fractions derive from different size classes, but they assumed following their hierachical model described above (chapter 2.4.3), that $OPOM_{<1.6}$, OPOM 1.6-1.8 g/cm³ and OPOM 1.8-2.0 g/cm³ derive from microaggregates and the fraction OPOM 1.8-2.0 g/cm³ also partly derives from macroaggregates where it acts as a binding agent between microaggregates. Therefore, as Ro-Grass (0-10 cm) contains a higher percentage of macroaggregates, the relative contribution of the fraction $OPOM_{1.6\text{-}2.0}$ to the total SOC was higher than at the cropped soils. Similar to the results in this thesis, studies in western Canada reported that application of N fertilizer significantly increased the carbon in light fractions in continuous cropping systems (BIEDERBECK ET AL., 1994).

5.2.3.4 Distribution of maize-derived carbon and ^{14}C in density fractions

Maize-derived percentages were highest in the $FPOM_{<1.6}$ with 22.9% at Ha-M_{NPK} and 25.9% at Ha-M_0. The lowest maize-derived percentages were in the $OPOM_{<1.6}$ with 1.34% at Ha-M_{NPK} and 2.3% at Ha-M_0. Maize-derived percentages in the $OPOM_{1.6\text{-}2.0}$ were 7.4% at Ha-M_0 and 4.1% at Ha-M_{NPK}. After the separation of the lighter fractions, the remaining mineral fraction >2.0 g cm^{-3} contained 16.4% (Ha-M_{NPK}) and 11.4% (Ha-M_0). Absolute standard deviations of the maize-derived percentages were highest at $FPOM_{<1.6}$, due to the high heterogeneity in this fraction.

Maize-derived percentages of Ro-M_{NPK} and Ro-M_{org} were highest at $FPOM_{<1.6}$ with 59.1% at Ro-M_{NPK} and 55.7% at Ro-M_{org} and lowest at $OPOM_{<1.6}$ with 25.4% at Ro-M_{NPK} and 17.4% at Ro-M_{org}. The fraction $OPOM_{1.6\text{-}2.0}$ showed intermediate values with 38.3% at Ro-M_{NPK} and 40.4% at Ro-M_{org}. The mineral fraction had maize-derived percentages of 31.5% at Ro-M_{NPK} and 34.8% at Ro-M_{org}.

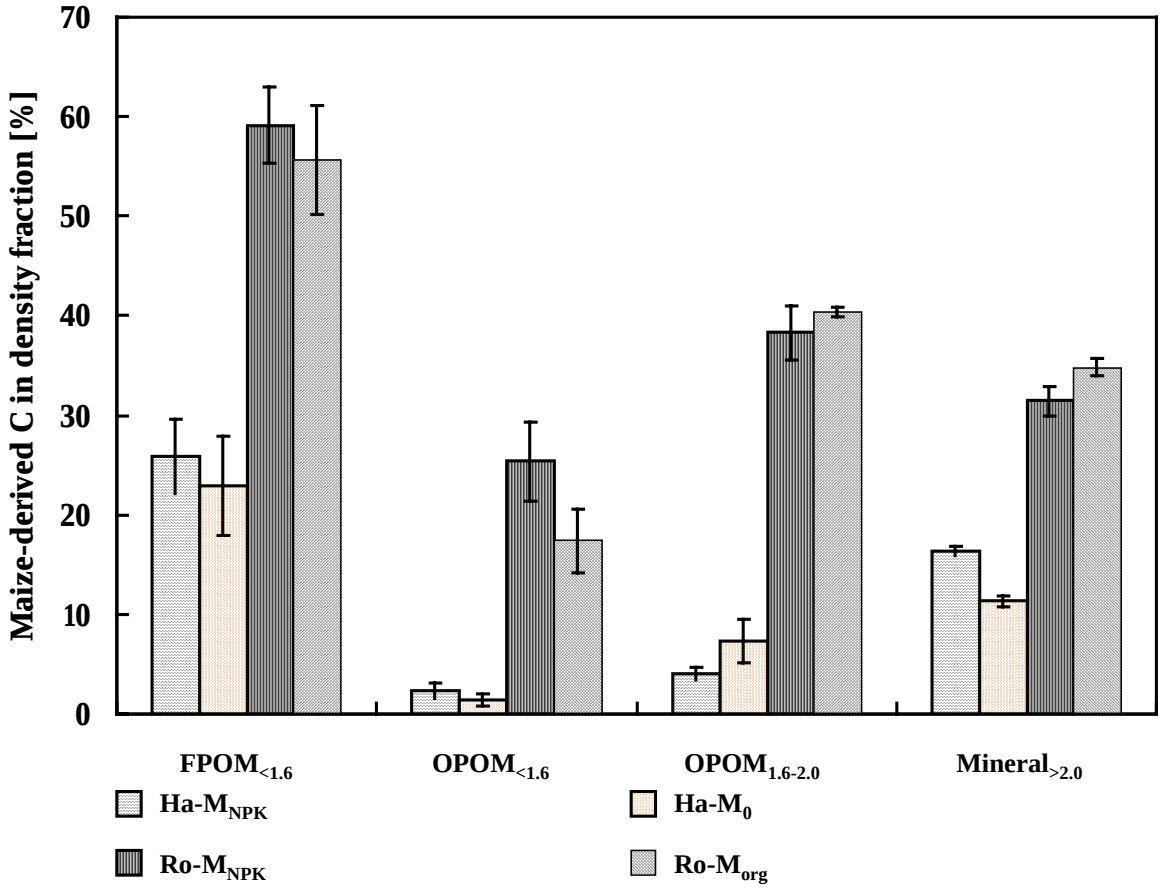

Figure 5.11: Distribution of maize-derived C among density fractions of Ha-M_0 and Ha-M_{NPK} (0-10 cm, respectively), Ro-M_{NPK} and Ro-M_{org} (0-30 cm, respectively). Means and SE (n=4).

Both sites featured a similar pattern concerning the distribution of young organic carbon among the density fractions. The % C of total C in the soil were highest in the mineral fraction, followed by $OPOM_{1.6-2.0}$, $FPOM_{<1.6}$ and $OPOM_{<1.6}$. The high percentage of maize-derived carbon in the $FPOM_{<1.6}$ was due to the unprotected position in the soil and the resulting higher turnover rate. However, maize-derived percentages in the density fractions were higher at Rotthalmünster due to the higher input of maize residues and the subsequent higher carbon turnover at this site.

^{14}C-analysis of different density fractions of Halle proposed prominent age differences. However, the age of all density fractions was well below the actual pMC (Figure 5.12). This indicated the accumulation of black carbon in the density fractions. The highest accumulation occurred at $OPOM_{<1.6}$. The trend of the age was the same as for the ^{13}C analysis (Figure 5.11), however, similar to the ^{13}C and ^{14}C measurements in the size fractions, care has to be taken when comparisons between these two methods are made due to the high anthropogenic pollution. In contrast to the results from Halle, the ^{14}C contents of different density fractions from Rotthalmünster were all close to the actual pMC, thus indicating a fast turnover of the

aggregates. The light fractions of Ro-W_{NPK} were younger than those of Ro-M_{NPK}, indicating a higher carbon turnover. Contrary to this finding, $Mineral_{>2.0}$ was older at Ro-W_{NPK} than at Ro-M_{NPK}. Again, $OPOM_{<1.6}$ was the oldest fraction, due to its protected position in the soil. No difference could be found between $Mineral_{>2.0,}$ $FPOM_{<1.6}$ and $OPOM_{1.6\text{-}2.0}$. The high age of the fractions <2.0 g cm^{-3} at the Halle soils as compared to the Rotthalmünster is also in line with the observations under the microscope (Figure 5.9).

The results comply the hypothesis of GOLCHIN ET AL. (1997) who proposed that the FPOM has the highest turnover rate, followed by the occluded organic matter (chapter 2.4.3). Using ^{13}C CP/MAS NMR, GOLCHIN ET AL. (1994 a, b) found that the largest proportion of the organic carbon contained in the free light fractions of these soils was O-alkyl, followed by alkyl, aromatic and carbonyl carbon, respectively. There was more alkyl, aromatic and carbonyl carbon in the $OPOM_{<1.6}$, but less O-alkyl carbon. Thus their results proved that the OPOM was further degraded than the $FPOM_{<1.6}$. Thus, BALDOCK ET AL. (1992) suggested that the three successive stages of decomposition were loss of O-alkyl carbon leading to exposure and loss of aromatics, with alkyl materials being the most stable. BESNARD ET AL. (1996) found that POM occluded inside microaggregates turned over slowly, in contrast to POM in macroaggregates.

The analysis of the light fraction (<2.0 g cm^{-3}) of an Ah horizon of a Gleysol by Py-FIMS resulted in mass spectra and thermograms similar to those of primary plant materials. The corresponding heavy fraction (>2.0 g cm^{-3}) was characterized by larger abundances of carbohydrates, lignin decomposition products, alkylaromatics, N-containing compounds and peptides. Their volatilization at +40 to +70 K higher pyrolysis temperatures suggested stronger chemical bonds within humic macromolecules or to minerals (SCHULTEN & LEINWEBER, 1999). When comparing the organic structure of the free and occluded fractions in the red brown earth to the chemical composition of sand- and silt-sized aggregates, GOLCHIN ET AL. (1994 a) found remarkable similarities. This indicated that at least some of the material separated as silt-size aggregates were occluded organic particles released as the result of aggregate disruption by sonification.

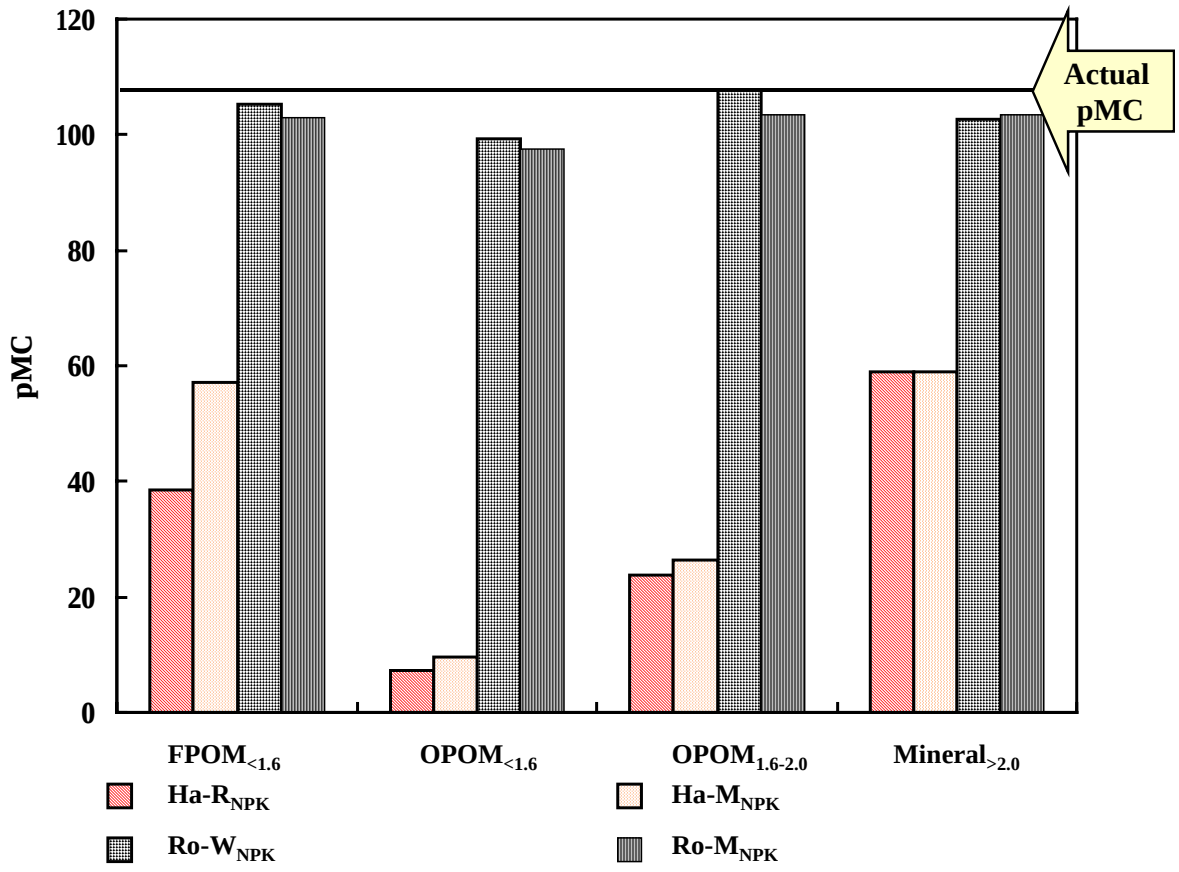

Figure 5.12: Distribution of ^{14}C among density fractions from Ha-M_0 and Ha-M_{NPK} (0-10 cm, respectively), Ro-M_{NPK} and Ro-M_{org} (0-30 cm, respectively). Measurements of composite samples.

5.3 Carbon turnover in the microbial biomass

5.3.1 Methodical aspects

The comparison of the methods for the killing and extraction of the microbial biomass as well as the determination of maize-derived percentages in the extracts was an important aspect of this thesis. Thus, an in-depth discussion of the methods is given at the beginning of this chapter.

5.3.1.1 Killing of the microbial biomass

Studies on the decomposition of ^{14}C labeled rye grass showed that a significant fraction with strong isotope enrichment was extractable after killing of the microorganism in the soil after chloroform fumigation. The fumigation of soil material with chloroform causes the breakup of cellular membranes of living organisms. During the following 24 h incubation a degradation of polymers to oligomers and monomers by autolytic processes takes place, that

produces a higher percentage of extractable material in the soil (JENKINSON, 1966). The development of the chloroform-incubation (CFI) method (JENKINSON & POWLSON, 1976) allowed soil scientist to become increasingly skilled at quantifying the soil microbial biomass C compared with older techniques of plate counting and microscopic enumeration (HANEY ET AL., 2001). Underestimation of the microbial biomass in recently amended, low pH, or waterlogged soils with the CFI method with substraction of a control prompted the development of the chloroform fumigation extraction method to try to overcome these difficulties (HANEY ET AL., 2001). Both, the fumigation-incubation (CFI) and the fumigation-extraction (CFE) method give direct access to the soil microbial tissue (JENKINSON, 1988). Further methods of measuring the soil microbial biomass include the substrate-induced respiration (SIR) and the physiological analyses of the soil microbial biomass, such as extractable phospholipid fatty acids (PLFA) (BAILEY ET AL., 2002).

Trace levels of chloroform C may remain in fumigated extracts from the CFE procedure. Although such contamination is insignificant with respect to the determination of C_{fum}, it may be significant in the determination of $\delta^{13}C$ values of the fumigated extracts. Thus, a different approach to the measurement of the microbial biomass C is the direct extraction of freeze-dried soil as proposed by ISLAM ET AL. (1997). With no protective additives, freeze-drying is lethal to most living systems, thus the underlying principle of that method is that rehydrating a freeze-dried soil releases cytoplasmic organic compounds from desiccated and disrupted microbial cells. An overview of the processes governing the killing of the biomass by freeze-drying is given by ISLAM ET AL. (1997): An initial rapid cold shock alters the permeability of the cell due to a phase transition in the membrane lipoproteins, subsequent rapid crystillization within the membrane lipid bilayer causes degradation of cellular constituents into smaller components and thus creates hypophilic channels that allow solutes to escape from the cell. Following this, nucleated by extracellular ice crystals that have grown through hydrophilic channels in the cell membrane the intracellular freezing of the cold cytoplams occurs. These intracellular ice crystals cause conglomeration of membrane macromolecules and exert pressures that cause mechanical rupture of plasma membranes. Additionally, rapid desiccation occurs by sublimation of ice crystals and partial loss of bound water from the hydration layer of membranes. This drying changes the configuration of the biological macromolecules, thus altering the permeability and stability of the microbial cells.

5.3.1.2 Molarity of the extracting agent

The typical extractant in the CFE method has been the 0.5 M K_2SO_4 (VANCE ET AL., 1987; HANEY ET AL., 2001). Potassium sulfate was selected for extracting soluble organic C in many laboratories after the discovery that Cl^-, such as in KCl, interfered with colorimetric determination of soluble organic C when oxidized with potassium dichromate (QUINN & SALOMON, 1964). The reason for the usage of 0.5 M K_2SO_4 rather than a more dilute extactant or water seems to be unclear and the choice seems to have been arbitrarily selected despite the

common use of water as an extractant for soluble organic C in many studies (HERBERT & BERTSCH, 1993; HANEY ET AL., 2001). The findings of the study of POWLSON & JENKINSON (1976), who used 0.5 M K_2SO_4 before and after chloroform fumigation of soils prompted further investigations into extracting chloroform-labile C (HANEY ET AL., 2001). An advantage of the high salt concentration is that microbial decomposition of very easily decomposable $CHCl_3$ labile organic material is prevented (POTTHOFF ET AL., 2003). The disadvantage of the high concentration of 0.5 M K_2SO_4 is that it has an osmotic effect on living cells during extraction (GREGORICH ET AL., 2000). Nevertheless, if microbial biomass N (N_{mic}) has to be determined simultaneously, the use of 0.5 M K_2SO_4 is inevitably necessary (SHEN ET AL., 1984; BROOKES ET AL., 1985).

The K_2SO_4 concentrations in the extractant were reduced in numerous studies to minimize the amounts of salt entering the combustion chamber of the EA-IRMS. The concentrations in the extracts range from pure water (GREGORICH ET AL.; 2000, LIANG ET AL., 2002), 0.03 M K_2SO_4 (GAILLARD ET AL., 1999), 0.05 M K_2SO_4 (ANGERS ET AL., 1995), to 0.25 M K_2SO_4 (BRUULSEMA & DUXBURY, 1996; ROCHETTE ET AL., 1999, TRINSOUTROT ET AL., 2000).

When investigating the effect of extractant molarity (distilled water and 0.001, 0.01, 0.1, and 0.5 M K_2SO_4) on the flush of C with the CFE method in 12 soils of different pH, HANEY ET AL. (2001) found large variations in extractable C in both fumigated and unfumigated samples with changes in extractant molarity. The CFE flush (i.e. fumigated minus control) across the 12 soils was an average of 129 mg C kg^{-1} soil in water, 159 mg C kg^{-1} soil in 0.001 M K_2SO_4, 161 mg C kg^{-1} soil in 0.01 M K_2SO_4, 136 mg C kg^{-1} soil in 0.1 M K_2SO_4 and 125 mg C kg^{-1} in 0.5 M K_2SO_4. However, the variability was dependent on the pH: In four out of six soils with the pH below 7, the concentration of extractable carbon was higher after extraction with water than after extraction with 0.5 K_2SO_4. On the contrary, in five out of six soils, the extractable carbon was lower after water extraction than after extraction with K_2SO_4 in soils with a pH above 7. JÖRGENSEN (1995) found that the amount of $CHCl_3$ labile organic C extracted with a 0.01 M $CaCl_2$ solution did not differ from a 0.5 M K_2SO_4 solution. GREGORICH ET AL. (2000) found that the C extracted by water or 0.125 M K_2SO_4 solution was similar in control soils and fumigated soils.

The extraction efficiency of the microbial biomass carbon using 0.5 M K_2SO_4 solution was estimated using an extraction efficiency coefficient k_{EC} (i.e. extractable part of microbial biomass C) factor (chapter 4.6). When assessing the k_{EC} factors on the basis of 153 soils (94 arable, 46 grassland and 13 forest soils) by indirect calibration using the fumigation-incubation (FI) method, JÖRGENSEN (1996) concluded that single k_{EC} values ranged from 0.23 to 0.84, with 70% of the soils ranging from 0.35-0.55 and confirmed the k_{EC} value of 0.45 of previous authors (VANCE ET AL., 1987; WU ET AL., 1990). VORONEY ET AL. (1993) and SPARLING ET AL. (1990) recommended a k_{EC} factor of 0.35. GREGORICH ET AL. (2000) and

LIANG ET AL. (2002) applied the k_{EC} factor of 0.35 after a water extraction in spite of the fact that they were determined for 0.5 M K_2SO_4 and not for water as extracting agent.

The k_{EC} factors for the extraction of freeze-dried soils using 0.5 M K_2SO_4 were calculated as 0.152 (ISLAM ET AL., 1997). The data set for the k_{EC} were 19 agricultural soils in central and southern Maryland, USA, with a pH ranging from 5.1 to 7.5.

In this study, a k_{EC} factor of 0.45 was solely applied for the calculation of C_{mic} in the Halle soils.

5.3.1.3 Measurement of $\delta^{13}C$ values in the microbial labile C

When measuring the $\delta^{13}C$ values of the microbial biomass C of a grassland soil, the 0.5 M concentration of K_2SO_4 hampered accurate mass spectrometric analysis of dried extracts by EA-IRMS. The large quantities of salt (with a relatively small amount of organic C) impaired the flash combustion in the elemental analyzer (POTTHOFF ET AL., 2003). Thus they did not obtain reliable $\delta^{13}C$ values for dried samples (oven-dried at 70 °C) containing more than 80 mg K_2SO_4. This problem was also described by GREGORICH ET AL. (2000).

To reduce the high salt concentrations of the CFE extracts for the measurement of $\delta^{13}C$ values, WANNIARACHCHI (1997) and ROCHETTE ET AL. (1999) used a dialysis membrane to remove the salt. However, POTTHOFF ET AL. (2003) found that a considerable part of the extracted C was lost by this procedure. About 25% of the C from the extract was lost after 1 h and about 70% after 5 h although dialysis membranes with a lower cut-off point (molecular weight of 1000) than the membrane proposed by WANNIARACHCHI (1997) (molecular weight of 3500) were utilized. Similar results were reported by BALESDENT & MARIOTTI (1996) who lost about 20 to 30% of fulvic acid C by applying dialysis to Na-hexametaphosphate extracts.

RYAN & ARAVENA (1994) and RYAN ET AL. (1995) proposed an off-line sample preparation technique to purify CO_2 evolved during the sample oxidation. The oxidation was performed by combustion of freeze-dried FE extracts (0.5 M K_2SO_4) at 550 °C, the produced CO_2 was purified cryogenically, and the isotopic composition ($^{13}C/^{12}C$) was determined with a dual-inlet IRMS. They obtained standard deviations of the $\delta^{13}C$ values between 0.1 and 0.9‰ PDB for the FE extracts and between 0.9 and 1.9‰ PDB for the calculated microbial C.

POTTHOFF ET AL. (2003) also described an off-line preparation technique with liquid oxidation and cryogenic purification of CO_2 with following analysis by dual-inlet IRMS that resulted in significantly smaller standard deviations of the $\delta^{13}C$ values as compared with the other methods tested (EA-IRMS or liquid oxidation with freeze-trapping of CO_2 and GC-IRMS analysis). For this thesis, the off-line preparation technique was applied for the measurement of some extracts of the microbial biomass extracted from Halle soils (data not shown). This method has a high precision due to repeated measurements of sample and reference gases

during a single isotope ratio determination, the large amount of C and homogeneity of the samples (no pulverisation is necessary), and a minimal risk of sample contamination and ^{13}C discrimination during the oxidation and CO_2 purification process. This method seems to be superior if small differences in $\delta^{13}C$ have to be detected. However, this method is laborious and comprehensive security measures are indispensable.

The UV catalysed liquid oxidation of the extracts with following detection of $^{13}C/^{12}C$ by GC-IRMS that was applied in this study for the extracts of the Halle soils has the advantages that the K_2SO_4 does not interfere with the measurements and that the sample preparation is not as time-consuming as the cryogenic purification of the CO_2 described above. Nevertheless, the method has sources of error: Because the needles are prone to freeze up, the freezing process needs to be time-limited. Therefore, freezing of the CO_2 evolving from the oxidizer was started only after a threshold value was exceeded. After the CO_2 peak had evolved, freezing was stopped when the threshold value was reached which happened before the oxidizing process ended. Therefore the peak of evolving CO_2 was only partly trapped. Nevertheless, POTTHOFF ET AL. (2003) recommend this method if a large number of samples has to be analyzed and if the extraction was done with 0.5 M K_2SO_4.

The freeze-drying of extracts that was applied for the samples of Rotthalmünster offers the advantage that it comprises all carbon in the extracts. No C is lost by dialysis or during the liquid oxidation with subsequent trapping of the evolving CO_2. Moreover, it is a very easy to use and fast procedure. The disadvantages of this method are (i) the samples might be difficult to weigh in due to an electrostatic charge, (ii) the method is only applicable to solutions with low salt concentrations, and (iii) no k_{EC} values that are applicable for a wide range of soils exist for this method. No grinding is necessary or possible due to the low amount of material that is left after the freeze drying of the water extracts.

A comparison of the results of ^{13}C-measurements of percolates with the UV-catalyzed and the freeze-drying of extracts showed that standard deviations were less with the freeze-drying method, however, no significant difference between the two methods in respect of $\delta^{13}C$ values could be found (chapter 5.4.2). From the experiences that were made during this thesis, if no N_{mic} has to be determined simultaneously and water or another extractant with a low molarity are applied for extraction, the method of freeze-drying extracts was superior to all other methods in terms of rapidity of measurements, simplicity and safety of usage.

5.3.2 Microbial biomass C at Halle and Rotthalmünster

5.3.2.1 Total extractable microbial biomass C

For the determination of the extractable microbial C of the Halle soils, the CFE method with 0.5 M K_2SO4 as extractant was employed. For the soils at Rotthalmünster, the CFE method

was compared with the freeze-drying method using distilled water as extractant. On average, the freeze-drying method resulted in 3.3 ± 0.7 times higher yields than the CFE method for soils from Rotthalmünster (Figure 5.14). There was one exception of the subsoils of Ro-M_{NPK} and Ro-W_{NPK} where the order was reversed (Table 10.8). However, the difference in the subsoils of Ro-M_{NPK} and Ro-W_{NPK} was not significant. Thus, the freeze-drying method could be either more effective in killing the microbial biomass or the higher yields in soluble carbon from the freeze-drying method were due to physical processes which made more carbon available for the extraction. ISLAM ET AL. (1997) found that freeze-drying caused a 74% decrease in the microbial activity of the soil. Optical absorbance measured at 410 nm was almost identical for extracts of both freeze-dried and field-moist soils, suggesting that rehydration of freeze-dried soil released only intracellular biomass C from the lysed cells, and did not break down nonbiomass humic C in soil. HERRMANN & WITTER (2002) estimated that up to 65% of a C flush following freeze-thaw cycles originated from the microbial biomass of the soil. The k_{EC} determined for the CFE method is 0.45 (JÖRGENSEN, 1994), it was three times higher than the k_{EC} for the freeze-drying (0.152, ISLAM ET AL., 1997), thus a higher extraction efficiency after fumigation than after freeze drying would have been expected for the soils at Rotthalmünster. This was just opposite to the results of this study. In surface mine soils under 14-year-old pine and 37-year-old red oak containing lignite and recent organic matter, freeze-drying resulted in 0.87 and 1.11 times the extraction efficiency of the CFE-method (RUMPEL ET AL., 2001). As the data base is limited, no final conclusions can be drawn from the results of this study and the cited literature concerning the question which method possessed a higher killing efficiency of the microbial biomass.

When correlating the yields of the microbial labile C of all agricultural soils of Rotthalmünster for the freeze-drying method with those of the CFE method, a correlation of $r^2 = 0.87$ could be found. A correlation of the mean values of surface soils of the agricultural soils resulted in a correlation of $r = 0.99$. Likewise, a very close relationship ($r = 0.99$) could be found in lignite-containing mining soils when comparing the mean values of the CFE-method with the mean values of the freeze-drying method and using 0.01 M $CaCl_2$ as an extracting agent (RUMPEL ET AL., 2001).

Both at Halle and Rotthalmünster (Figure 5.14), the extractable C_{mic} was significantly dependent on the SOC present in the soil (Halle (Figure 5.13): $r(C_{extr\_fum}) = 0.89$; Rotthalmünster (Figure 5.14): $r(C_{extr\_freeze}) = 0.91$, $r(C_{extr\_fum}) = 0.95$).

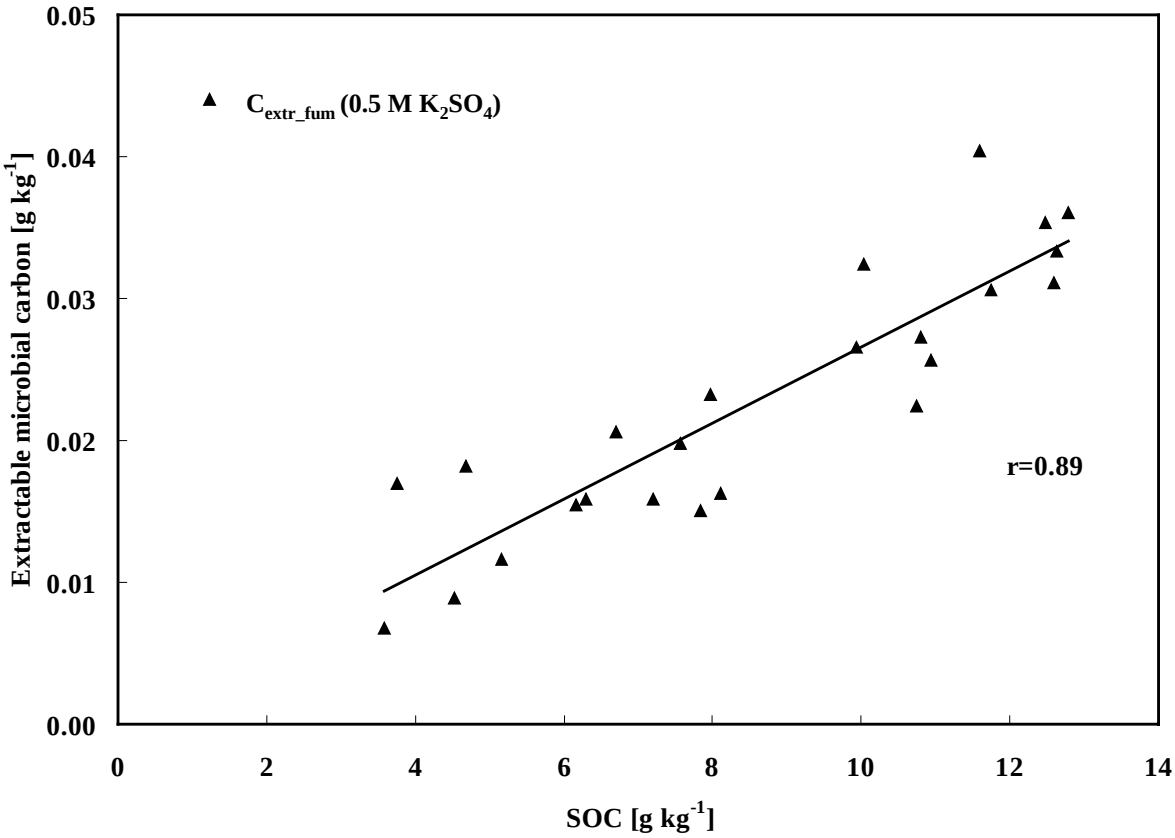

Figure 5.13: 0.5 M K_2SO_4 extractable microbial biomass after chloroform-fumigation extraction (C_{extr_fum}) correlated with SOC (soil organic carbon) for the surface soils (0-10 cm) and subsoils (30-40 cm) of Ha-M_{NPK}, Ha-M_0, Ha-R_{NPK}, and Ha-R_0. All data points.

At Halle, due to the higher input of organic matter, C_{extr_fum} was significantly higher under NPK fertilization than without fertilization in the surface soils and subsoils of all plots, whereas the crop type had no significant influence on C_{extr_fum}. For both fumigated and freeze dried soils, in the surface soils and subsoils of Rotthalmünster, the microbial biomass was highest at Ro-Grass, followed by Ro-M_{org}, Ro-M_{NPK} and Ro-W_{NPK}. Extractable microbial carbon was significantly lower in the subsoils than in the surface soils due to the reduced substrate availability both at Halle and at Rotthalmünster (Table 10.7; Table 10.8). The higher microbial activity at Ro-Grass compared to the other sites may be explained by its higher percentage of macroaggregates: A breakdown of macroaggregates by cultivation results in a release of labile SOM and its increased availability for microbial decomposition. The increased microbial activity depletes SOM, which eventually leads to lower microbial biomass and activity and consequently a lower production of microbial-derived binding agents and a loss of aggregation (SIX ET AL., 2000). After three years of manure application, ROCHETTE & GREGORICH (1998) found that C_{mic} was increased by a factor of two to three compared to a control without fertilizers, whereas N fertilization had only little effects.

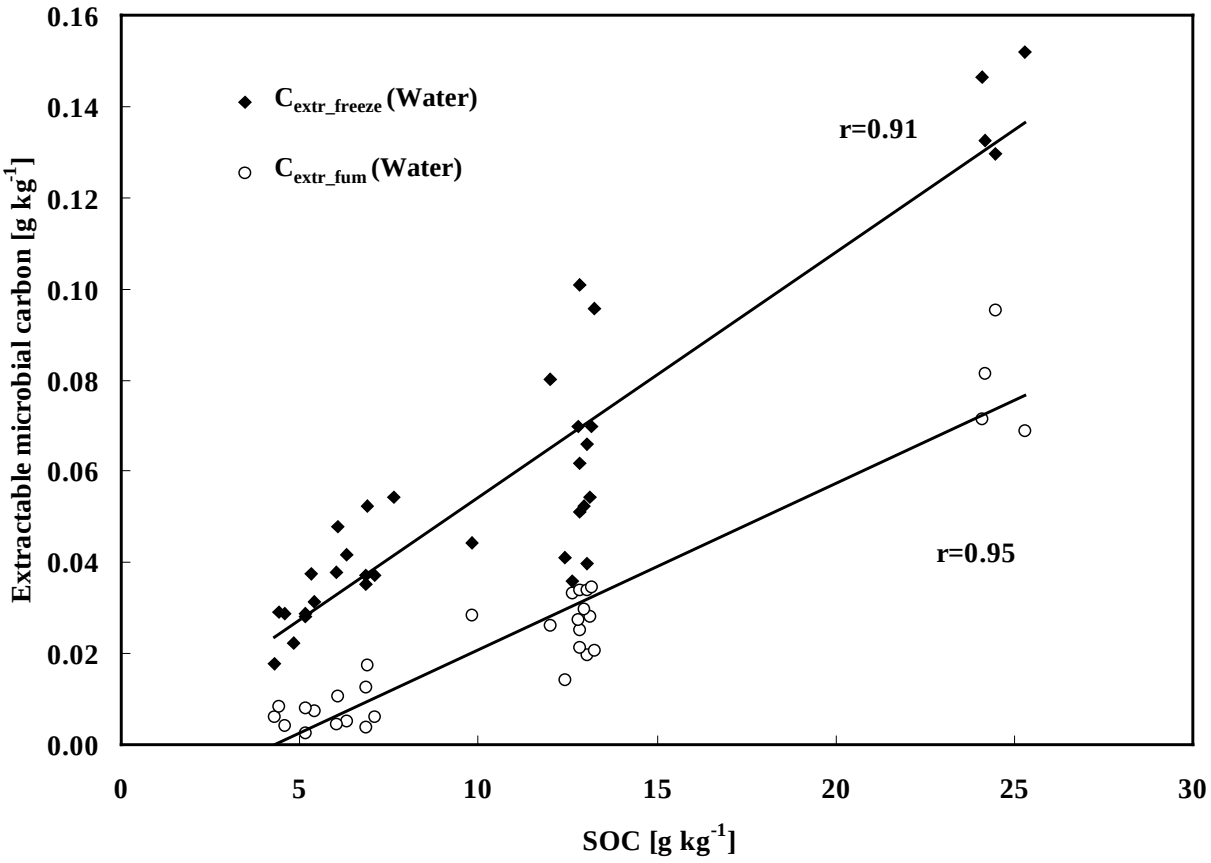

Figure 5.14: Water extractable microbial biomass after chloroform-fumigation extraction (C_{extr_fum}) and after freeze drying (C_{extr_freeze}) correlated with SOC (soil organic carbon) for the surface soils and subsoils of Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org} (0-30 cm and 30-45 cm, respectively) and Ro-Grass (0-10 cm, 10-20 cm and 30-45 cm). All data points.

Higher concentrations of C_{mic} under inorganic fertilization compared to no fertilization were also found by CAMPBELL ET AL. (1999) and BRELAND & ELTUN (1999). The C_{mic} was higher under pasture than under a maize field with conventional tillage in Upper Marlboro, Maryland, USA, microbial biomass content was highest under pasture followed by wheat and maize cultivation under conventional tillage in Clarksville, Maryland (HANEY ET AL., 2001).

In this study, the concentration of the C_{mic} was low compared to other studies (JÖRGENSEN 1996; POTTHOFF ET AL., 1999; ŠANTRŮČOVÁ ET AL., 2000). The low C_{mic} content at the Halle soils might be caused by the high sand content of the soil and thus the reduced habitat for soil microorganisms. Another explanation for the low microbial biomass content at both Rotthalmünster and Halle was the long-term monoculture with its reduced yields and subsequent lower input of biomass to the soil. ANANYEVA ET AL. (1999) found for a mollisol that soil management with long-term monoculture resulted in the greatest reduction of microbial biomass compared with either virgin soil or soils managed by crop rotation.

5.3.2.2 $\delta^{13}C$ values and maize-derived percentages of microbial biomass C

C_{mic} was ^{13}C-enriched against SOC at all variants and depths at Halle by 0.6 to 1.7‰ PDB at Ha-R_{NPK} and Ha-R_0 and 4.5 to 6.1‰ PDB at Ha-M_{NPK} and Ha-M_0. For all surface soils of Rotthalmünster, a ^{13}C-enrichment was measured that ranged in the surface soils from 0.3 to 2.2‰ PDB from C_3-variants and 0.8 to 2.6‰ PDB in the C_4-variants. At Rotthalmünster, no ^{13}C-enrichment could be found for some subsoils (30-45 cm): for the freeze-drying method at Ro-W_{NPK} (-0.5‰ PDB) and Ro-Grass (-1.1‰ PDB), for the fumigation method at Ro-M_{org} (-0.5 PDB) and Ro-Grass (-1.1‰ PDB). POTTHOFF ET AL. (2003) found for grassland soils that microbial biomass C (chloroform labile C) was ^{13}C-enriched by ca. 2‰ PDB compared with the total soil organic C. The same ^{13}C enrichment in the soil microbial biomass was described by ŠANTRŮČKOVÁ ET AL. (2000) who analysed 21 tropical and temperate grassland soils. RYAN ET AL. (1995) found a difference in $\delta^{13}C$ of 1.8‰ PDB between soil microbial biomass C and total soil organic matter for an arable soil in Canada. GLEIXNER ET AL. (1993) detected $\delta^{13}C$ values for basidiomycetes (fungi) being 1.5 to 6.0‰ PDB higher than their substrate (wood tissue). Comparable values (3.5‰ PDB enrichment of ^{13}C) were also obtained for heterotrophic bacteria (*Vibrio harveyi*) by MACKO & ESTEP (1984). The ^{13}C enrichment in microbial biomass C was a result of isotope discrimination during biosynthesis of new biomass and isotopic composition of organic compounds preferentially used by soil microorganisms (POTTHOFF ET AL., 2003). The depletion of ^{13}C in the respired CO_2 compared with biomass C indicate that catabolic reactions prefer light isotopes (ŠANTRŮČKOVÁ ET AL., 2000).

At Halle, the maize-derived C in C_{mic} was higher in the surface soil (Ha-M_{NPK}: 45.6% of the total, Ha-M_0: 38.1%) than in the subsoil (Ha-M_{NPK}: 32.3% of the total, Ha-M_0: 22.7%), however, the differences were not significant. In the surface soils of Rotthalmünster, maize-derived percentages in Ro-M_{org} were 60.2% (freeze-drying) and 58.5% (CFE), they were lower at Ro-M_{NPK} with 50.8 and 47.4%, respectively. No significant differences could be found for the maize-derived percentages of the two methods for the killing of the microbial biomass. Maize-derived percentages were less in the subsoil with significant differences among the freeze-drying and CFE method. In the subsoil, no significant differences could be found between Ro-M_{org} and Ro-M_{NPK}: Maize-derived percentages at Ro-M_{NPK} were 34.0% (freeze-drying) and 25.2% (CFE), they were not significantly lower at Ro-M_{org} with 31.3% (freeze-drying) and 24.3% (CFE). Similarly, HERRMANN & WITTER (2002) found that the C-flush after freeze-thaw cycles was short-lived and had a narrow C/N ratio, thus indicating a high degradability.

The correlation of C_4-derived extractable microbial C of the respective methods was r = 0.90 (Figure 5.15b), the plotting for the C_3-derived extractable microbial C for both methods resulted in two distinct scatterplots for the surface soils and subsoils (Figure 5.15a). This

indicates that the sources for the C_4-derived extractable carbon for both methods were less dependent on the soil depth than the sources of C_3-derived extractable carbon.

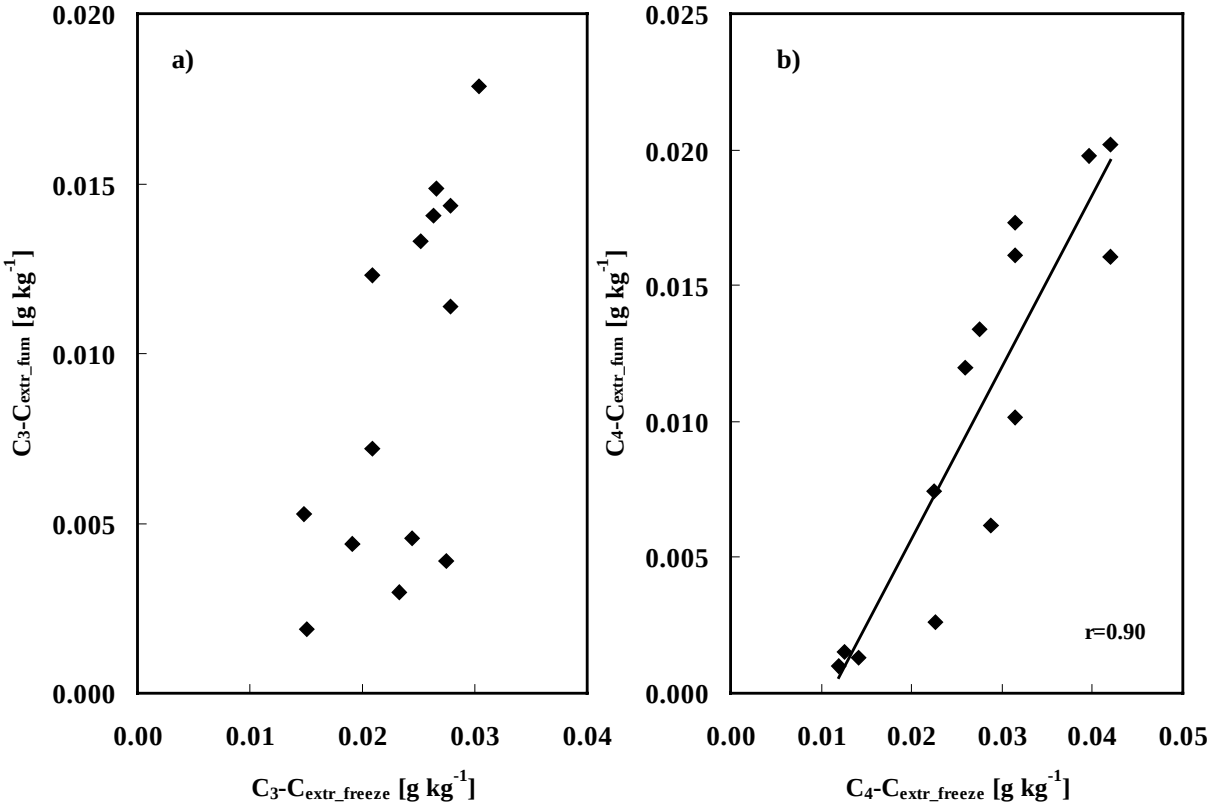

Figure 5.15: Scatterplots of a) C_3- and b) C_4-microbial labile C yielded by the freeze-drying and by the CFE-method for all data points of the surface soils (0-30 cm) and subsoils (30-45 cm) of Ro-M_{NPK} and Ro-$M_{org.}$

POTTHOFF ET AL. (2003) noted that it is completely unknown to what extent $\delta^{13}C$ values differ between the chloroform-labile and the non labile part of microbial biomass C, although such differences are likely. It is likely, that the microbial labile carbon extracted with the freeze-drying method is equivalent to the microbial labile carbon extracted with the fumigation method plus an additional part of the microbial biomass which can only be attained by freeze-drying plus an additional input of extractable carbon that can only be reached by freeze drying. It is also possible that the groups of microorganism reached by either method only partly overlap.

Before using the freeze-drying method to kill the microbial biomass for further studies, a thorough investigation concerning the processes that release extractable carbon would be advised. Probably the method of freeze-drying is not applicable for the killing of the microbial biomass as not only carbon deriving from the microbial biomass but additionally carbon deriving from physical processes was measured.

5.3.2.3 Specific production of microbial biomass C from SOC

The specific production of C_{mic} at Halle is given in chapter 5.4.6. At Rotthalmünster, the fraction of C_{extr_freeze}/SOC ranged from 0.3% to 0.7% at the surface soils and subsoils of Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org} (0-30 cm and 30-45 cm, respectively) and Ro-Grass (0-10 cm, 10-20 cm and 30-45 cm). The specific production was lower for the fumigation method, so C_{extr_fum}/SOC ranged from 0.1% to 0.3%. For the freeze-drying method, the fraction C_3-C_{extr_freeze}/C_3-SOC ranged from 0.3% to 0.4%. The fraction C_4-C_{extr_freeze}/C_4-SOC was clearly dependent on soil depth, it was 0.63% (Ro-M_{NPK}) and 0.84% (Ro-M_{org}) at the surface soils and higher in the subsoils with 1.25% (Ro-M_{NPK}) and 2.12% (Ro-M_{org}). After fumigation, C_3-C_{extr_fum}/C_3-SOC was higher in the surface soils (0.18% at Ro-M_{NPK} and 0.16% at Ro-M_{org}) than in the subsoils (0.07% at Ro-M_{NPK} and 0.09% at Ro-M_{org}). The fraction C_4-C_{extr_fum}/C_4-SOC ranged from 0.1 to 0.6 with no clear pattern concerning its interrelation to soil depth.

5.4 Carbon and nitrogen turnover in microcosm experiments with soils from Halle

5.4.1 Methodical aspects

$\delta^{13}C$ values of the DOC were determined after its liquid oxidation and freeze-trapping of the released CO_2 (Figure 4.3). To assess the quality of this method, additionally, the DOC solutions of the surface soils of Ha-M_{NPK} and Ha-R_{NPK} were freeze-dried and the $\delta^{13}C$ values were determined after flash combustion (DELTA^{plus}). With liquid oxidation (n = 5), the mean values and standard deviations for $\delta^{13}C$ values were –22.3 ± 0.6‰ PDB for Ha-M_{NPK} and -27.2 ± 0.4‰ PDB for Ha-R_{NPK}, after freeze-drying (n=4), they were –22.6 ± 0.4‰ PDB for Ha-M_{NPK} and –27.5 ± 0.2‰ PDB for Ha-R_{NPK}. The two methods did not produce significantly different results, thus, the liquid oxidation was applicable for measurements of the DOC. However, the errors were reduced with the freeze-drying method.

5.4.2 DOC leaching

DOC production was highest in the first two weeks following the rewetting of the soil. Afterwards, it remained constant (Figure 5.16 a, c). The cumulative DOC production was higher under fertilization, it decreased in the surface soil in the order Ha-R_{NPK} > Ha-M_{stalk} > Ha-M_{NPK} > Ha-R_0 = Ha-M_0, in the subsoil, the order was Ha-M_{NPK} > Ha-R_{NPK} > Ha-M_0 ≈ Ha-R_0 (Table 5.4). Similar to this findings, CAMPBELL ET AL. (1999) found after 38 years of continuous wheat cropping that water soluble carbon was less in an unfertilized soil compared to a soil with NP-fertilization.

Calculated according to BALESDENT & MARIOTTI (1996), the initial percentage of maize-derived DOC was higher at Ha-M_{NPK} and Ha-M_{stalk} than at Ha-M_0 at the surface soil (30.1% and 29.1% versus 20.9% of the total DOC) and higher at Ha-M_{NPK} than at Ha-M_0 for the

subsoil (23.4% versus 15.4% of the total DOC) (Figure 5.16 b, d). However, it decreased to 24.7% (Ha-M_{stalk}), 19.7% (Ha-M_{NPK}) and 12.9% (Ha-M_0) in the surface soil and to 6.1% (Ha-M_{NPK}) and 4.8% (Ha-M_0) in the subsoil after 230 days of incubation. A higher maize-derived percentage in water soluble organic carbon (23%) compared to SOC (12%) was also found by LIANG ET AL. (2002) in a greenhouse study where maize was grown for 110 days on a loamy sand previously managed with C_3-plants.

The total leaching of C_4-derived DOC was 0.61 g m^{-2} for Ha-M_{stalk} and 0.52 g m^{-2} for Ha-M_{NPK}. Calculated as difference, the surplus DOC leaching from Ha-M_{stalk} compared to Ha-M_{NPK} was 0.34 g DOC m^{-2} and a total of 0.86 g DOC m^{-2} or 34.8% of the total DOC was C_4-derived. C_3-derived C in the DOC was less when calculated as differences with 63% as opposed to 75% when calculated according to equation 3.4. No significant difference ($p<0.05$) among the two calculation methods was determined using a two-tailed two-sample t-test. After incubation, the mean carbon content of the remaining recent maize residues of Ha-M_{stalk} was 124 ± 13 g m^{-2}. During the incubation period over 230 days with irrigation 29.8 g CO_2-C and 0.34 g DOC m^{-2} were lost from these residues when calculated as difference between Ha-M_{stalk} and Ha-M_{NPK}. Thus, the mean biomass of the fresh residues in Ha-M_{stalk} at the beginning of the irrigation was approximately 155 ± 16 g C m^{-2}. Only 20% of these residues were lost as CO_2 or DOC during the incubation period. When incubating ground roots (<2 mm) of *Brachiaria humidicola* and *Desmodium ovalifolium* in sand at 28 °C, after 119 days, 31% and 34%, respectively, had been mineralized as CO_2 (SCHWEIZER ET AL., 1999). AJWA & TABATABAI (1994) found that 27% of maize residues (<850 µm) were mineralized after 30 days at 20 °C. The faster degradation of maize residues in these studies was probably due to chopping and mixing of residues with the soil and the higher incubation temperatures.

No significant differences of the calculations regarding the source of the DOC at Ha-M_{stalk} were found, thus indicating that no priming effect occured during the degradation of the fresh material. Since dissolved organic substances deriving from the degradation of the maize stalk are more easily decomposable than substances deriving from the degradation of the SOC, they are for the major part mineralized to CO_2, thus the much higher production of CO_2 from Ha-M_{stalk} as compared to Ha-M_{NPK} (5.4.3) and the low, though not significant, surplus production of DOC from the maize stalk as compared to the CO_2 production. This finding was in line with ZSOLNAY (1996) who concluded that much of the fresh DOC introduced or produced in the soil has a high substrate value for microbes. BRANDT ET AL. (1997) found only very small plant-derived DOC outputs from the mineral soil (40 cm depth) with ^{14}C-labeled oat straw which was incorporated in the upper 5 cm of a Luvisol and irrigated with increased amount of rainfall (1700 mm a^{-1}). After adding *Calamagrostis epigeios* litter to a Spodic Dystic Cambisol soil columns and incubating them for 130 days, LUDWIG ET AL. (2000b) measured an only slightly higher production of DOC when compared to bare soil and concluded that during soil passage much of the young DOC might have been rapidly

decomposed or sorbed. I conclude that what remains in the DOC and is finally leached out of the soil, is the more recalcitrant part that was not used by the microorganisms, thus the percentages of carbon deriving from the C_3-sources were similar for Ha-M_{stalk} and Ha-M_{NPK}.

The greater production of DOC at the rye plot could be due to the preceding tillage that favored C and N mineralization.

Table 5.4: Mean values of C_3- and C_4-derived stocks of SOC, leached DOC, respired CO_2-C and C_{mic} (microbial biomass for the surface soils and subsoils of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK} (n = 5) and for Ha-M_{stalk} (n = 4). DOC and CO_2-C are cumulative values over the incubation period of 230 days, the values for SOC and C_{mic} are from a single sampling date in September 2000

Experimental plot and depth	Origin of C	OC	DOC	CO_2-C	C_{mic}
(cm)			(g/m²)		
Ha-M_0, 0-25	Total soil	3654^{b}	1.66^{b}	16.09^{b}	21.61^{d}
	C_3	3308^{m}	1.42^{m}	7.12^{m}	13.37^{n}
	C_4	346^{w}	0.24^{x}	8.97^{y}	8.23^{x}
Ha-M_0, 25-50	Total soil	3475^{b}	1.22^{a}	5.80^{a}	16.55^{c}
	C_3	3277^{m}	1.11^{mn}	2.60^{n}	11.20^{m}
	C_4	198^{w}	0.11^{w}	3.20^{w}	5.35^{w}
Ha-M_{NPK}, 0-25	Total soil	4711^{c}	2.12^{c}	23.25^{c}	28.74^{c}
	C_3	4046^{m}	1.60^{no}	7.78^{m}	15.64^{o}
	C_4	666^{x}	0.52^{y}	15.47^{z}	13.11^{y}
Ha-M_{NPK}, 25-50	Total soil	3570^{b}	1.82^{bc}	8.16^{a}	21.62^{ab}
	C_3	3312^{n}	1.63^{no}	3.16^{n}	16.72^{no}
	C_4	258^{w}	$0.19w^{x}$	5.00^{x}	4.90^{w}
Ha-M_{stalk}, 0-25	Total soil plus stalk	4870^{c}	2.45^{c}	53.1^{e}	
	C_3	4046^{m}	1.84^{o}	9.31^{o}	
	C_4	820	0.61y	43.8z	
Ha-R_0, 0-25	Total soil	3830^{bc}	1.66^{b}	31.32^{d}	21.87^{d}
Ha-R_0, 25-50	Total soil	2561^{a}	1.20^{a}	3.82^{a}	12.49^{bc}
Ha-R_{NPK}, 0-25	Total soil	4368^{c}	2.59^{c}	47.30^{e}	28.18^{c}
Ha-R_{NPK}, 25-50	Total soil	2884^{a}	1.65^{b}	4.82^{a}	18.83^{a}

Within columns, values followed by the same letter (a-e for total amounts m-o for C_3-derived carbon and w-z for C_4-derived carbon) are not significantly different ($p<0.05$) between experimental plots and depths for SOC, DOC, CO_2-C, and C_{mic}. Maize-derived percentages of C_{mic} were extrapolated from measurements of the depth 0-10 cm and 30-40 cm, respectively.

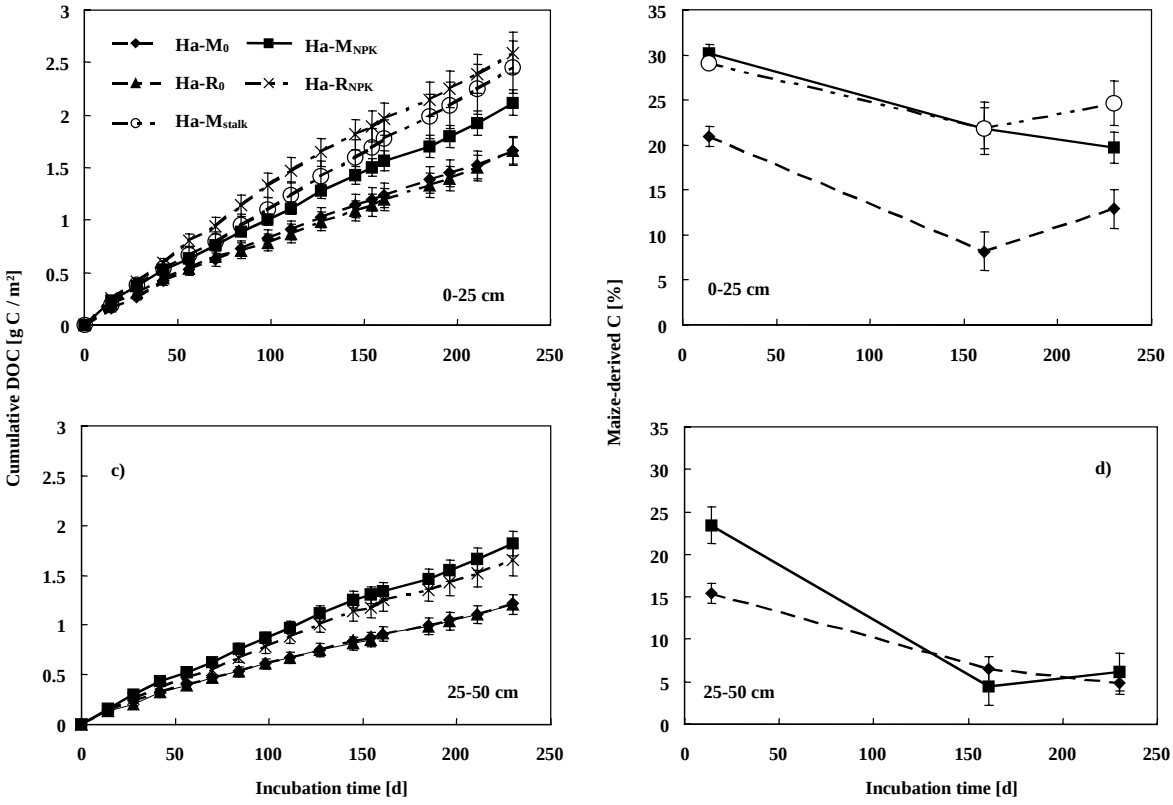

Figure 5.16: Cumulative DOC (dissolved organic carbon) leaching of the a) surface soils of Ha-M_0, Ha-M_{NPK}, Ha-M_{stalk}, Ha-R_0, Ha-R_{NPK} and c) subsoils of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK} and time dynamics of the maize-derived C [%] in the DOC of the b) surface soils of Ha-M_0, Ha-M_{NPK}, Ha-M_{stalk}, and d) subsoils of Ha-M_0 and Ha-M_{NPK}. Mean values and SE (Ha-M_{stalk}: n = 4; all other sites: n=5).

5.4.3 Soil respiration

CO_2 respiration was decreasing over time, indicating a decreasing activity of soil microorganisms (Figure 5.17 a, c). For the surface soil, CO_2 respiration was decreasing in the order of Ha-M_{stalk} > Ha-R_{NPK} > Ha-R_0 > Ha-M_{NPK} > Ha-M_0 (Table 5.4). This order reflects the decreasing availability of fresh crop residues in the soil columns: Maize residues were accumulated in areas with maize stubble (Ha-M_{stalk}), and the amount of maize residues were considerable less between maize rows where only a few roots were found (Ha-M_{NPK}, Ha-M_0). At the rye sites, crop residues were evenly distributed by tillage. The higher CO_2 production of the fertilized plots may be caused by the higher C input, the subsequent higher SOC content and the higher DOC content at these sites (Table 5.4). In the subsoil, the respiration was reduced compared to the surface soil due to the reduced substrate availability below the plough-horizon, with no significant differences between the plots (Table 5.4).

The percentage of maize-derived CO_2 was approximately constant over time (Figure 5.17 b, d). It was higher at Ha-M_{NPK} with 60 to 79% in the surface soil and 57 to 75% in the subsoil than at Ha-M_0 with 42 to 64% and 43 to 62%, respectively. Thus, the maize-derived SOC was faster mineralized than the older C_3-derived SOC. STEMMER ET AL. (2000) analyzed the availability of different SOC pools by ^{14}C labeling. They found that from a Calcic Chernozem where ^{14}C-labeled farm yard manure had been applied thirty years ago, the ^{14}C content of the SOC was 0.4% under crop rotation and 0.5% under bare fallow. In contrast, the ^{14}C content of the emitted CO_2 was 0.8% at the crop rotation and 1.0% at the bare fallow. Thus, after 30 years, the labeled C compounds still remained more mineralizable than the non-labeled SOC pool.

The mineralization of fresh maize residues (root and stubble) of Ha-M_{stalk} was calculated from the total amount of CO_2-C produced and the isotopic composition ($^{13}C/^{12}C$) of the respired CO_2 but also as the difference between the CO_2-C emission of Ha-M_{stalk} and Ha-M_{NPK}. Calculated as maize-derived percentages according to equation 3.1, the total production of C_4-derived CO_2-C of Ha-M_{stalk} was 43.8 g m^{-2} (Table 5.4) or 82% (Figure 5.17 b). Calculated as differences between Ha-M_{stalk} and Ha-M_{NPK}, 29.8 g CO_2-C m^{-2} of the produced CO_2 originated directly from the fresh maize residues accumulated in Ha-M_{stalk}. This was equal to 56% of the total CO_2 emission and resulted in a total amount of maize derived CO_2-C (from fresh residues and older maize-derived SOC) of 45.3 g CO_2-C m^{-2}. Fifteen percent of the total carbon dioxide produced by Ha-M_{stalk} were C_3-derived when calculated as difference, whereas 18% were C_3-derived when calculated according to equation 3.1, however, using a two-tailed two-sample t-test ($p<0.05$), no significant differences among the two calculation methods could be found. Thus, similar to the DOC production, no priming effect resulting in a higher production of CO_2 from SOC occurred during the degradation of the fresh organic matter in the soil. Contrary to this, LIANG ET AL. (1999) determined in Chicot sandy clay loam previously cropped to C_3-plants that 20% of the respired CO_2-C was deriving from maize residues as calculated by an isotopic expression. In contrast, the mineralization of added maize residues was 30% when calculated by difference, thus they concluded that the difference was due to the mineralization of the indigenous soil organic C.

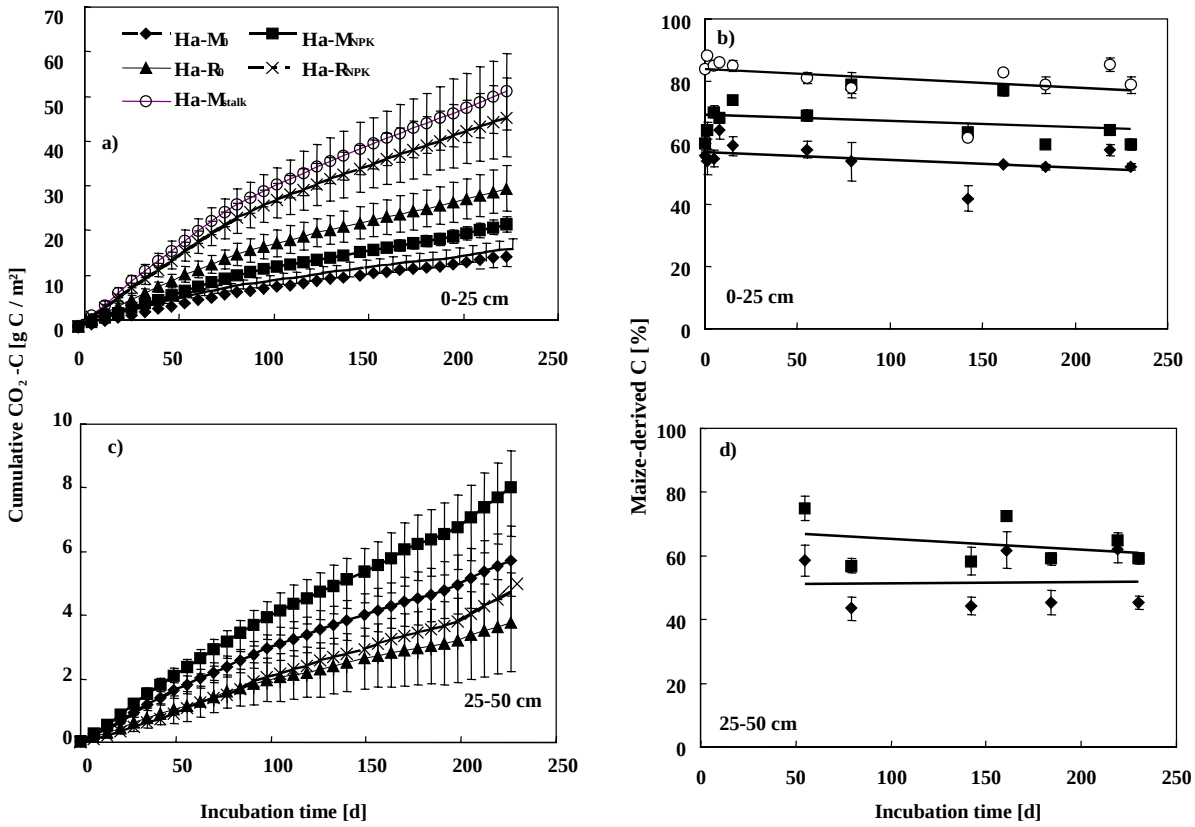

Figure 5.17: Cumulative CO_2-C production of the a) surface soils of Ha-M_0, Ha-M_{NPK}, Ha-M_{stalk}, Ha-R_0, Ha-R_{NPK} and c) subsoils of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK} and time dynamics of the maize-derived C [%] in the CO_2-C of the b) surface soils of Ha-M_0, Ha-M_{NPK}, Ha-M_{stalk}, and d) subsoils of Ha-M_0 and Ha-M_{NPK}. Mean values and SE (Ha-M_{stalk}: n = 4; all other sites: n=5).

For the Halle soils, maize-derived C in C_{mic} was less than in the respired CO_2. FLESSA ET AL. (2002) found that the indigenous microflora present on plant residues produces more CO_2 than the autochtonous microflora in the soil. LADD ET AL. (1995) hypothesized that the C_{mic} in soil is not uniform and that it is composed of various fractions, each having different levels of activity and turnover times. One of these fractions would be formed from the decomposition of fresh residues and have a rapid turnover. The results of this study were in agreement with this hypothesis, since the greater proportion of maize C in CO_2 than in C_{mic} indicates that the C_{mic} consists of a very active population relying primarily on maize-derived SOC and a less active population that mineralizes substrate with a higher proportion of older carbon derived from former C_3-vegetation. This is also in accordance with HAIDER (1999), who proposed that the predominant part of the C_{mic} is in dormancy.

5.4.4 DON and NO_3^--N leaching

The DON-production in the surface soil was decreasing as Ha-R_{NPK} > Ha-R_0 >Ha-M_{stalk} > Ha-M_{NPK} > Ha-M_0. DON production was lower in the subsoil where no significant differences among the experimental plots was found. MURPHY ET AL. (2000) found under drainage water from the Broadbalk continuous wheat experiment at Rothamsted that the loss of DON was higher in N-fertilised plots (144 kg N a^{-1}) than in the nil-N plot. At Ha-M_{NPK}, the specific DON leaching from N_t was 0.04% compared to a specific leaching of 1.27% for DON associated with the decomposition of fresh maize residues at Ha-M_{stalk}.

Table 5.5: Mean values of N_t, leached NO_3^--N, leached DON and fraction of DOC/DON for the surface soils and subsoils of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK} (n = 5) and for Ha-M_{stalk} (n = 4). NO_3^-N and DON are cumulative values over the incubation period of 230 days, the values for N_t are from a single sampling date in September 2000

Experimental plot and depth	Origin of C or N	N_t	NO_3^--N	DON	DOC/ DON
[cm]			[g m^{-2}]		[%]
M_0, 0-25	Total Soil	266^{ab}	2.7^{ab}	0.08^{ab}	21.7
M_0, 25-50	Total Soil	338^{c}	1.1^{a}	0.06^{a}	27.1
M_{NPK}, 0-25	Total Soil	304^{bc}	3.5^{bc}	0.12^{abc}	17.4
M_{NPK}, 25-50	Total Soil	329^{c}	1.2^{a}	0.05^{a}	63.5
M_{stalk}, 25-50	Total soil plus stalk	307^{bc}	3.9^{bc}	0.16^{bcd}	15.0
R_0, 0-25	Total Soil	297^{bc}	5.1^{c}	0.19^{cd}	9.4
R_0, 25-50	Total Soil	245^{a}	1.6^{a}	0.04^{a}	32.1
R_{NPK}, 0-25	Total Soil	293^{abc}	7.6^{d}	0.22^{c}	12.0
R_{NPK}, 25-50	Total Soil	260^{ab}	1.7^{a}	0.08^{ab}	20.6

Within columns, values followed by the same are not significantly different ($p<0.05$) between experimental plots and depths for N_t , NO_3^--N and DON.

The ratio of DOC/DON was always higher in the subsoils (20.6 – 63.5) than in the surface soils (9.4 – 21.7). In the surface soils, nitrate leaching was decreasing in the same order as DON with Ha-R_{NPK} > Ha-R_0 > Ha-M_{stalk} > Ha-M_{NPK} > Ha-M_0, no significant was found among the subsoils. Similarly, MACDONALD ET AL. (2001) found at Broadbalk continuous wheat experiment at Rothamsted, UK, that the production of nitrate was higher under NPK-fertilization than under the nil fertilization plot. The leaching of DON accounted for 4-14% of the total N leached from the wheat field, which is in the magnitude of the 2.9–3.7% measured at the Halle field. Using the electro-ultrafiltration method (EUF), MERCIK & NÉMETH (1985) determined that after 60 years of annual applications of inorganic NPK (90 kg N ha^{-1}) on a Polish sandy luvisol cropped with rye the EUF-N_{org} was 1.9 times higher in the surface soil (0-25 cm) and 3.5 times higher in the subsoil (50–75%) than under PK fertilization. EUF-

NO_3^- was 4.5 times higher under N-fertilization in the surface soil, but fertilization exhibited no influence on nitrate production in the subsoil.

Similar to the DOC production, the greater production of DON and NO_3^- at the rye plot could be due to the preceding tillage.

5.4.5 Correlations of soil constituents and CO_2 for Halle

Correlations between SOC, C_{mic}, DOC and CO_2 were calculated using time-weighed averages of maize-derived and C_3-derived C for DOC and CO_2. The correlations indicated that the formation of DOC, CO_2 and C_{mic} from the C_4-SOC pool was dependent on the amount of C_4-SOC whereas the relationship between the formation of DOC, CO_2 and C_{mic} from the C_3-pool was not as pronounced (e.g Figure 5.15 a,b). This might be due to the higher bioavailability of the C_4-SOC pool as compared to the C_3-SOC pool. This difference may be explained by the greater stabilization of the older C_3-SOC pool. COLLINS ET AL. (1999) concluded that chemical effects (clay stabilization, humification and aromaticity) strongly affect the turnover of older SOC, while younger materials are more dependent on soil management and physical factors such as aggregation. Additionally, the pyrogen C present in the soils (BRODOWSKI ET AL., 2003) may have contributed to these results.

DOC plays an important role as a substrate for microbial activity (JANDL & SOLLINS, 1997). Our results confirm a close relationship between the amount of C_{mic} and the DOC and CO_2 production. The relationship was less pronounced for the C_3-derived than for the C_4-derived pools (Figure 5.15 c, d, e f). However, it is difficult to determine whether microbial activity occurs because DOC is present or vice versa (NEFF & ASNER, 2001).

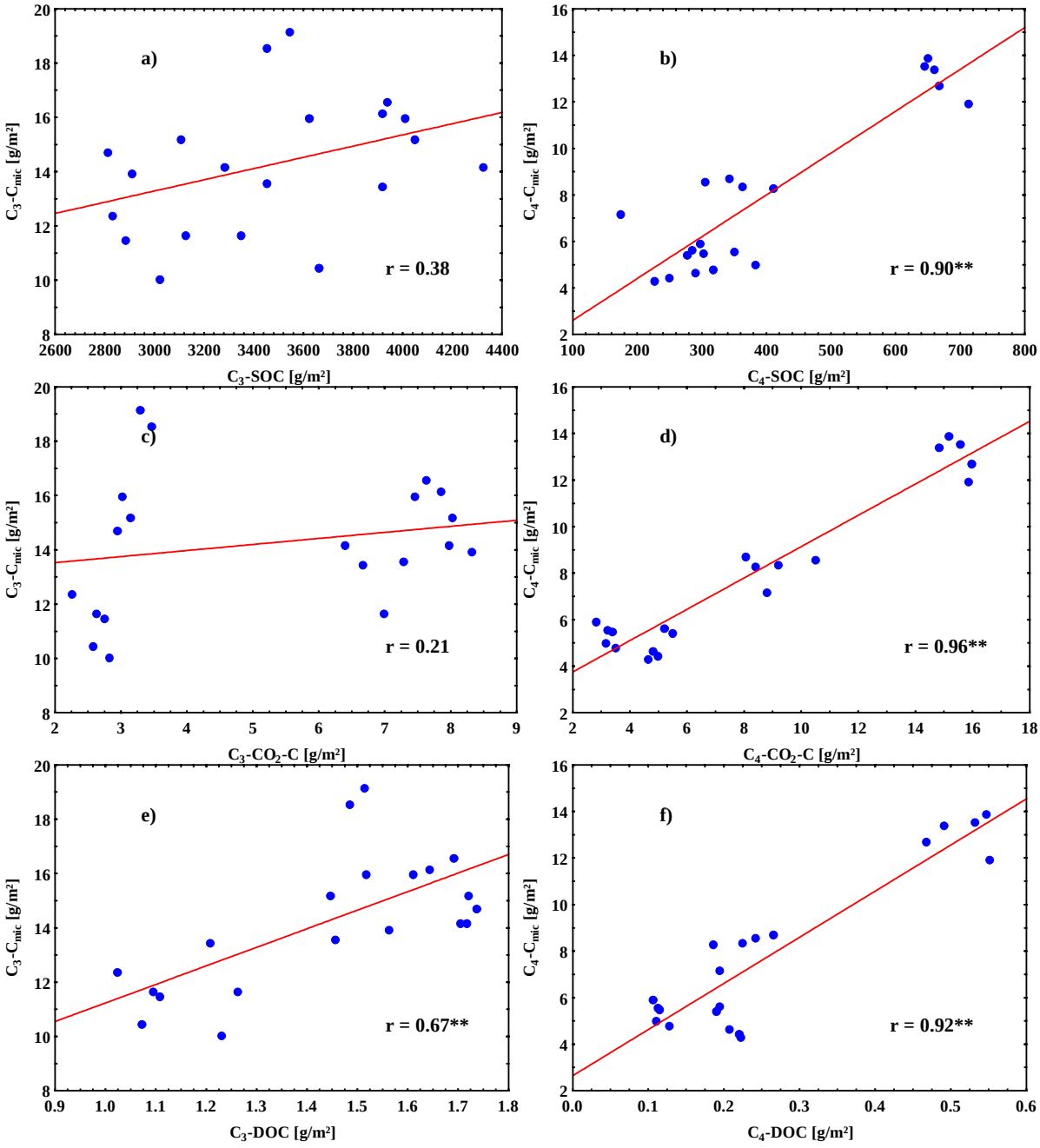

Figure 5.18 a-f: **Scatterplots between C_3-,C_4-C_{mic} (microbial biomass), to C_3,C_4-SOC (soil organic carbon), C_3,C_4-CO_2-C and C_3,C_4-DOC (dissolved organic carbon), respectively, for all data of the surface soils (0-25 cm) and subsoils (25-50 cm) of Ha-M_0 and Ha-M_{NPK}. All data points.**

5.4.6 Specific production rates of microbial C, DOC and CO_2 from SOC at Halle

The fraction of C_{mic}/SOC [%] is a measure for the amount of SOC stored in the microbial biomass. For Halle, it ranged from 0.5 to 0.7% in the surface soils and subsoils. The specific stock of C_3-C_{mic} to C_3-SOC ranged from 0.3 to 0.5% in all soils, the stock of C_4-C_{mic} to C_4-SOC ranged from 1.9 to 2.7% in all soils. The results indicated that the microorganisms mainly fed upon younger SOC.

From the Halle soils, the specific DOC leaching rate (fraction of DOC/SOC) ranged between 0.04% and 0.06% for all sites, thus about 0.05% of the total SOC was leached as DOC over a period of 230 days (Table 5.6). Specific DOC production rates were calculated (Table 5.6) by relating the production of C_3-DOC and C_4-DOC to their corresponding stocks of C_3-SOC and C_4-SOC.

For the surface soils, the specific DOC production from C_4-SOC was 1.9 and 1.6 times higher than the DOC-production from C_3-SOC for M_{NPK} and M_0. In the subsoil, it was 1.5 times and 1.7 times for the respective plots. This indicated that the younger, C_4-derived C was more readily available for the formation of DOC. The specific DOC leaching (0.22%) during the decomposition of the fresh maize residues in M_{stalk} was higher than the specific leaching rates of C_3-DOC and C_4-DOC from their corresponding stocks of C_3-SOC and C_4-SOC with 0.04 for C_3-DOC/C_3-SOC [%] and 0.08 for C_4-DOC/C_4-SOC, respectively.

The specific CO_2-C production rate (fraction of CO_2-C/SOC in percent) calculated from the cumulative CO_2 production during the incubation period (230 days) is an indicator for the availability of different SOC pools. It ranged from 0.4% to 1.1% in the surface soils and was 0.2% in the subsoils. The specific CO_2 production rate from C_4-SOC was 20 times (surface soils) or 12 times (subsoils) higher than the CO_2-production from the C_3-SOC (Table 5.6). The soil columns of M_{stalk} contained an additional substrate, the fresh maize residues. The specific mineralization rate of these residues was much greater (19.3%) than that of older C_4-SOC or C_3-SOC pools (Table 5.4).

The fraction of DOC/CO_2-C [%] is a measure to compare the relevancy of DOC and CO_2 as media to export C from the soil. For the surface soils, the fraction of DOC/CO_2-C was about 10% for the soils under maize and about 5% for the soils under rye, whereas for the subsoils, it was about 20% (maize plots) and 30% (rye plots) (Table 2). The DOC/CO_2-C ratio for the decomposition of the fresh maize residues in Ha-M_{stalk} was 1.13%. Thus, the DOC production relative to the CO_2 production was minor and the relative importance of DOC leaching increased with depth. For the surface soils of Ha-M_{NPK} and Ha-M_0, the fraction of C_3-DOC/C_3-CO_2-C was about 20%, whereas for the subsoils, it reached 52% (Ha-M_{NPK}) and 43% (Ha-M_0). The fractions of C_4-DOC/C_4-CO_2-C were much smaller (3 to 4%, Table 2) which indicated the higher bioavailability of C_4-DOC compared to C_3-DOC and a subsequent

higher turnover of C_4-DOC. The high bioavailabilty of C_4-DOC was also reflected by the small fraction of C_4-DOC/C_4-C_{mic} (2 to 4%) compared to a fraction of C_3-DOC/C_3-C_{mic} of 10 to 11% (Table 5.6). Overall, with increasing age and decreasing microbial availability of the OM in the soil, the relative relevance of DOC leaching compared to CO_2 emission for the export of carbon from the soil increased. This results are in line with the observations of FLESSA ET AL. (2000) who found that the DOC/CO_2 ratio was three times greater for older SOC stocks as compared to younger SOC pools.

Table 5.6: Mean values of C_3- and C_4-derived stocks of and fractions between the soil organic constituents SOC (soil organic carbon), leached DOC (dissolved organic carbon), C_{mic} (microbial biomass) and respired CO_2-C for the surface soils and subsoils of Ha-M_0, Ha-M_{NPK}, Ha-R_0, Ha-R_{NPK} (n = 5) and for Ha-M_{stalk} (n = 4). DOC and CO_2-C are cumulative values over the incubation period of 230 days, the values for SOC and C_{mic} are from a single sampling date in September 2000

Experimental plot and depth	Origin of C	DOC/ SOC	CO_2-C/ SOC	C_{mic}/ SOC	DOC/ CO_2-C	DOC/ C_{mic}	CO_2-C/ C_{mic}
(cm)				(%)			
Ha-M_0, 0-25	Total soil	0.045	0.44	0.59	10.33	7.69	74.46
	C_3	0.043	0.22	0.40	19.94	10.61	53.24
	C_4	0.070	2.59	2.38	2.71	2.95	108.93
Ha-M_0, 25-50	Total soil	0.035	0.17	0.48	21.03	7.36	35.02
	C_3	0.034	0.08	0.34	42.51	9.87	23.21
	C_4	0.057	1.61	2.70	3.56	2.13	59.76
Ha-M_{NPK}, 0-25	Total soil	0.045	0.49	0.61	9.11	7.37	80.87
	C_3	0.040	0.19	0.39	20.57	10.23	49.74
	C_4	0.078	2.32	1.97	3.34	3.95	118.02
Ha-M_{NPK}, 25-50	Total soil	0.051	0.23	0.61	22.27	8.41	37.75
	C_3	0.049	0.10	0.50	51.56	9.74	18.90
	C_4	0.073	1.94	1.90	3.77	3.85	102.11
Ha-M_{stalk}, 0-25	Total soil plus stalk	0.050	1.08		4.62		
	C_3	0.046	0.23		19.8		
	C_4	0.074	5.34		1.39		
Ha-R_0, 0-25	Total soil	0.043	0.82	0.57	5.29	7.58	143.18
Ha-R_0, 25-50	Total soil	0.047	0.15	0.49	31.46	9.63	30.60
Ha-R_{NPK}, 0-25	Total soil	0.059	1.08	0.65	5.48	9.20	167.86
Ha-R_{NPK}, 25-50	Total soil	0.057	0.17	0.65	34.31	8.78	25.59

The metabolic quotient of the C_{mic} (CO_2-C/C_{mic}) was higher in the surface soil than in the subsoil (Table 5.6), indicating the higher activity of microorganisms in the tilled horizon. There was a pronounced difference in the metabolic quotient calculated for the C_3 and the C_4

pool which testified a remarkably higher activity of the C_{mic} population which consumes the younger, C_4-derived SOC.

5.5 Modeling carbon dynamics using the Rothamsted Carbon Model

5.5.1 Model case I

In model case I, the amount of IOM was estimated using the equation by FALLOON ET AL. (1998) and the annual rye-C-input and maize-C-input were fitted to total SOC in 2000. For the Halle soils, the model suggested that after 39 years of continuous maize cropping 29% (Ha-M_0) and 37% (Ha-M_{NPK}) of the SOC were maize-derived which was in a marked contrast to the findings of the $\delta^{13}C$ analysis. Thus, model case I was inappropriate to estimate SOC dynamics in this soil.

5.5.2 Model case II

In model case II, the additional information from the ^{13}C analysis was used. At Halle, for Ha-M_{NPK}, the model calculated that an annual maize-C input of 0.089 kg m^{-2} was required to obtain a storage of 0.71 kg maize-derived C in the Ap horizon after 39 years. The input calculated was close to the maize-C input estimated by FLESSA ET AL. (2000) for this site (0.079 kg m^{-2}) by considering the mean dry matter yield (grains, cobs, leaves, stems) and assuming a C content of 45% and a (stubble and root biomass)/(aboveground yield) ratio of 0.20 according to the findings of BALESDENT & BALABANE (1992). In the estimate by FLESSA ET AL. (2000), rhizodeposition was not included. SCHULZE (1993) found in a long term ^{14}C-labeling experiment with maize, that the rhizodeposition extracted from soil in the end of the growing period may be as great as the root biomass. However, the decomposability of C stemming from rhizodeposition might be much greater than that of roots and most of the rhizodeposition-C might be respired and the contribution of rhizodeposition-C to the long term stabilization of SOC might be very small.

For Ha-M_0, the model calculated an annual maize-C input of 0.044 kg m^{-2} to obtain a storage of 0.35 kg maize-derived C in the Ap horizon after 39 years. The difference between the modeled maize-C inputs between the two treatments (annual maize-C input (Ha-M_{NPK}) / annual maize-C input (Ha-M_0) = 2.0) compares satisfactorily with the measured difference of the aboveground yields (aboveground yield (Ha-M_{NPK}) / aboveground yield (Ha-M_0) = 2.4). For M_0, relatively more C might have been allocated below ground than for M_{NPK} for a more efficient nutrient uptake. For instance, GEISLER & KRÜTZFELD (1984) and ANDERSON (1988) reported for maize that N fertilizer significantly decreased the root : shoot weight ratio.

The $\delta^{13}C$ analysis indicated for the maize plots, that the C_3-derived SOC decreased by 0.53 (Ha-M_0) or 0.86 kg m^{-2} (Ha-M_{NPK}) within 39 years of continuous maize cropping . Based on

these changes and by assuming that SOC stocks in the continuous rye plots represent steady state conditions and were the same on the maize plots 39 years ago, the annual rye-C inputs and the amounts of IOM were obtained without using adjustable parameters. The calculated amounts of IOM were 2.3 (Ha-R_0, Ha-M_0) or 2.5 kg C m^{-2} (Ha-R_{NPK}, Ha-M_{NPK}), suggesting that 64% (Ha-M_0) or 53% (Ha-M_{NPK}) of the total SOC in the Ap horizon of the maize plots were inert in 2000. These IOM amounts are much larger than the ones obtained using the equation suggested by FALLOON ET AL. (1998) (IOM (in t C ha^{-1}) = 0.049 $SOC^{1.139}$) which would have resulted in IOM amounts of 0.3 (Ha-R_0, Ha-M_0) or 0.4 kg C m^{-2} (Ha-R_{NPK}, Ha-M_{NPK}). The large IOM amounts of 2.3 or 2.5 kg C m^{-2} found in our study point to a large C sequestration by Haplic Phaeozems. The main reason for this large C sequestration might be an enhanced stabilization by interaction of SOC with inorganic soil colloids. Amounts of charcoal in the surface soil (0-25 cm) were 28% of the SOC (BRODOWSKI ET AL., 2003) and thus one important reason for the large C sequestration in this soil.

The equation suggested by RÜHLMANN (1999) (SOC of long-term bare fallow soils (in %) = 0.017 (percentage of soil particles <20 µm) – 0.001 * exp(0.075 * (percentage of soil particles <20 µm))) to obtain the IOM amounts for this site was tested. This equation gave considerably larger IOM amounts for both treatments (Ha-R_0, Ha-M_0, Ha-R_{NPK}, Ha-M_{NPK}: 1.3 kg C m^{-2}). In contrast to the approaches by RÜHLMANN (1999) and FALLOON ET AL. (1998), the equation given by KÖRSCHENS (1980) and KÖRSCHENS ET AL. (1998) (IOM (in %) = 0.04 * (percentage of soil particles <6.3 µm)) gave IOM amounts of 2.1 kg C m^{-2} for both treatments (Ha-R_0, Ha-M_0, Ha-R_{NPK}, Ha-M_{NPK}) which were close to the results obtained by using the Rothamsted carbon model. The main reason for the usefulness of the latter approach was probably that the data set used for the regression analysis included Haplic Phaeozems, whereas the data set used by RÜHLMANN (1999) did not include such a soil type (LUDWIG ET AL., 2003). However, the amount of IOM might not only depend on the soil texture, but also on climatic and paleoclimatic factors, base status and mineralogy (KONONOVA, 1966).

The model results for the changes with time in maize-derived C in the Ap horizon agreed well with the measured values of maize-derived C at 0-20 cm for both treatments (Ha-M_0, Ha-M_{NPK}) (Figure 2). Modeled results of maize-derived C were 9.8% for Ha-M_0 and 15.0% for Ha-M_{NPK} and measured values were 9.5% for Ha-M_0 and 14.0% for Ha-M_{NPK}.

5.5.3 Comparison of analytical and model C pools

BALESDENT (1996) suggested that SOC of the fraction 0 to 50 µm might represent the sum of the pools microbial biomass, humified OM and IOM of the ROTH-C model. In our study, at Halle, the measured fraction 0 to 63 µm of the total (C_3- and maize-derived) SOC amounts (9.8 g C kg^{-1} soil) agreed satisfactorily with the modeled sum of C_3- and maize-derived SOC amounts of microbial biomass, humified OM and IOM (11.8 g C kg^{-1} soil). Furthermore, the maize-derived amounts of the 0 to 63 µm fraction (1.1 g C kg^{-1} soil) were similar to the

modeled sum of maize-derived C in the pool microbial biomass and humified OM (0.9 g C kg^{-1} soil) which suggests the usefulness of the pool concept and of the physical fractionation to obtain meaningful pool sizes with respect to SOC dynamics.

Contrary to the findings of BALESDENT (1996) (for the fraction >50 µm), the fraction >63 µm in our study contained much less maize-derived SOC (0.3 g C kg^{-1} soil) than suggested by the model results for the RPM pool (0.9 g C kg^{-1} soil).

6 CONCLUSIONS

The method of natural ^{13}C abundance was a useful tool to determine the carbon turnover in soils. At Halle, the enrichment of younger carbon was higher under NPK-fertilization than without fertilization. The percentage of maize-derived carbon was higher at Rotthalmünster than at Halle due to the higher production of biomass, higher input of plant residues after harvest, higher NPK-fertilization, and the high percentage of silt and clay.

The stabilization of carbon and nitrogen was dependent on their position in the soil: The results of the size fractionation for the surface soils of the Halle site indicated that carbon and nitrogen enrichment factors (E_C and E_N) were highest in the clay fraction (E_C = 3.8, E_N = 5.7), followed by the silt fractions (E_C = 2, E_N = 2.9). This results agreed well with published equations (Leinweber, 1995; Christensen, 1996). Carbon and nitrogen enrichment was relatively high in the coarse sand due to its high content of fresh organic matter. C/N ratios and maize-derived percentages indicated that the fine sand fraction and the coarse silt fraction were the most stable fractions. A comparison to ^{14}C measurements of the size fractions showed a similar trend concerning the turnover of the size fractions, however, ^{14}C data had to be interpreted cautiously due to the high anthropogenic pollution of the Halle site.

In the topsoils of Rotthalmünster, the distribution of aggregate size classes was influenced by land cultivation, as tillage destroyed especially aggregates >1000 µm. For the tilled soils of the maize sites, the most important fractions were the microaggregates (53-250 µm). For wheat (conservation tillage since 1998) the smaller macroaggregates (250-1000 µm) and for the grassland and forest soils the megaaggregates (>2000 µm) were most important. At the grassland and forest, surface soils were more aggregated than subsoils. Aggregates protect carbon from decomposition as carbon content in all aggregate fractions 53 µm was higher than in the silt and clay fraction (<53 µm). The amount of carbon of one kg soil stored in the microaggregates was nearly independent of the amount of SOC in the bulk soil, and hence cultivation, while the amount of macroaggregates was highly dependent on the SOC. Water stable aggregates of the maize, wheat and grassland sites of Rotthalmünster had higher C-contents and lower maize-derived percentages in the microaggregates than in the macroaggregates, thus proving the concept of aggregate hierarchy.

With a density fractionation using sodiumpolytungstate for all soils of Halle and Rotthalmünster (excluding the forest site), the free organic matter <1.6 g cm^{-3} ($FPOM_{<1.6}$), occluded organic matter <1.6 g cm^{-3} ($OPOM_{<1.6}$) and from 1.6 to 2.0 g cm^{-3} ($OPOM_{1.6-2.0}$) and the mineral fraction >2.0 g cm^{-3} ($Mineral_{>2.0}$) were fractionated. The results suggested that in respect of the C-storage, of the light fractions $OPOM_{1.6-2.0}$ was most important (11.2-20.7%), followed by the $FPOM_{<1.6}$ (5.7-9.6%), whereas the $OPOM_{<1.6}$ was only of minor importance in respect of carbon storage (1.0-4.5%). The major part, however, was located in the mineral

fraction $Mineral_{>2.0}$. The high maize-derived percentages in the free particulate organic matter fractions of Halle (22.9-25.9%) and Rotthalmünster (55.7-59.1%) and the lower maize-derived percentages in the occluded organic matter fractions ($OPOM_{<1.6}$: Halle: 1.3-2.3%, Rotthalmünster: 17.4-25.4%; $OPOM_{1.6-2.0}$: Halle: 4.1-7.4%, Rotthalmünster: 38.3-40.4%;) emphasized the importance of physical protection for carbon storage. For the Halle soils, the fraction $OPOM_{<1.6}$ was the pool with the slowest turnover that could be measured in the entire study. As an independent verification of the ^{13}C data, ^{14}C data (J. Rethemeyer, Kiel, unpublished data) suggested that the $OPOM_{<1.6}$ was the oldest fraction both at Halle and Rotthalmünster, but similar to the size fractionation, the anthropogenic pollution of the Halle site has to be accounted for and is a great factor of uncertainty when estimating C turnover by ^{14}C data.

For the reconciliation of the results from different physical fractionation methods an integrated approach would be advisable, so the next step should be a combined fractionation of water-stable aggregates, a size fractionation and a density fractionation.

For the determination of the extractable microbial biomass, various methods were compared in this study. The microbial biomass of the Halle soils was determined using 0.5 M K_2SO_4 as extraction agent after a chloroform-fumigation extraction. For the determination of the microbial biomass of Rotthalmünster, the CFE-method was compared to a freeze-drying method, using water as extraction agent in both cases. Both at Halle and Rotthalmünster, the microbial biomass was low due to the adverse conditions of the monoculture. At Halle, the microbial biomass and their maize-derived percentages were higher in the fertilized soils, due to their higher input of organic residues. At Rotthalmünster, the microbial activity was highest in the grassland soil, followed by the maize sites and the wheat site. On average, the extractable carbon was 3.3 times higher after freeze-drying than after fumigation. The freeze-drying method probably extracted carbon from the killed biomass, but additionally carbon that was released from other processes due to the freeeze-drying. Maize-derived percentages were higher after freeze-drying than after chloroform-fumigation, however, significant differences could only be found in the subsoils. Before the two methods that were used for the Rotthalmünster soils can be applied as standard methods, a calculation of k_{EC} factors would be necessary to compare the results to other studies that use different methods for the determination of the microbial biomass.

The maize-derived percentages after 40 years of continuous maize cropping at the Halle site were highest in CO_2 (42 to 79%), followed by C_{mic} (23 to 46%), DOC (5 to 30%) and SOC (5 to 14%). Young, C_4-derived carbon showed a higher turnover than older, C_3-derived, more recalcitrant carbon. Strong correlations were found between C_4-derived C_{mic} and C_4-derived SOC, DOC and CO_2 ($r \geq 0.90$), whereas the relationships between C_3-derived C_{mic} and C_3-derived SOC, DOC and CO_2 were not as pronounced ($r \leq 0.67$). A comparison of the results

for surface soils and subsoils showed that the significance of DOC compared to CO_2 to export carbon from the soil was minor but increased with soil depth. When including soil columns with a standing stubble into the study for representing the inhomogeneity of maize residue distribution after harvest of maize for silage making, the results showed that the uneven distribution of maize residues resulted in a considerably increased heterotrophic activity within the maize rows as compared with soil between seed rows. However, there was no or only a marginal effect of maize stubble decomposition on leaching of DOC, DON and NO_3^-. The results about CO_2 and DOC losses emphasized the relative importance of DOC leaching for the loss of SOC increases with increasing age and stability of SOC.

The results of the study indicated that young carbon turned over much faster than the older carbon in the soil. Its turnover showed closer correlations among maize-derived soils constituents than among older soils constituents. The greater proportion of maize C in CO_2 than in C_{mic} indicated that the C_{mic} consisted of a very active population relying primarily on maize-derived SOC and a less active population that mineralizes substrate with a higher proportion of older carbon derived from former C_3-vegetation. The results also indicated that even though it might be possible to draw conclusions about the turnover of young carbon in the soil, a much wider scattering may be observed concerning the turnover of older SOC material, thus further research is needed concerning the different processes that steer the turnover of old and young soil organic matter in the soil.

The results of the ^{13}C natural abundance technique were successfully employed to model the SOC dynamics in the long-term maize cropping systems of Halle (NPK fertilization or unfertilized) without using adjustable parameters. The approach of KÖRSCHENS (1980) and KÖRSCHENS ET AL. (1998) to determine the size of the "inert organic matter" pool agreed well with the model results. Furthermore, the total as well the maize-derived fraction 0–63 µm agreed well with the total and maize-derived sums of the model pools "inert organic matter", "humified organic matter" and "microbial biomass".

The thesis showed that newly incorporated carbon has a considerably higher turnover than older carbon in the soil, thus questioning the long-term mitigation potential of soils. The results of the different soil carbon pools are a valuable source for the improvement of soil carbon models.

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8 OWN PUBLICATIONS WITH RESULTS OF THIS THESIS

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9 STUDY SITES AND ABBREVIATIONS

9.1 Study sites

Ha-M_0	continuous maize (since 1961) without fertilization
Ha-M_{NPK}	continuous maize plot (since 1961) with mineral NPK fertilization
Ha-M_{stalk}	soil with one cut maize stalk (length <5 cm) of Ha-M_{NPK}
Ha-R_0	continuous rye (since 1878) without fertilization
Ha-R_{NPK}	continuous rye (since 1878) with mineral NPK fertilization
Ro-Forest	spruce forest (since ~1920)
Ro-Grass	continuous grassland (since 1961) with mineral NPK fertilization
Ro-M_{NPK}	continuous maize plot (since 1979) with mineral NPK fertilization
Ro-M_{org}	continuous maize plot (since 1979) with mineral NPK fertilization and organic fertilization
Ro-W_{NPK}	continuous wheat plot (since 1969) with mineral NPK fertilization

9.2 Abbreviations

BC	black carbon
BP	years before present
C	carbon
C_3-plant	plant with the C_3 pathway of photosynthesis
C_4-plant	plant with the C_4 pathway of photosynthesis
C_c	extractable carbon of a control soil
C_{extr_freeze}	extractable microbial carbon from a freeze-dried soil after substraction of a control
C_{extr_fum}	extractable microbial carbon from a soil treated with CFE after substraction of a control
CFE	chloroform fumigation extraction
C_{freeze}	extractable microbial carbon from a freeze-dried soil
C_{fum}	extractable microbial carbon from a soil treated with CFE
C_{mic}	microbial biomass C
$\delta^{13}C$ [‰ PDB]	^{13}C:^{12}C ratio expressed relative to the PDB standard
DOC	dissolved organic carbon
DOC	dissolved organic matter

DON	dissolved organic nitrogen
DPM	decomposable organic matter
E_{C1_clay}	C enrichment factor for clay (LEINWEBER,1995)
E_{C1_silt}	C enrichment factor for medium and fine silt (LEINWEBER, 1995)
x_{clay}	average clay content
x_{silt}	average medium and fine silt content
E_{C2_clay}	C enrichment factor for clay (CHRISTENSEN, 1996)
E_{C2_silt}	C enrichment factor for medium and fine silt (CHRISTENSEN, 1996)
E_C	Enrichment factor (mass C per mass separate / mass C per mass soil)
E_N	Enrichment factor (mass N per mass separate / mass N per mass soil)
$FPOM_{<1.6}$	free particulate organic matter, density <1.6 g cm^{-3}
g	gravity accelaration
HUM	humified organic matter
IOM	inert organic matter
k_{EC}	extraction efficiency coefficient
$Mineral_{>2.0}$	mineral fraction, density <1.6 g cm^{-3}
N	nitrogen
N_{mic}	microbial biomass N
N_t	total soil organic carbon
OM	organic matter
$OPOM_{<1.6}$	occluded particulate organic matter, density <1.6 g cm^{-3}
$OPOM_{1.6-2.0}$	occluded particulate organic matter, density 1.6-2.0 g cm^{-3}
PDB	Pee Dee Belemnite, standard for ^{13}C analysis
pMC	percent modern carbon
POM	particulate organic matter
ppb	parts per billion
ppm	parts per million
RothC	Rothamsted Soil Carbon Model
rpm	rotations per minute
RPM	resistant organic matter
RSOM	refractory organic matter
SE	Standard error
SOC	soil organic carbon
SOM	soil organic matter
TOC	total organic carbon

10 APPENDIX

Table 10.1: Size fractionation method I: Distribution of yield [%], C [%], EC, EN, C/N [%], $\delta^{13}C$ [‰ PDB], maize-derived C [%] and pMC for the size fractions from the surface soils (0-10 cm) of Ha-M_{NPK}, Ha-M_0, Ha-R_{NPK}, and Ha-R_0. Means and SE (n = 4).

µm	Yield [%]	C [%]	EC	EN	C/N	$\delta^{13}C$ [‰ PDB]	C_4- C [%]	pMC	Yield [%]	C [%]	EC	EN	C/N	$\delta^{13}C$ [‰ PDB]	corr. pMC
	Ha-M_{NPK}								Ha-R_{NPK}						
630-2000	4.1	0.86^{ab}	0.7	0.4	23.7	-19.9	36.4^{e}		4.1	0.70^{a}	0.6	0.8	11.5	-26.0	
	(0.1)	(0.141)			(0.1)	(1.0)	(8.2)		(0.3)	(0.154)			(0.1)	(0.9)	
200-630	30.3	0.21^{a}	0.2	0.2	15.9	-23.6	11.7^{bc}		33.9	0.24^{a}	0.2	nd	nd	-25.5	
	(0.2)	(0.021)				(0.1)	(1.3)		(0.2)	(0.054)				(0.2)	
63-200	30.7	0.28^{a}	0.2	0.1	28.2	-23.9	7.8^{b}		31.8	0.28^{a}	0.2	0.2	22.3	-25.2	
	(0.5)	(0.011)				(0.2)	(1.4)		(0.7)	(0.028)			(0.1)	(0.2)	
20-63	13.7	1.74^{cd}	1.4	0.7	28.8	-23.7	11.9^{bc}		11.3	1.66^{bc}	1.4	0.9	23.3	-25.7	
	(0.3)	(0.130)			(0.2)	(0.0)	(0.5)		(0.2)	(0.072)			(0.1)	(0.1)	
2-20	10.9	3.52^{fg}	2.8	2.6	16.9	-23.8	9.8^{bc}		10.3	3.48^{fg}	3.0	2.9	15.0	-25.5	
	(0.4)	(0.241)			(0.8)	(0.1)	(1.4)		(0.1)	(0.129)			(0.4)	(0.2)	
<2	8.6	4.25^{gh}	3.4	5.1	10.4	-22.8	16.5^{c}		7.0	4.62^{h}	4.0	5.5	10.7	-25.6	
	(0.0)	(0.420)			(1.8)	(0.1)	(0.6)		(0.4)	(0.406)			(1.9)	(0.1)	
	Ha-M_0								Ha-R_0						
630-2000	4.1	1.01^{abc}	0.9	0.3	42.2	-22.0	24.7^{d}	47.63	4.6	0.75^{a}	0.7	0.4	27.7	-26.2	77.37
	(0.3)	(0.364)			(0.4)	(0.4)	(5.3)	(0.22)	(nd)	(0.043)				(0.8)	
200-630	30.9	0.17^{a}	0.2	nd	nd	-24.0	8.1^{b}	24.79	33.5	0.22^{a}	0.2	nd	nd	-25.3	33.08
	(0.3)	(0.018)				(0.1)	(0.9)	(0.21)	(0.4)	(0.047)				(0.1)	
63-200	29.6	0.26^{a}	0.2	0.1	25.4	-24.0	5.3^{ab}	nd	32.3	0.24^{a}	0.2	0.2	19.7	-24.9	23.72
	(0.7)	(0.003)			(0.0)	(0.1)	(0.8)		(0.6)	(0.010)			(0.0)	(0.1)	
20-63	15.0	1.69^{bcd}	1.6	0.9	26.5	-24.0	7.1^{ab}	32.75	10.3	1.68^{bcd}	1.7	0.9	28.9	-25.2	31.91
	(1.4)	(0.064)			(0.1)	(0.0)	(0.7)	(0.21)	(0.4)	(0.099)			(0.2)	(0.1)	
2-20	9.7	2.55^{de}	2.4	2.3	16.1	-24.2	8.2^{b}	49.60	10.4	3.33^{ef}	3.3	3.1	16.1	-25.5	50.59
	(1.2)	(0.054)			(0.1)	(0.2)	(1.4)	(0.23)	(0.2)	(0.043)			(0.1)	(0.0)	
<2	9.2	3.75^{fgh}	3.5	5.6	9.6	-23.6	10.9^{bc}	67.18	7.6	4.41^{h}	4.4	6.8	9.7	-25.4	69.50
	(0.2)	(0.056)			(0.2)	(0.0)	(0.4)	(0.20)	(0.1)	(0.060)			(0.3)	(0.1)	

corr. pMC indicates that the fraction of modern (1950) carbon was corrected for fractionation using simultaneous ^{13}C measurements.
Within columns, values followed by the same letter are not significantly different ($p<0.05$) between experimental plots and size fractions for C [%]. N [%] and maize-derived C [%]

Table 10.2: Size fractionation method II: Distribution of yield [%], C [%], EC, EN, C/N [%], $\delta^{13}C$ [‰ PDB], maize-derived C [%] for the size fractions from the surface soils (0-10 cm) of Ha-M_{NPK} and Ha-R_{NPK}. Means and SE (n = 4).

µm	Yield [%]	C [%]	EC	EN	C/N	$\delta^{13}C$ [‰ PDB]	C_4- C [%]	Yield [%]	C [%]	EC	EN	C/N	$\delta^{13}C$ [‰ PDB]
				Ha-M_{NPK}							Ha-R_{NPK}		
200-630	29.8 (0.9)	0.3 (0.0)	0.2	0.2	17.3 (0.0)	-22.8 (0.1)	20.6 (1.1)	30.4 (0.3)	0.3 (0.1)	0.3	0.3	13.5 (2.1)	-26.3 (0.3)
63-200	32.1 (0.3)	0.5 (0.0)	0.4	0.3	22.0 (0.7)	-23.6 (0.0)	9.2 (0.4)	34.7 (0.3)	0.5 (0.0)	0.4	0.3	21.3 (1.4)	-25.1 (0.1)
20-63	19.0 (0.3)	1.5 (0.1)	1.2	0.7	26.2 (0.2)	-24.2 (0.2)	5.9 (0.9)	17.2 (0.2)	1.8 (0.1)	1.6	1.0	27.3 (0.8)	-25.2 (0.1)
0.2-20	11.2 (0.3)	5.1 (0.0)	4.1	4.8	13.2 (0.2)	-23.7 (0.1)	14.7 (1.0)	10.9 (0.1)	5.9 (0.0)	5.1	6.3	13.3 (0.2)	-26.2 (0.1)
<0.2	2.8 (0.2)	4.1 (0.2)	3.3	5.1	9.8 (0.2)	-22.4 (0.1)	19.4 (0.7)	2.1 (0.3)	4.9 (0.3)	4.2	7.1	9.7 (0.2)	-25.7 (0.1)

Table 10.3: Rotthalmünster: Total Yield [%], C [%], N [%], C [g] and N [g] in aggregate fraction from 1 kg soil, C/N, $\delta^{13}C$ and maize-derived C in waterstable aggregates from Ro-W_{NPK}, Ro-M_{NPK}, and Ro-M_{org}. Means and SE (n = 4).

Plot	Aggregate Size [µm]	Yield [%]	C [%]	N [%]	C/N	C [g] in aggregate fraction of 1 kg soil	N [g] in aggregate fraction of 1 kg soil	$\delta^{13}C$ [‰ PDB]	C_4- C [%]
Ro-W_{NPK},	>2000	5.6 (1.6)	3.50 (0.05)	0.23 (0.01)	15.5	1.44	0.09	-27.1 (0.3)	
0-30	1000-2000	7.7 (2.7)	1.68 (0.13)	0.22 (0.01)	7.7	1.35	0.16	-26.6 (0.0)	
	250-1000	41.3 (3.4)	1.41 (0.03)	0.20 (0.01)	6.9	5.83	0.84	-26.6 (0.0)	
	53-250	26.8 (4.7)	1.27 (0.02)	0.19 (0.01)	6.6	3.42	0.52	-26.6 (0.1)	
	<53	17.7 (2.5)	0.96 (0.05)	0.16 (0.01)	6.0	1.71	0.28	-26.1 (0.1)	
Ro-M_{NPK},	>2000	10.9 (4.7)	1.33 (0.16)	0.15 (0.04)	9.0	1.74	0.22	-20.4*	47.2*
0-30	1000-2000	3.4 (0.8)	1.50 (0.26)	0.19 (0.02)	7.6	0.54	0.07	-20.0 (0.4)	46.9 (2.8)
	250-1000	27.7(3.0)	1.49 (0.05)	0.20 (0.01)	7.4	4.11	0.56	-21.2 (0.2)	38.2 (1.2)
	53-250	35.0 (2.8)	1.23 (0.04)	0.16 (0.00)	7.4	4.40	0.59	-21.9 (0.2)	32.7 (1.5)
	<53	22.8 (0.5)	0.81 (0.01)	0.11 (0.01)	7.5	1.85	0.25	-23.1 (0.1)	21.1 (0.7)
Ro-M_{ORG},	>2000	5.9 (2.9)	1.45 (0.14)	0.15 (0.03)	9.6	1.29	0.14	-19.9*	51.2*
0-30	1000-2000	3.4 (0.5)	1.53 (0.09)	0.19 (0.01)	8.1	0.52	0.07	-19.9 (0.4)	47.6 (2.6)
	250-1000	30.6 (4.8)	1.59 (0.09)	0.21 (0.01)	7.7	4.80	0.63	-21.1 (0.1)	38.8 (0.9)
	53-250	34.3 (3.3)	1.29 (0.05)	0.18 (0.01)	7.3	4.48	0.61	-21.5 (0.1)	35.6 (0.8)
	<53	23.4 (4.9)	0.88 (0.08)	0.13 (0.02)	7.1	2.12	0.31	-22.7 (0.1)	24.0 (0.5)

* value determined from composite sample

Table 10.4: Rotthalmünster: Total Yield [%], C [%], N [%], C [g] and N [g] in 1 kg soil, C/N, $\delta^{13}C$ and maize-derived C in waterstable aggregates from Ro-W_{NPK}, Ro-M_{NPK}, and Ro-M_{org}. Means and SE (n = 4).

Plot	Aggregate Size [µm]	Yield [%]	C [%]	N [%]	C/N	C [g] in aggregate fraction of 1 kg soil	N [g] in aggregate fraction of 1 kg soil	$\delta^{13}C$ [‰ PDB]
Ro-Grass,	>2000	38.3 (6.0)	2.66 (0.12)	0.30 (0.01)	8.8	10.03b	1.15	-28.2 (0.0)
0-10	1000-2000	16.4 (0.9)	2.62 (0.06)	0.29 (0.00)	9.0	4.28	0.48	-28.0 (0.0)
	250-1000	26.7 (1.3)	2.69 (0.05)	0.32 (0.01)	8.5	7.18	0.85	-27.9 (0.0)
	53-250	15.3 (2.2)	2.43 (0.01)	0.28 (0.00)	8.6	3.72	0.43	-27.9 (0.0)
	<53	8.8 (2.6)	1.18 (0.06)	0.17 (0.02)	7.3	1.02	0.16	-27.4 (0.0)
Ro-Grass,	>2000	3.9 (0.8)	1.45*	0.14*	10.2	0.45	0.04	
10-30	1000-2000	6.5 (1.4)	1.20*	0.12*	10.4	0.73	0.07	
	250-1000	36.8 (1.3)	1.00 (0.06)	0.10 (0.01)	9.6	3.68	0.38	
	53-250	31.7 (2.2)	0.84 (0.06)	0.09 (0.01)	9.2	2.67	0.29	
	<53	21.4 (2.6)	0.62 (0.02)	0.07 (0.00)	8.6	1.51	0.18	
Ro-Forst,	>2000	41.7 (2.4)	5.16 (0.17)	0.26 (0.02)	20.1	21.61a	1.09	-25.5*
0-7	1000-2000	13.5 (0.9)	4.73 (0.61)	0.27 (0.03)	17.5	6.29	0.36	-25.5 (0.0)
	250-1000	19.9 (1.3)	4.32 (0.15)	0.27 (0.02)	16.2	8.57	0.53	-25.7 (0.1)
	53-250	16.8 (2.2)	4.97 (0.21)	0.29 (0.01)	17.4	8.33	0.48	-25.8 (0.1)
	<53	7.9 (1.0)	2.32 (0.09)	0.15 (0.00)	15.4	1.82	0.12	-25.9 (0.1)
Ro-Forst,	>2000	11.0 (2.2)	nd	nd				
7-25	1000-2000	10.0 (0.2)	1.27 (0.02)	0.05 (0.00)	25.2	1.27	0.05	
	250-1000	21.0 (1.0)	0.99 (0.04)	0.05 (0.00)	20.9	2.08	0.10	
	53-250	22.1 (1.2)	0.78 (0.03)	0.04 (0.00)	18.0	1.71	0.09	
	<53	36.7 (2.0)	0.39 (0.02)	0.03 (0.00)	13.3	1.45	0.11	

* value determined from composite sample

Table 10.5: Halle: C [g] and in 1 kg soil $\delta^{13}C$ [‰ PDB], maize-derived C [%] and pMC in density fractions from Ha-M_{NPK}, Ha-M_0, Ha-R_{NPK}, and Ha-R_0. Means and SE (n = 4).

Plot	Density fraction	C [g] in aggregate fraction from 1 kg soil	$\delta^{13}C$ [‰ PDB]	Maize-derived C [%]	corr. pMC
Ha-M_{NPK}	$FPOM_{<1.6}$	1.20 (0.06)	-22.3 (0.5)	25.9 (3.7)	
	$OPOM_{<1.6}$	0.55 (0.04)	-25.5 (0.1)	2.3 (0.8)	
	$OPOM_{1.6-2.0}$	2.24 (0.33)	-24.5 (0.1)	4.0 (0.6)	
	$Mineral_{>2.0}$	7.98 (0.32)	-23.1 (0.0)	16.4(0.5)	
Ha-M_0	$FPOM_{<1.6}$	0.69 (0.12)	-22.3 (0.7)	22.9 (5.0)	57.21
	$OPOM_{<1.6}$	0.48 (0.01)	-25.5 (0.1)	1.3 (0.6)	9.64
	$OPOM_{1.6-2.0}$	1.74 (0.23)	-24.0 (0.3)	7.4 (2.2)	26.28
	$Mineral_{>2.0}$	7.28 (0.44)	-23.6 (0.0)	11.4 (0.5)	58.93
Ha-R_{NPK}	$FPOM_{<1.6}$	0.74 (0.03)	-26.6 (0.3)		
	$OPOM_{<1.6}$	0.31 (0.08)	-25.9 (0.1)		
	$OPOM_{1.6-2.0}$	2.39 (0.17)	-25.2 (0.1)		
	$Mineral_{>2.0}$	6.91 (0.37)	-25.9 (0.1)		
Ha-R_0	$FPOM_{<1.6}$	0.97 (0.14)	-26.2 (0.4)		38.47
	$OPOM_{<1.6}$	0.45 (0.04)	-25.7 (0.1)		7.14
	$OPOM_{1.6-2.0}$	1.55 (0.11)	-25.2 (0.1)		23.85
	$Mineral_{>2.0}$	6.91 (0.35)	-25.6 (0.1)		58.89

Corr. pMC indicates that the fraction of modern (1950) carbon was corrected for fractionation using simultaneous ^{13}C measurements.

Table 10.6: Rotthalmünster: C [g] and in 1 kg soil, $\delta^{13}C$ [‰ PDB], maize-derived C [%] and pMC in density fractions from Ro-W_{NPK}, Ro-M_{NPK}, Ro-M_{org} and Ro-Grass. Means and SE (n = 4).

Plot	Density fraction	C [g] in aggregate fraction from 1 kg soil	$\delta^{13}C$ [‰ PDB]	Maize-derived C [%]	corr. pMC
Ro-W_{NPK}	$FPOM_{<1.6}$	0.41 (0.04)	-26.5 (0.3)		105.36
	$OPOM_{<1.6}$	0.06 (0.01)	-27.4 (0.1)		99.26
	$OPOM_{1.6-2.0}$	1.18 (0.08)	-27.4 (0.0)		107.73
	$Mineral_{>2.0}$	8.62 (0.01)	-26.5 (0.1)		102.67
Ro-M_{NPK}	$FPOM_{<1.6}$	0.56 (0.12)	-18.0 (0.4)	59.1 (3.8)	102.87
	$OPOM_{<1.6}$	0.14 (0.06)	-23.9 (0.6)	25.4 (3.9)	97.6
	$OPOM_{1.6-2.0}$	1.01 (0.08)	-22.0 (0.4)	38.3 (2.7)	103.5
	$Mineral_{>2.0}$	8.75 (0.04)	-22.1 (0.1)	31.5 (3.0)	103.48
Ro-M_{org}	$FPOM_{<1.6}$	0.36 (0.03)	-18.6 (0.7)	55.7 (5.4)	
	$OPOM_{<1.6}$	0.07 (0.01)	-25.0 (0.4)	17.4 (3.2)	
	$OPOM_{1.6-2.0}$	1.03 (0.04)	-21.7 (0.0)	40.4 (0.4)	
	$Mineral_{>2.0}$	8.72 (0.01)	-21.6 (0.2)	34.8 (1.8)	
Ro-Grass	$FPOM_{<1.6}$	0.86 (0.03)	-28.9 (0.1)		
	$OPOM_{<1.6}$	0.29 (0.06)	-28.6 (0.1)		
	$OPOM_{1.6-2.0}$	2.13 (0.38)	-28.7 (0.1)		
	$Mineral_{>2.0}$	15.42 (0.07)	-28.0 (0.1)		

Corr. pMC indicates that the fraction of modern (1950) carbon was corrected for fractionation using simultaneous ^{13}C measurements.

Table 10.7: Halle: Total, C_3- and C_4-derived C_{extr_fum}, $\delta^{13}C$ values of C_c, C_{fum}, and C_{extr_fum} for Ha-M_{NPK}, Ha-M_0, Ha-R_{NPK}, and Ha-R_0. Means and SE (n = 4). For the Calculation of C_{mic} from C_{extr_fum}, the values need to be divided by k_{EC} = 0.45.

Depth [cm]	Origin of C	C_{extr_fum}	$\delta^{13}C$ C_c	$\delta^{13}C$ C_{fum}	$\delta^{13}C$ C_{extr_fum}	C_{extr_fum}	$\delta^{13}C$ C_c	$\delta^{13}C$ C_{fum}	$\delta^{13}C$ C_{extr_fum}
		[g m^{-2}]	‰ PDB	‰ PDB	‰ PDB	[g m^{-2}]	‰ PDB	‰ PDB	‰ PDB
		Ha-M_{NPK}				Ha-M_0			
0-10	Total	4.63 (0.30)	-20.3 (0.1)	-23.9 (0.2)	-17.2 (0.2)	3.57 (0.25)	-21.6 (0.4)	-24.2 (0.4)	-18.5 (0.6)
	C_3	2.52 (0.16)				2.21 (0.15)			
	C_4	2.11 (0.14)				1.36 (0.10)			
10-20	Total	5.69 (0.25)				4.20 (0.20)			
20-30	Total	5.23 (0.34)				3.90 (0.26)			
30-40	Total	3.62 (0.08)	-22.9 (0.2)	-24.5 (0.3)	-20.2 (0.4)	2.86 (0.21)	-22.9 (0.2)	-25.1 (0.1)	-18.8 (0.2)
	C_3	2.80 (0.06)				1.93 (0.14)			
	C_4	0.82 (0.02)				0.92 (0.07)			
40-50	Total	3.49 (0.39)				2.64 (0.19)			
50-60	Total	2.79 (0.36)				2.79 (0.39)			
		Ha-R_{NPK}				Ha-R_0			
0-10	Total	4.93 (0.19)	-25.6 (0.5)	-26.4 (0.1)	-24.9 (0.5)	3.96 (0.17)	-25.6 (0.5)	-26.2 (0.1)	-24.9 (0.5)
10-20	Total	5.21 (0.38)				4.02 (0.10)			
20-30	Total	5.09 (0.31)				3.74 (0.29)			
30-40	Total	2.72 (0.23)	-25.6 (0.1)	-26.1 (0.3)	-24.0 (0.3)	2.05 (0.36)	-25.6 (0.3)	-26.1 (0.1)	-24.3 (0.3)
40-50	Total	3.21 (0.31)				1.57 (0.37)			
50-60	Total	2.99 (0.26)				1.18 (0.25)			

Table 10.8: Rotthalmünster: Total, C_3- and C_4-derived $C_{extr\ \_freeze}$ and C_{extr_fum}, $\delta^{13}C$ values of C_c, C_{freeze}, C_{fum}, $C_{extr\ \_freeze}$, and C_{extr_fum} and fractions between SOC to $C_{extr\ \_freeze}$ and C_{extr_fum}, respectively. Means and SE (n = 4).

	Depth [cm]	Origin of Carbon	$C_{extr\ \_freeze}$	C_{extr_fum}	$\delta^{13}C$ C_c	$\delta^{13}C$ C_{freeze}	$\delta^{13}C$ C_{fum}	$\delta^{13}C$ $C_{extr\ freeze}$	$\delta^{13}C$ C_{extr_fum}	$C_{extr\ freeze}$ / $C_{extr\ fum}$ SOC	/SOC
			[g m^{-2}]	[g m^{-2}]	[‰ PDB]	[‰ PDB]	[‰ PDB]	[‰ PDB]	[‰ PDB]	[%]	[%]
Ro-W_{NPK}	0-30	Total	17.49 (0.75)	10.36 (1.88)	-27.4 (0.4)	-26.6 (0.1)	-25.9 (0.5)	-25.8 (0.6)	-24.4 (0.9)	0.34	0.20
	30-45	Total	5.79 (0.65)	1.12 (0.43)	-26.8 (0.5)	-26.7 (0.0)	-26.3 (0.3)	-26.6 (0.1)	-25.6 (0.6)	0.54	0.11
Ro-M_{NPK}	0-30	Total	23.02 (1.13)	12.06 (0.91)	-22.2 (0.7)	-21.1 (0.1)	-21.4 (0.1)	-20.2 (0.3)	-20.7 (0.2)	0.43	0.23
		C3	11.33 (0.55)	6.34 (0.48)						0.33	0.18
		C4	11.70 (0.57)	5.72 (0.43)						0.61	0.30
	30-45	Total	8.72 (0.38)	1.16 (0.12)	-25.6 (0.1)	-23.7 (0.2)	-24.4 (0.0)	-22.0 (0.7)	-23.3 (0.1)	0.57	0.08
		C3	2.96 (0.25)	0.29 (0.09)						0.44	0.07
		C4	5.75 (0.13)	0.87 (0.03)						1.25	0.12
Ro-M_{org}	0-30	Total	27.87 (1.81)	13.54 (0.73)	-23.6 (0.0)	-20.9 (0.2)	-21.0 (0.0)	-18.9 (0.7)	-19.1 (0.1)	0.50	0.24
		C3	16.76 (0.72)	7.92 (0.30)						0.31	0.16
		C4	11.11 (1.09)	5.63 (0.43)						0.84	0.40
	30-45	Total	10.29 (0.88)	2.65 (0.63)	-25.8 (0.1)	-23.9 (0.1)	-24.4 (0.2)	-22.4 (0.5)	-23.4 (0.4)	0.68	0.17
		C3	6.19 (0.35)	1.55 (0.26)						0.34	0.09
		C4	4.10 (0.53)	1.10 (0.37)						2.12	0.52
Ro-Grass	0-10	Total	17.28 (0.66)	9.78 (0.74)	-28.0 (0.4)	-27.0 (0.7)	-27.8 (0.1)	-26.5 (1.9)	-27.7 (0.1)	0.57	0.32
	10-20	Total	12.18 (1.53)	2.51 (0.86)	-27.2 (0.1)	-26.3 (0.5)	-27.1 (0.1)	-26.0 (0.7)	-27.1 (0.1)	0.72	0.14
	30-45	Total	6.91 (0.47)	0.99 (0.43)	-26.7	-26.9 (0.1)	-26.9 (0.3)	-27.0 (0.3)	-27.0 (0.6)	0.60	0.09

11 CURRICULUM VITAE (IN GERMAN)

Name	John, Bettina Maria
Geboren am/in	19.3.1973 in Mannheim
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Schulausbildung

8/1979 – 6/1983	Goethe-Grundschule in Viernheim
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Hochschulausbildung

10/1992 – 11/1999	Studium der Geoökologie an der Technischen Universität Braunschweig
10/1994	Vordiplom in Geoökologie
9/1995 – 6/1996	Studium der Environmental Sciences an der Western Washington University in Bellingham, Washington, USA
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Berufspraktika

9/1993	Praktikum beim Verein zum Schutz von Hiddensee und Boddenlandschaft e.V. auf Hiddensee
7/1996 – 9/1996	Praktikum bei der Seattle Audubon Society, Seattle, Washington, USA
3/1997	Praktikum beim Zentrum für Agrarlandschafts- und Landnutzungsforschung (ZALF) e.V.
9/1997 – 10/1997	Praktikum bei der Hoechst Schering AgrEvo GmbH, Frankfurt, Abteilung Umweltforschung – Ökochemie

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12/1999 – 2/2000	Projektmitarbeiterin bei Aventis CropScience, Frankfurt, Abteilung Environmental Risk Assessment
3/2000 – 9/2000	Wissenschaftliche Angestellte am Institut für Ökologische Chemie und Abfallanalytik der TU Braunschweig
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