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Management effects on carbon distribution in soil aggregates and its consequences on water repellency and mechanical strength

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A	aggregate
AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
Al	aluminium
ANOVA	Analysis of variance
A_t	CO_2 efflux
$a_{1,}$ a_2	amount of CO_2
B	bulk soil
Bc	Bucken
c	concentration
C	carbon
C-H	aliphatic carbon – hydrogen bonds
CEC	cation exchange capacity
C_F	centrifugal force
C=O	carboxylic carbon – oxygen bonds
C_{org}	organic carbon
C/N	carbon to nitrogen ratio
CO_2	carbon dioxide
CT	conventional tillage
CnT	conservation tillage
d_a	diameter of aggregate
D_0	diffusion coefficient
DRIFT	diffuse reflectance Fourier transform infrared spectroscopy
ex	external aggregate region
E_s	erosive strength
f	carbon derived von maize
F	force
Fe	iron
g	gravitativen forces
GAFLOCOD	gas flow compaction device
h	capillary rise height

H	homogenized sample
d_B	bulk density
in	internal aggregate region
J	mass flow
k	hydraulic conductivity
k_1, k_2	coefficients of the release rate of CO_2
K	potassium
m	mass
M	maize
Mn	manganese
N	nitrogen
n	number of samples
Na	sodium
NO_2	nitrogen dioxide
p	significance probability
PDB	Pee Dee Belemnite, carbonate standard for ^{13}C analysis
pH	negative decadic logarithmic of the proton activity
pF	logarithm of the negative tension
PLFA	phospholipids fatty acid
q	water flow
r	pore radius
rpm	rotations per minute
R	repellency index
R_a	radius of the aggregate
R_{SK}	radius of the rotary shaker
R_{SAE}	radius of the erosion chamber
Rm	Rotthalmünster
Rz	Ritzereu
SAE	soil aggregate erosion chamber
S_e	sorptivity of ethanol
S_w	sorptivity of water
SOC	soil organic carbon
SOM	soil organic matter
st.err	standard error of the mean

st.dev	standard deviation
t	time
TOC	total organic carbon
tr	transitional aggregate region
T_s	tensile strength
W	wheat
α	contact angle
γ	surface tension
ρ	density
μ	viscosity
ω	angular velocity
μ_f	frictional coefficient
$\delta^{13}C$	^{13}C:^{12}C ratio in ‰ expressed relatively to the PDB standard
Ψ_w	hydraulic gradient
Ψ_m	matric potential
Ψ_g	gravitation potential

Summary

Agricultural soils should have the ability to support plant growth by providing nutrients, gas, water, heat and a rootable pore system. Soil structure has a major influence on these properties, but human activities often cause severe changes in soil structure which may have detrimental impacts on soil functions. Soil structure mediates many physical and biological processes like porosity, infiltration, water availability for plants and mineralization by microorganisms.

In structured soils porosity is categorized into inter-aggregate and intra-aggregate pores latter leading to preferential flow of soil solution and root growth within coarse pores as well as development of chemical and physical gradients of the soil matrix. In most aggregated soils the hierarchical arrangement of soil particles to larger aggregate units are recognised; single particles form small domains, assembling microaggregates which in turn are arranged to macroaggregates with organic matter as a main binding agent.

Soil organic matter (SOM) has been reported to play an important role in global carbon cycling and has a high capacity to sequestrate large amounts of C_{org}. Changes in the carbon reservoir in agricultural soils induced by management practices can cause increased decomposition rates of soil organic matter and, in consequence, cause the loss of carbon as CO_2. Stabilization of SOM in soils is affected by the quantity and quality of plant substrates deposited in soil and its protection against microbial and oxidative degradation.

Although the processes responsible for organic carbon distribution and its accessibility have been investigated for many years it is still not fully understood how the management of the soil influences the distribution of organic carbon in soils and how the presence of organic substances affects the aggregate stability and movement of water in soil.

The purpose of this study was to investigate the physico-chemical heterogeneity of structured soils by analysing bulk soil, soil aggregates and homogenized material from arable soils (conservation and conventional tillage) in comparison to grassland soils. Soil samples were collected from an experimental field in Rotthalmünster in south Germany from silty loam Anthrosol and Luvisol at different soil horizons; in addition soil aggregates were collected from Ap horizon of Cambisoil of agricultural site in Ritzerau and Sw-Al horizon of stagnic Luvisol (forest site) in Bucken.

The organic carbon distribution of the investigated soils showed higher contents in the topsoil and decreased with depth. Organic carbon distribution varied not only between soil horizons, but also between aggregates of different sizes. The highest contents of organic carbon were found in small aggregates (<2mm) after segregation by dry sieving. The determination of carbon using δ^{13}C identified that in the smallest fraction mostly fresh organic carbon was deposited. Percolation with Na-pyrophosphate solution the most influenced the smallest aggregates and more organic carbon was lost than in other aggregate fractions. Those findings suggest that the organic carbon present in those aggregates was not associated with mineral fraction and was most easily removable from the soil.

The determination of organic carbon distribution and the δ^{13}C signal within soil aggregates have shown only a slight tendency of higher C_{org} accumulation in the exterior aggregate region in comparison to the interior ones. Neither the depletion of C_{org} after percolation nor the enrichment of fresh C_{org} in aggregates after greenhouse experiment have shown any significant differences in distribution of carbon between the exterior and the interior regions of soil aggregates.

In contrast to the soil material from Rotthalmünster the analyses of organic carbon distribution in the Sw-Al horizon of a stagnic Luvisol from Bucken have shown reduced contents of C_{org} in the aggregate exteriors in comparison to the interior regions.

Differences in the contents of hydrophobic and hydrophilic groups between the exterior and the interior regions of aggregates of Rotthalmünster soils were found. Most investigated soil aggregates showed higher amounts of hydrophilic groups in the exterior regions of aggregates than in the interior regions.

Further differences between aggregate interior and exterior were found in chemical element content distribution; K, Fe and Al have shown reduced contents in exterior regions in comparison to the interior regions, in contrast to the Na had a higher content on the aggregate surface. The microorganism distribution also resulted in a higher concentration of bacteria and fungi on the aggregate surface and a depletion in the aggregate center. In addition the measurements of water repellency on the outer surface of the aggregates have shown in the Anthrosol (maize) and in the Ap horizon of the Luvisol (wheat) higher repellency indices than in the aggregate interior probably due to higher microbiological activity at aggregate surfaces.

Water repellency investigation has shown that the Rotthalmünster soil showed only a slightly reduced infiltration rate. At field moisture water contents the values of water repellency index did not change strongly, however aggregates were mostly analysed under air dry conditions. Higher levels of repellency were detected in topsoil horizon and decreased with soil depth; in addition smaller aggregates of cultivated soils had higher repellency than larger ones.

Aggregate size had also a high effect on aggregate strength. The tensile strength of air dry aggregates was not only affected by the depth of the soil (aggregates from the subsoil were more stable), but also in most cases smaller aggregates were stronger than the larger ones. Field moist aggregates had significantly lower tensile strengths than air-dry aggregates.

Soil use and management influence the physical properties of the soil. In this research the largest differences were detected between grassland soils and arable soils, while the differences between conventional and conservation tillage systems were less pronounced. In cultivated soils especially in topsoil horizons the higher heterogeneity of physical properties was found than in undisturbed horizons or grassland soils. Due to different crops on the conventional and conservation sites in some cases it was not possible to recognize whether the vegetation type or the tillage system had a higher influence on distribution of organic carbon or water repellency. In addition the conservation tillage system was introduced for relatively short time and it may not have been long enough to recognize significant differences in soil properties. The most pronounced changes were detected during the percolation experiment where in conventional tilled soils the hydraulic conductivity was much higher in comparison to conservation tillage, as an effect of reduced hydraulic conductivity the loss of organic carbon was also much smaller.

Zusammenfassung

Landwirtschaftliche Böden sollen die Fähigkeit aufweisen, das Pflanzenwachstum zu unterstützen und dieses mit Nährstoffen, Gas, Wasser und einem gut durchwurzelbaren Porensystem zu versorgen. Die Bodenstruktur beeinflusst diese Eigenschaften, jedoch verursachen menschliche Tätigkeiten nachhaltige Veränderungen in der Bodenstruktur, was wiederum negative Auswirkungen auf die Bodenfunktionen haben kann. Die Bodenstruktur beeinflusst physikalische und biologische Prozesse wie Porosität, Infiltration und Wasserverfügbarkeit für Pflanzen sowie Mineralisierung durch Mikroorganismen.

In strukturierten Böden klassifiziert man die Porosität in intra-aggregat- und inter-aggregat-Poren. Präferenzieller Fluss der Bodenlösung, sowie das Wurzelwachstum in den Grobporen werden vom Interaggregatporensystem beeinflusst. In aggregierten Böden ist die hierarchische Anordnung von Bodenpartikeln zu größeren Einheiten bekannt, d.h., einzelne Partikel finden sich zu kleinen Domänen die sich zu Mikroaggregaten und größeren Makroaggregaten verbinden, wobei die organischen Substanzen als Hauptbindemittel fungieren.

Die organische Substanz des Bodens (SOM) spielt eine wichtige Rolle im globalen Kohlenstoffkreislauf und weist eine große Kapazität zur organischen Kohlenstoffstabilisierung auf. Bodenbearbeitung verursacht eine Veränderung der gespeicherten organischen Bodensubstanz, sie führt zum Abbau bzw. zum Verlust der organischen Substanz in Form von CO_2. Kohlenstoffstabilisierung in Böden wird durch die Menge und die Art des Pflanzenmaterials bestimmt. Des Weiteren wird der mikrobielle und oxidative Abbau im Boden verhindert. Die unterschiedlichen Prozesse, die zur Stabilisierung und zum Abbau von Kohlenstoff beitragen, sind trotz vieler Untersuchungen noch nicht ganz geklärt. Hierbei ist die Frage nach der Bedeutung des Bodenmanagement für die Verteilung des organischen Kohlenstoffs und das Vorhandensein der organischen Substanzen ebenso zu klären wie die Aggregatstabilität und die Bewegung des Wassers im Boden beeinflusst werden.

Ziel dieser Arbeit war es, die physiko-chemikalische Heterogenität des strukturierten Bodens in Vergleich von Gesamtboden, Bodenaggregaten und homogenisiertem Material von Ackerböden (konventionell und konservierend bearbeiteten Flächen) sowie von Grünlandböden zu untersuchen. Die Bodenproben stammen aus unterschiedlichen Horizonten des Versuchsfeldes in Rotthalmünster in Süddeutschland. Es handelt sich um einen tonig-schluffigen Luvisol (Pseudogley Kolluvisol) und einen Anthrosol (Pseudogley Parabraunderde) aus Löss. Außerdem wurden noch Bodenaggregaten vom Ap-Horizont des Standortes Ritzerau sowie vom Sw-Al-Horizont in Bucken untersucht.

Die organische Kohlenstoffverteilung zeigt höhere Gehalte im Oberboden und nahm mit zunehmender Tiefe ab. Nicht nur zwischen den Bodenhorizonten variiert die organische Kohlenstoffverteilung, sondern auch zwischen den Aggregaten unterschiedlicher Größe. Der höchste Gehalt an organischem Kohlenstoff wurde in den kleineren Aggregaten (<2 mm) nach trockener Siebung nachgewiesen. Mit der Methode der natürlichen ^{13}C Abundanz wurde nachgewiesen, dass in der kleinsten Aggregatgrößenklasse sich frischer organischer Kohlenstoff akkumuliert. Des Weiteren verloren die kleinsten Aggregate (<2 mm) am meisten an organischen Kohlenstoff durch die Na-Pyrophosphatperkolation. Es kann davon ausgegangen werden, dass der organische Kohlenstoff, der in dieser Fraktion vorhanden ist, nicht mit Mineralpartikeln oder Aggregaten verbunden ist und leicht vom Boden entfernbar ist. Obwohl die größeren Aggregate weniger organischen Kohlenstoff besitzen, kann man sie als relativ reich an organischem Kohlenstoff bezeichnen, da sich der C_{org}-Gehalt vor und nach der Perkolation kaum verändert, im Gegensatz zum relativ großem C_{org}-Verlust der kleineren Aggregate.

Die Untersuchung der organischen Kohlenstoffsverteilung und die ^{13}C Abundanz innerhalb der Bodenaggregaten haben gezeigt, dass nur in wenigen Aggregaten des untersuchten Bodens ein geringfügig höherer C_{org}-Gehalt an der Aggregatoberfläche als im Innenbereich nachgewiesen werden konnte. Die Verringerung des C_{org}-Gehalts nach der Perkolation und auch die Anreichung von frischem Corg während des Gewächshausexperiment hat zu keinem signifikanten Unterschied in der Verteilung des Kohlenstoffes innerhalb der

Bodenaggregate geführt. Im Gegensatz zu dem Bodenmaterial des Luvisols und des Anthrosols aus Rotthalmünster haben die Analysen der organischen Kohlenstoffsverteilung im Sw-Al Horizont eines stagnic Luvisol verringerte C_{org}-Gehalte des gesamten Außenbereichs im Vergleich zum Innenbereich gezeigt.

Allerdings wurden Unterschiede bezüglich des Inhalts der hydrophoben und hydrophilen Gruppen zwischen den Außen- und Innenregionen der Aggregate des Bodens gefunden. Die meisten untersuchten Bodenaggregate zeigten höhere Mengen der hydrophilen Gruppen in den Außenregionen als in den Innenregionen.

Unterschiede zwischen Aggregatinnerem und -äußerem wurden auch in der Verteilung verschiedener chemischer Elemente gefunden; K, Fe und Al wiesen geringere Gehalt in den Außenregionen im Vergleich zu den Innenregionen auf, dagegen war Na hauptsächlich an der Aggregatoberfläche angesammelt. Ferner ergaben Untersuchungen eine höhere Konzentration an Bakterien und Pilzen auf der Aggregatoberfläche, die zum Inneren hin abnahm. Die Benetzungshemmung war auf der Oberfläche der Aggregate des Anthrosol und im Ap Horizont des Luvisol größer als im Aggregatinneren. Dies lässt sich auf die erhöhte mikrobiologische Tätigkeit an der Aggregatoberfläche zurückführen.

Feldfeuchte und luftgetrocknete Aggregate zeigten nur eine geringe Abnahme der Infiltrationsraten. Jedoch war eine höhere Benetzungshemmung von Aggregaten aus dem Oberboden im Vergleich zum Unterboden erkennbar. Des Weiteren ist die Variabilität der Benetzungshemmung von der Aggregatgröße abhängig. Kleinere Aggregate vor allem in den bearbeiteten Flächen weisen eine höhere Hydrophobie als große Aggregate auf.

Die Aggregatgröße hat zudem einen großen Effekt auf die Zugfestigkeit von Bodenaggregaten. Die Zugfestigkeit der lufttrockenen Aggregate ist nicht nur vom Horizont (Aggregate aus dem Unterboden sind stabiler) beeinflusst, sondern auch von der Aggregatgröße. In den meisten Fällen waren kleinere Aggregate stabiler. Feldfeuchte Aggregate wiesen generell eine geringere Zugfestigkeit im Gegensatz zu trockenen Aggregate auf.

Bodenbearbeitung beeinflusst die physikalischen Eigenschaften des Bodens. In dieser Arbeit wurden die größten Unterschiede zwischen Boden unter Grünland und unter Ackernützung ermittelt. Dagegen waren die Unterschiede zwischen der konventionellen und konservierenden Bodenbearbeitung weniger ausgeprägt. Die größte Heterogenität der Bodeneigenschaften wiesen die Oberböden der Ackerflächen, im Vergleich zu den ungestörten Horizonten im Unterboden oder der Grünlandböden auf. Aufgrund der unterschiedlichen Vegetation auf den konventionellen und konservierenden bearbeiteten Flächen, war es teilweise nicht möglich zu entscheiden, ob die Vegetationsart oder die Bodenbearbeitung einen größeren Einfluss auf bestimmte Bodeneigenschaften hatte. Des Weiteren wurde erst 1998 auf konservierende Bodenbearbeitung umgestellt, so dass noch keine signifikanten Veränderungen der Bodeneigenschaften zu erkennen waren. Ausgeprägte Veränderungen wurden während des Perkolationsexperimentes ermittelt. Der konventionell bearbeitete Boden zeigt eine höhere hydraulische Leitfähigkeit im Vergleich zum konservierend bearbeiteten Boden. Folglich führen kleinere Werte der Wasserleitfähigkeit zu einer geringeren Auswaschung von Kohlenstoff.

Streszczenie pracy

Wpływ zagospodarowania gleb na rozmieszczenie węgla organicznego w agregatach glebowych oraz jego efekt na hydrofobowość i wytrzymałość mechaniczną gleb

Gleba należy do jednego z najcenniejszych zasobów Ziemi, gdyż warunkuje ona życie roślin a w konsekwencji istnienie życia zwierząt i człowieka. Dzięki glebie zachodzi przepływ energii i obieg materii w ekosystemie; jej ważna rola w obiegu węgla w przyrodzie może mieć bezpośredni efekt na emisję dwutlenku węgla do atmosfery co w konsekwencji może wywoływać zmiany klimatyczne.

Głównym zadaniem gleb uprawnych jest umożliwienie wzrostu roślinom poprzez zapewnienie im składników odżywczych, powietrza, wody, ciepła oraz porowatego systemu do rozwoju korzeni. Ważne znaczenie na w/w właściwości ma struktura gleby, bowiem pośredniczy w wielu biologicznych i fizycznych procesach jak infiltracja, dostępność wody dla roślin jak również wrażliwość na erozję. Naturalna stuktura gleby jest często zakłócana poprzez działalność człowieka co może znacznie ograniczać niektóre funkcje gleby.

Gleby strukturalne agregatowe charakteryzują się porowatością, która dzieli się na międzyaggregatową oraz wewnątrzagregatową. Porowatość międzyaggregatowa to z reguły gołym okiem widoczne rysy i makropory tworzące najczęściej połączony system, w przeciwieństwie do wewnątrzagregatowych porów o znacznie mniejszych rozmiarach, często odseparowanych od siebie. Obecność tych dwóch rodzajów porów prowadzi do preferencyjnego przepływu roztworów glebowych oraz rozwoju korzeni roślinnych pomiędzy aggregtami. W większości gleb agregatowych widoczne jest hierarchiczne rozłożenie glebowych partykułów, czyli pojedyncze ziarna gleby tworzą małe domeny, następnie mikroaggergaty i większe makroagregaty, w których materia organiczna funkcjonuje jako główny składnik cementujący. Rola materii organicznej jest nie tylko bardzo znacząca dla samej gleby, ale również dla całego ekosystemu. Dlatego rozmieszczenie i dostępnośc materii organicznej jest tematem wielu badań naukowych, jak również określenie jakie znaczenie ma jej dystrybucja na przepływ wody w systemie glebowym oraz jej właściwości stabilizacyjne dla agregatów glebowych.

Celem przeprowadzonych pomiarów było badanie wpływu dystrybucji węgla organicznego na zwilżalność gleby oraz mechaniczną wytrzymałość agregatów, w zależności od typu zagospodarowania gleby. Do przeprowadzonych analiz wykorzystano próbki o nienaruszonej strukturze, pojedyńcze agregaty glebowe o różnych rozmiarach oraz shomogenizowany materiał glebowy. Próbki glebowe zostały pobrane z eksperymentalnego pola w Rotthalmünster na południu Niemiec z pyłowo-gliniastych gleb Luvisol i Anthrosol (klasyfikacja FAO), z trzech horyzontów glebowych i z czterech różnie zagospodarowanych pól: bezorkowa uprawa pszenicy, orkowa uprawa kukurydzy oraz dwa rodziaje gleby łąkowych.

Badanie rozmieszczenia węgla organicznego w glebie wykazało, że górne horyzonty glebowe są znacznie wzbogacone w świeży materiał organiczny, w zależności od typu uprawy najwyższe zawratości węgla organicznego w wierzchniej warstwie znaleziono w glebach łąkowych, następnie w glebach systemu bezorkowego i najniższe w konwencjonalnie uprawianej ziemi. Poza znaczną różnorodnością w zawartości materii organicznej w poszczególnych horyzontach zauważono również zależność zawartości węgla od wielkości agregatów glebowych. W mniejszych agregatach glebowych (separacja w warunkach suchych) znaleziono wyższe zawartości węgla, szczególnie węgla świeżego (metoda różnic sygnału $\delta^{13}C$) w prównaniu do agregatów o większych średnicach. Przeprowadzenie procesu perkolacji z Na-pirofosforanem również pokazało największy wpływ na najmniejszą frakcję agregatową, podczas gdy w agregatach o większych średnicach efekt był dużo mniejszy. Doprowadziło to do wniosku, że węgiel organiczny powiązany z mineralną fazą glebową w agregatach glebowych jest mniej narażony na wymywanie niż luźna materia organiczna.

Badania dotyczące dystrybucji węgla organicznego przeprowadzono również wewnątrz pojedynczych agregatów glebowych, gdyż preferencyjny przepływ roztworów glebowych oraz korzeni roślin może prowadzić do powstawania gradientów pomiędzy zewnętrznym i wewnętrznym regionem agregatów. Korzystając z mechanicznego urządzenia do separacji materiału z poszczególnych wartstw agregatu oddzielono materiał z zewnętrzenej powierzchni agregatu, od jego centrum i przeprowadzono analizy chemiczne tj. zawartość: C_{org}, Na, K, Al, Fe, Mn, grup hydrofobowych i hydrofilowych; dystrybucja mikroorganizmów; hydrofobowość poszczególnych warstw agregatu; oraz na podstawie prędkości izolowania materiału wyznaczono erozyjną wytrzymałość poszczególnych warstw agregatu. W/w analizy wykazały, że zewnętrzna warstwa agregatów charakteryzuje się nieznacznym wzrostem zawartości węgla organicznego, większą akumulację K, Fe i Al oraz hydrofilowych i hydrofobowych grup węgla; zwiększoną aktywnością mikroorganizmów oraz w większości mierzonych agregatów również niższą zwilżalnością (wyższą hydrofobowością). Wnętrza agregatów miały wyższą gęstość objętościową oraz większą wytrzymałość erozyjną niż zewnętrzne warstwy.

Pomiary zwilżalności glebowych wykonane na agregatach glebowych o różnej wielkości wykazały, zredukowaną infiltrację zwaną niezwilżalnością subkrytyczną, która może mieć pozytywny wpływ na stabilizację struktur agregatowych glebie, jak również sekwestrację węgla. Wyższe wartości niezwilżalności zanotowano w wierzchniej warstwie gleby i spadek jej wartości razem z głębokością. Dodatkowo zanotowano znaczne różnice w zwilżalności w zależności od wielkości agregatów, szczególnie w tych glebach gdzie uprawa była bardziej intensywna. Nie znaleziono jednak korelacji pomiędzy zawartością grup hydrofobowych oraz niezwilżalności.

Mechaniczne właściwości agregatów glebowych były badane na podstawie próby na zgniatanie (crushing test) i znaleziono, że gleba pochodząca z głębszych warstw ma wyższą wytrzymałość niż agregaty z horyzontów wyższych, bardziej narażonych na działanie warunków zewnętrznych. Mniejsze agregaty były z reguły bardziej wytrzymałe niż większe, co dowodzi hierarchicznemu rozmieszczeniu jednostek strukturalnych. Nie znaleziono jednak pozytywnego wpływu zawartości substancji orgnicznych na wytrzymałość agregatów w suchych warunkach, co może oznaczać, że materia orgniczna, która w warunkach wilgotnych ma właściwości stabilizujące, w warunkach suchych traci te właściwości, a wręcz przyczynia się do powstawania rys w miejscach akumulacji materii organicznej.

Próba znalezienia zależności między sposobem zagospodarowania gleb i wpływem na jej fizyczne właściwości doprowadziła do wniosku, że najbardziej widoczne są różnice między glebami uprawnymi i łąkowymi, podczas gdy różnice między systemem orkowym i bezorkowym są mniej zaznacznone. Różnice te są najbardziej widoczne w wierzchniej warstwie gleby, gdzie uprawa ma największy wpływ na heterogenizację właściwości. Najbardziej widoczne zmiany zaobserwowano na podstawie przeprowadzonego procesu perkolacji, gdzie różnice między hydrauliczną przewodnością między systemem konwencjonalnym i bezorkowym były bardzo znaczne i prowadziły do zmniejszonej ilości wypłukanego węgla w próbkach z uprawy bezorkowej.

W związku z tym, że bezorkowy i orkowy typ uprawy były zagospodarowane przez różne rośliny, podczas analizy właściwości tych gleb trudno było odróżnić, czy większe znaczenie miał typ uprawy, czy raczej rodzaj wegetacji. Poza tym system bezorkowej uprawy wprowadzony został zaledwie przed kilku laty (1998), dlatego efekt tej zmiany może być jeszcze nie do końca widoczny.

I General introduction

1 Introduction

Stable soil structure which provides nutrients, gas, water and beneficial thermal properties, and a sufficient rootability for plant growth is important and needed for agricultural practices. However, some practices like soil tillage can have a destructive effect on soil, and during cultivation the natural soil conditions are changed and former structure disrupted. Intensive and not appropriate soil management can lead to depletion of organic carbon, erosion of the soil and poor water and aeration conditions.

Soils are reported to have a high capacity of carbon sequestration in form of soil organic matter and the management of the soils has a significant influence on the mineralization of organic carbon to CO_2 and its respiration to the atmosphere. Several properties are reported to have a direct or indirect influence on carbon sequestration in soils. One of the aspects is the physical protection of organic carbon in soil aggregates due to reduced accessibility of microorganisms in structured soils. Although this aspect has been investigated repeatedly, it is still not totally understood how the usage of the soil affects the organic matter distribution and its accessibility in soils. Furthermore, the question how the distribution of organic material affects the stability of soil structure and water movements is also not finally solved and led to the following investigations.

2 Objectives

The general objective of this study was to find out how the distribution of organic carbon is affected by soil management and which consequences it has on water repellency and mechanical strength.

The detailed objectives of each experiment have been stated in each chapter and the investigation focuses on following questions:

- Chapter III: Does preferential flow and plant roots distribution in aggregated soils cause chemical, microbiological and physical gradients? Which effect has soil depth and the vegetation type on the wettability and aggregate strength? Is there any effect of mechanical soil strength on gas fluxes and microbial activity?
- Chapter IV: Does the surface of soil aggregates contain more hydrophobic material than the bulk soil? Do higher concentrations of hydrophobic material induce higher levels of repellency on the surface of soil aggregates? Is there any difference in carbon content and distribution of functional groups in aggregate exterior and interior? What is the effect of arable soil management on the distribution of hydrophobic compounds?
- Chapter V: Does the erosive strength change according to different concentric layers of aggregates? Are the tensile and erosion strength of aggregates affected by different soil management and soil depths? What is the relationship between aggregates strength and other soil properties?
- Chapter VI: How far the conventional and conservation tillage systems influence the accessibility of organic carbon in soil during percolation with water and pyrophosphate solution? How far the loss of organic carbon during the percolation processes affects the distribution of organic carbon in aggregates from different size classes and within aggregates? Does the depletion of organic carbon due to percolation processes effect the bulk density and tensile strength of single aggregates?
- Chapter VII: How the organic carbon is distributed in aggregates of different sizes and concentric layers of single aggregates? Is the six weeks period of C_4 plant growth on soil with C_3 vegetation enough to detect the accumulation of the fresh organic matter in soil aggregates?

II Literature overview

1 Characteristic of structured soils

Soil can not be considered as a group of individual soil particles, but as a composite body, in which the various particles are packed and held together to form a continuous spatial network, which is commonly called the soil matrix. The arrangement or organization of the particles in the soil is called soil structure (Hillel, 1998) which can be also defined as the spatial heterogeneity of the different components or properties of soil (Dexter, 1988).

1.1 Size and shape of aggregates

The structural units of soil structure are aggregates which can vary in size and shape. The hierarchical concept of soil aggregation considers that large aggregates are composed of smaller ones defined as microaggregates, clusters, domains and finally smallest clay particles which again are composed from single mineral particles (Hadas, 1987; Oades and Waters, 1991; Jastrow and Miller, 1998; Six *et al.*, 2000; Six *et al.*, 2004). The shapes of aggregates observed in the field described by Hillel (1998) are as follows: platy (horizontally layered, thin and flat), prismatic (vertically oriented pillars, often six-sided, up to 15 cm in diameter), blocky (cube-like blocks, up to 10 cm in size, sometimes angular with well-defined planar faces) and spherical (rounded, generally not larger than 2 cm in diameter).

1.2 Aggregate formation

The processes of aggregate formation are results of the changes in water content (wetting and drying of the soil) as well as biological activity of the microorganisms (Hillel, 1980; Horn, 1990; Anderson and Domsch, 1995). Dexter (1988) proposed that the soil structure may be created either by the grouping of structural elements of lower hierarchical order or by fragmentation of larger structural elements. Shrinkage of the soil causes the formation of cracks which defines the boundaries of the aggregates, and even after wetting the cracks between aggregates remain planes of weakness (Dexter, 1988).

Changes in water content of the soil, especially when the soil dries causes that mineral particles are tied together by capillary forces, which increase the number of points of contact and result in the formation of inter- and intra-aggregate pores (Horn and Dexter, 1989). The intra-aggregate pores are the narrow pores within aggregates which include micropores and capillary pores, while the inter-aggregate pores include partly capillary pores and macropores (Hillel, 1998).

1.3 Water flow in structured soils

Flow of water in soil depends on the size, form and continuity of pores. Following the Hagen-Poiseuille Law (Eq. II-1) the dominant role for water flow (q_w) plays pore radius (r), then viscosity (μ) of the liquid and the distance (l) of the flow.

$$q_w = r^4 \frac{\pi \cdot \partial \Psi h_w / \partial y}{8 \cdot \mu \cdot l} \qquad \textit{Eq. II-1}$$

The hydraulic gradient ($\vartheta \Psi h_w / \vartheta y$) is the driving force for water flow in soil and is completed from the matric (Ψ_m) and gravitation gradients (Ψ_g).

$$\Psi_w = \Psi_m + \Psi_g \qquad \textit{Eq. II-2}$$

The determination of pore size distribution and interconnectivity of pores is usually not feasible; therefore the macroscopic approach is used to for describing flow in soil. Darcy’s law postulates that the water flow through a porous medium is proportional to the hydraulic gradient and also proportional to the ability of conducting medium to transmit the liquid called hydraulic conductivity (k).

$$q_w = -k_w \frac{\partial \Psi h_w}{\partial y} \qquad \textit{Eq. II-3}$$

The hydraulic conductivity (k) is different for saturated and unsaturated conditions in soil. Under saturated conditions hydraulic conductivity is a function of fluid and soil properties, whereas under unsaturated conditions the conductivity also depends on the matric suction head $k=k(\Psi)$

1.4 Mechanisms of solutes transport in structured soils

In heterogenic porous aggregated soils the soil solutions flow has been classified to mobile and immobile phases (van Genuchten and Wierenga, 1976;

Beven and Germann, 1982). The mobile phase is limited to the centres and the inner peripheries of macropores (Becher, 1985) and the immobile phase percolates slowly through the micropores in the aggregates (Hantschel et al., 1988). The transport through macropores is mostly due to the convection (mass flow) (Selim et al., 1985), whereas flow from the inter-aggregate pores to the intra-aggregate pores is due to the process of diffusion.

The convection of soil water caring the solutes is described by following equation called also Darcian flow:

$$J_c = qc = -c\left(k\frac{dH}{dx}\right) \qquad \textit{Eq. II-4}$$

where J_c is a mass of solute passing through a unit cross-sectional area of a soil body per unit time, q following Darcy's flow is a volume of solution flowing through a unit area per time (k - hydraulic conductivity, dH/dx - hydraulic gradient) and c is the concentration of solution (mass of solute per unit volume of solution).

Diffusion process occurs in consequence of the random thermal motion and repeated collisions and deflections of molecules in the fluid (Hillel, 1998). Nonuniform distribution of solutes throughout a solution causes the concentration gradients, and solutes tend to diffuse from zones where their concentration is higher to where it is lower. The rate of diffusion (J_d) is related by Fick's first low to the gradient of the concentration (c):

$$J_d = -D_0\frac{dc}{dx} \qquad \textit{Eq. II-5}$$

in which D_0 is the diffusion coefficient for a particular solute and dc/dx is the effective concentration gradient of the solute.

In inter- and intra-aggregate pore systems solution flow with different velocities, the hydraulic conductivity in bulk soil is higher in comparison to slower flow inside aggregates (Horn, 1990). Such variation result also in different chemical compositions of soil solutions between single aggregates, bulk soil and homogenised material.

The importance of soil structure for cation exchange processes were studied by Hartmann *et al.* (1998), who found lower amount of exchangeable cations in water from saturated structured soil compared to a homogenized sample of the same material. Hantschel *et al.* (1988) also reported that the extracts of homogenized soil contains more alkaline cations than the soil extracts from percolation. Such large differences between structured and homogenised soils were due to larger accessible surface area of homogenised material and high pores tortuosity in structured soils which decreases the accessibility of intra-aggregate surfaces (Horn, 1987).

1.5 Gradients in soil aggregates

The preferential flow in structured soils concerns not only the domination of solution flow in inter-aggregate pore system, but also presence of gases, roots and litter and microorganisms between aggregates (Horn, 1994; Augusitin *et al.*, 1995). Presented in Figure II-1 schema show that due to the preferential distribution of liquids, gases, microorganisms and roots between aggregates chemico-physical gradients in soil aggregates can be formed (Augusitin *et al.,* 1995).

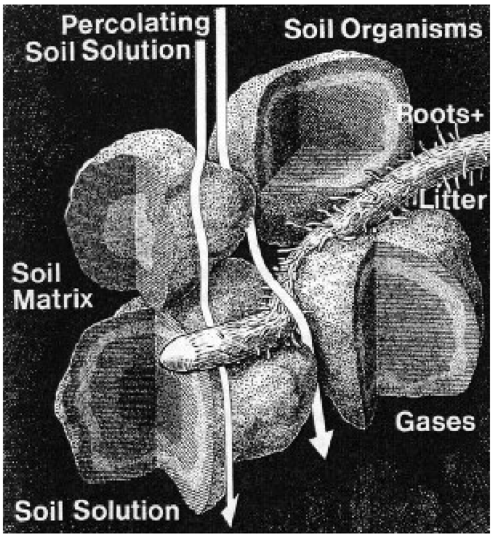

Figure II-1 *Schematic diagram of different gradients in aggregated soils (Augustin et al., 1995)*

Several authors reported great differences between the exterior, transitional and the interior region of soil aggregates. Horn (1987) reported accumulation of fine textured particles on aggregates surface and coarse ones in aggregates center. Gerke and Köhne (2002) evaluated the hydraulic properties of the aggregate exterior and the interior and found significant reduction of water absorption rates at the aggregate surface. Park and Smucker (2005a) established the greater porosities in exterior layers of soil aggregates from different managements and lowest intraaggregate porosities in the central regions of conventionally tilled aggregates. Wilcke *et al.* (1999) examined the deposition of heavy metals in aggregated soils and found higher concentrations of metals in the aggregate exteriors than the interiors. In temperate soils, which do not show illuviation phenomena such as clay or humus coating on aggregate surfaces, the aggregate exteriors contain less organic C, less Mn and Fe oxides, and have a lower cation exchange capacity than the interiors (Amelung and Zech, 1996; Wilcke and Kaupenjohann, 1997). Santos *et al.* (1997) found significant difference in concentration gradients for Ca and Mg between external and internal regions of aggregates. Significantly higher contents of organic carbon at the surface of soil aggregates were found by Ellerbrock and Gerke (2004) and Park and Smucker (2005a). Several authors described an accumulation of organic substances and microorganisms at the surface of soil aggregates (Allison, 1968; Hattori, 1988; Christensen et al., 1990; Augustin, 1992).

1.6 Stability of soil structure

The structural stability of soil aggregates and the pores between them affect the infiltration, movement, and storage of water; aeration; erosion; plant root and microbiological activities; and crop productivity (Tisdall, 1996). The ability of soil to preserve the arrangement of solid and void space when exposed on different stresses is called structural stability (Kay and Angers, 2000). The stability of soil structure is specific for the structural form and the type of stress which is applied. Thus, the stresses applied on soil may be caused by tillage, traffic and wetting or drying processes.

Horn *et al.* (1995) analyzed increased mechanical aggregate strength due to swelling and shrinkage and assumed that the mechanical strength of the aggregates is affected by pore heterogeneity and diameter of the aggregates.

The aggregate strength depends on capillary forces, intensity of shrinkage, number of swelling and shrinkage cycles, mineral particle mobility and bounding energy between particles in or between aggregates or in the bulk soil (Horn, 1994). Dexter (1988) reported that larger aggregates have a greater porosity and are weaker than smaller aggregates which in contrast are denser and stronger.

Many studies have focused on the relations between organic materials and soil structural stability. Some of these studies reported positive effects of total OM (Tisdall and Oades, 1982) on structure stability while it increases the cohesion of aggregates, through the binding of mineral particles by organic polymers, or through the physical surrounding of particles by fine roots or fungi (Tisdall and Oades, 1982; Dorioz *et al.*, 1993). Several authors suggested that organic matter increases the aggregate stability by reduced water uptake of aggregates due to water repellency (Piccolo and Mbagwu, 1999; Chenu *et al.*, 2000). Organic materials composed of hydrophobic constituents are reported to be more effective and long-lasting aggregate binding agents than those mainly made of hydrophilic compounds such as in root exudates or as polysaccharides of plant tissues (Piccolo and Mbagwu, 1999).

2 Soil organic matter

Soil organic matter (SOM) is defined as all dead material in or lying on the soil that contain carbon (Sollins *et al.*, 1996). Its amount depends on the balance between the rate of deposition of plant residuals in or on soil and the rate of mineralization of the residue C by soil biota (Baldock and Nelson, 2000). SOM plays a very important role in the development and maintenance of soil fertility, mainly through the cycling, retention, and supply of plant nutrients (Stevenson, 1994).

The primary resource for OM formation in soil is provided by plant litter materials (Kögel-Knabner, 2002). Its amount, composition and properties control the formation of SOM and humification processes. In addition the significant part of terrestrial biomass is formed by microorganisms and their residuals (Haider, 1992).

2.1 Role of soil organic matter in carbon cycle

Soil organic matter is a major component of the terrestrial carbon cycle and consequently soils are considered as a major reservoir of carbon and an important sink (Swift, 2001). It has been proposed that better management of soils may sequestrate large amounts of organic carbon in form of soil organic matter (IPCC, 2001). There are three main mechanisms of SOM stabilizations which decrease the mineralization and respiration of CO_2 to the atmosphere: chemical, physical and biochemical protection (Christensen, 1996).

Chemical stabilisation is the result of the chemical or physicochemical binding between SOM and soil minerals, a good relationship exists between SOM fractions and clay or silt content (Hassink, 1997).

Biochemical stabilization or protection of SOM occurs due to the complex chemical composition of the organic materials (Six *et al.*, 2002).

The physical protection indicates a positive effect of SOM association with aggregates (Tisdall and Oades, 1982; Oades *et al.*, 1988; Jastrow *et al.*, 1996; Six *et al.*, 2000). In soil aggregates the substrate is separated from microbial biomass; the diffusion of oxygen into aggregates is reduced (Sextone *et al.*, 1985), which leads to a reduced activity within the aggregates (Sollins *et al.*, 1996) and the microbial biomass is separated from microbial grazers (Six *et al.*, 2002).

2.2 Age and origin of SOM

Not only the distribution of total organic carbon but also its age and its origin are important to be understood by examination of the carbon sequestration. One of the effective methods to trace soil organic carbon inputs is the natural stable isotope composition ^{12}C and ^{13}C (Balesdent *et al.*, 1987). Carbon derived from a C_4 plant can be distinguished from that of C_3 plants by its isotopic composition (Smith and Epstein, 1971). The cropping of maize, a C_4 plant, on soils with previously C_3 vegetation provides a natural label of SOM, which can distinguish young SOM derived from the crop and older SOM from the previous C_3 crops (Puget *et al.*, 1995). Plants with the C_3 pathway of photosynthesis (almost all temperate species and trees) have $\delta^{13}C$ values ranging from approximately -32 ‰ PDB to -22 ‰ PDB, with a mean of -27 ‰ PDB and C_4 plants (most of tropical species) have $\delta^{13}C$ values ranging from approximately -17 ‰ PDB to -9 ‰ PDB, with a mean of -13 ‰ PDB (O'Leary, 1988; Boutton, 1991). PDB is the reference material used for isotopic determination with $\delta^{13}C = 0‰$.

Using ^{13}C abundance Puget *et al*. (1995) qualified the carbon derived from maize in silty soils after 23 and 6 years of maize cultivation and found that young carbon composed of decomposing plant residues and mineral-associated carbon tends to accumulate in larger aggregates acting as a binding agent. Balesdent *et al*. (1990) reported a 20% enrichment of C from maize in the Ap horizon after 17 years of maize cropping and Flessa *et al.* (2000) found 15% of maize derived carbon after 37 years of continuous maize cropping in sandy soils. Horn and Smucker (2005) suggested that due to the plant roots accumulation of C on surfaces of soil aggregates can be identified for periods as short as 6 weeks under greenhouse conditions, or 20 months in rotational field studies.

2.3 Organic matter as soil structure binding agent

Organic matter is reported as very important for soil structure due to its binding mechanism for soil particles and aggregates at different scale. Three main groups based on the age and degradation of the organic matter are considered as binding agents for soil aggregates: transient, temporary and persistent (Tisdall and Oades, 1982). Transient binding agents are organic materials which are decomposed rapidly by microorganisms. The most important group are the polysaccharides including: microbial polysaccharides produced when various organic materials are added to soil, and some of the polysaccharides associated with roots and the microbial biomass in the rhizosphere. Temporary binding agents are roots and hyphae which build up in the soil within a few weeks or months as the root systems and associated hyphae grow and they are affected by soil management. Persistent binding agents consist of degraded, aromatic humic material associated with amorphous iron, aluminium and aluminosilicates to form the large organomineral fraction (Tisdall and Oades, 1982).

The importance of plant roots and microbes exudates for stabilizing of soil aggregates have been reported by several authors. The increase of the aggregation and its stability were detected after addition of mucilage (Tisdall and Oades, 1982). Czarnes *et al.* (2000) examined the effect of mucilage of plant and microbial origin on hydrophobicity of soil and aggregate strength. They found that both the mucilage of plant and microbial origin together with wetting and drying cycles stabilize the soil structure by reducing water repellency of the soil. Chenu *et al.* (2000) also found that organic matter associated to clay minerals gave them increased hydrophobicity and stabilize the aggregates.

Another specific component of soil organic carbon important for aggregate stability is a glomalin, a glycoprotein produced by arbuscular mycorrhizal fungi (Wright *et al.*, 1996; Wright and Upadhyaya, 1996). Glomalin acts as a glue to hold the soil particles together which significantly influence aggregation processes (Haddad and Sarkar, 2003b). Several studies from differing locations and management practices have shown positive correlation between glomalin content and soil aggregation (Wright *et al.*, 1999; Franzluebbers *et al.*, 2000; Haddad and Sarkar, 2003a; Haddad and Sarkar, 2003b)

3 Water repellency in soils

The wettability of soils is an important property while it influences water movement especially through the altered water infiltration. Water repellency of soil is defined to occur when free water is prevented from entering the pores of dry soil (Marshall and Holmes 1979 cited by Tillman *et al.*, 1989). It has been found that soil water repellency is a wide-spread phenomena and has been reported in most continents of the world for varying land uses and climatic conditions (Ritsema and Dekker, 2003). In most soils low levels of water repellency have been observed and described as subcritical water repellency which means that water infiltrates into the soil but its rate is reduced (Tillman *et al.*, 1989). Severe soil water repellency often leads to surface runoff and erosion, rapid leaching of surface-applied agrichemicals, and losses of water and nutrient availability for crops (Ritsema and Dekker, 2003). On the other hand the slight reduction in infiltration rates through water repellency can cause an increase in soil aggregate stability, and results in the heterogeneity of overland flow and water infiltration at the field scale (Hallett and Young, 1999).

3.1 Physics of water repellency

The liquid placed on the dry, solid surface spread over to a certain extent and the edge of the drop forms a typical angle with the surface of the solid it is defined as contact angle (Figure II-2a). In porous media such as soils, the contact angle is conceptually the effective angle formed by a water meniscus in contact with the soil pore walls (Figure II-2b) (DeBano, 1969). The solid-water contact depends on the solid surface free energy and the surface tension of the soil solution. If the contact angle (α) is greater than 90° there is no infiltration of liquid into the soil and is called hydrophobic, when the contact angle has values between 0-90° the soil is subcritical water repellent (Tillman et al., 1989).

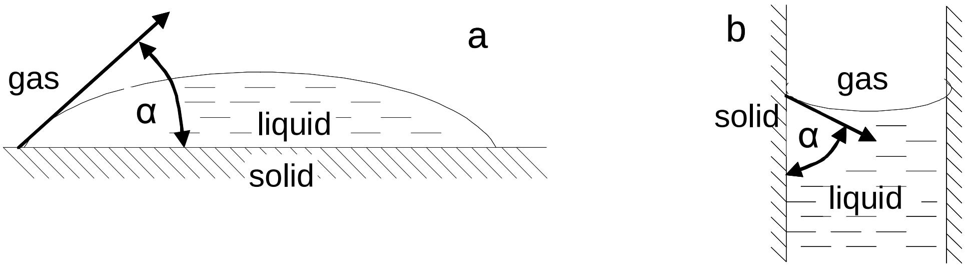

Figure II-2 *The contact angle of a drop resting on the solid surface (a) and in soil pores (b) (Hillel, 1998)*

In order to determine contact angle in soils the infiltration rate and a capillary rise technique must be applied (Letey et al., 1962). Assuming that the soil is characterized by cylindrical tubes the Poiseuille's approximation is used to determine the contact angle (α) where the rate of solution capillary rise (*h*) into a soil column is related to the physical properties like surface tension (γ), density of the solution (ρ), and the effective pore radius (*r*).

$$h = \frac{2\gamma \cos\alpha}{\rho g r} \qquad \text{Eq. II-6}$$

Assuming that ethanol wets soil with a contact angle equal to zero the value of contact angle for water can be assumed using the equation (Eq. II-7) (Letey *et al.*, 1962).

$$\cos\alpha = \frac{h_w \gamma_e \rho_w}{h_e \gamma_w \rho_e} \qquad \text{Eq. II-7}$$

where,

h_w, h_e - capillary rise height

γ_w, γ_e, - surface tension of water (w) and ethanol (e)

ρ_w, ρ_e - density of water (w) and ethanol (e)

This assumption has been used to measure the water repellency of materials which have an initial contact angle less than 90° (Letey *et al.*, 1962; Tillman *et al.*, 1989).

The determination of water repellency of single soil aggregates was proposed by Hallett and Young (1999) by measuring the rate of water and ethanol sorptivity which gives the water repellency index (R) (Eq.II-8).

$$R = 1.95 \frac{S_e}{S_w} \qquad \text{Eq. II-8}$$

where the value 1.95 is the calculation of surface tension (γ_e, γ_w) and viscosity (μ_e, μ_w) of these two liquids (Eq. II-6).

$$S_w = \left[\frac{\left({}^{\mu_e}\!/\!_{\gamma_e} \right)^{1/2}}{\left({}^{\mu_w}\!/\!_{\gamma_w} \right)^{1/2}} \right] S_e \qquad \textit{Eq. II-9}$$

Soils which have repellency index R< 1.95 are totally wettable (Hallett *et al.*, 2001), and those with repellency index R> 1.95 are subcritical water repellent. The use of repellency index better identify the reduced rate of infiltration than the contact angle determination.

3.2 Hydrophobic groups responsible for water repellency

The chemical origin of hydrophobicity has been investigated by several studies showing a correlation between carbon content and soil hydrophobicity (Chenu *et al.*, 2000; Mataix-Solera and Doerr, 2004), but this has been refuted by studies on other soils (Horne and McIntosh, 2003). Since not all carbon compounds are hydrophobic, it is proposed to consider the type of organic carbon present in the soil rather than simply the total amount of organic carbon (McKissock *et al.*, 2003). Long chain, aliphatic compounds have been linked to soil hydrophobicity, specifically long chain acids, alcohols, and wax esters with extensive polymethylene chains (Ma'shum *et al.,* 1988). In addition, fatty acids, alcohols, and esters, together with alkanes, phytols, phytol derivatives, and sterols, have all been isolated from water repellent soils and are associated with water repellency (Franco *et al.*, 2000).

Capriel *et al*. (1995) and Ma’shum *et al.* (1988) used reflectance Fourier transform infrared spectrometer (DRIFT) for quantifying hydrophobicity and found a linear relationship between the amount of an aliphatic soil extract and the area of alkyl C-H peak at 3000-2800 cm^{-1}. The area of the peak is proportional to the concentration of aliphatic C present (Capriel *et al.,* 1995). Capriel (1997) found also that the agricultural management clearly influences the number of aliphatic C-H units and implicitly the hydrophobicity of the soil organic matter. Ellerbrock *et al.* (2005) used infrared spectroscopy to indicate the amount of hydrophobic and hydrophilic functional groups in relation to soil hydrophobicity and found the higher ratio of hydrophobic to hydrophilic groups indicate higher water repellency. On the other hand Doerr *et al.* (2005) conducted the DRIFT analyses on soils with different hydrophobicity and concluded that the amount of aliphatic C-H in soil material does not determinate the water repellency of a soil.

Von Wandruszka (1998) presented the specific formation of micellar structures by humic substances in soil, whereby molecules have hydrophobic (nonpolar) and hydrophilic (polar) parts. Hydrophobic bonding can cause humic molecules to associate in micelle-like aggregates. In some situations the hydrophobic groups orientate towards each other and the interior, and the hydrophilic functionalities are on the outside (Figure II-3). Polar groups can be on the inside, and in such cases, interactions such as hydrogen bonding will decrease the hydrophilic character of the polar groups. The hydrophilic groups (inside or outside) in the micelle structures can interact through hydrogen bonding and dipole-dipole interactions with the solvent (water). Entropy increases as water structure is disrupted and decreases with micelle formation (Hayes and Clapp, 2001). The spatial arrangement of the functional groups at the molecular scale (carboxylic, aliphatic, hydroxylic groups) is responsible for chemical reactivity and sorptivity of SOM as well as hydrophobicity (Capriel et al., 1995; Ellerbrock and Gerke, 2004).

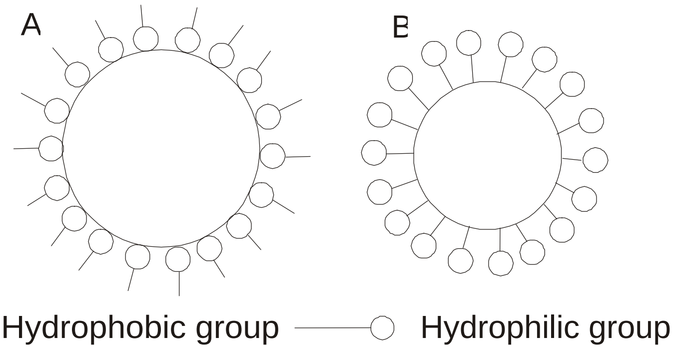

Figure II-3 *Schematic presentation of spatial orientation of hydrophobic and hydrophilic groups of organic matter in soil (A) hydrophobic center with hydrophilic ending pointing out; (B) hydrophilic center with hydrophilic ending pointing outside*

The relations between water repellency, aggregate stability and organic matter distribution are still not completely understood even it has been studied by many scientists. Following study is conducted to add new information about these soil properties and help to understand the processes happening in structured soils.

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III Heterogeneity of physico-chemical properties in structured soils and its consequences

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1 Abstract

Structured soils are characterized by the presence of inter- and intra-aggregate pore systems and aggregates, which show varying chemical, physical, and biological properties depending on the aggregate type and land use system. How far these aspects also affect the ion exchange processes and to what extent the interaction between the carbon distribution and kind of organic substances affect the internal soil strength as well as hydraulic properties like wettability are still under discussion. Thus, the objective of this research was to clarify the effect of soil aggregation on physical and chemical properties of structured soils at two scales: homogenized material and single aggregates. Data obtained by sequentially peeling off soil aggregates layers revealed gradients in the chemical composition from the aggregate surface to the aggregate core. In aggregates from long term untreated forest soils we found lower amounts of carbon in the external layer, while in arable soils the differentiation was not pronounced. However, soil aggregates originating from these sites exhibited a higher concentration of microbial activity in the outer aggregate layer and declined towards the interior. Furthermore, soil depth and the vegetation type affected the wettability. Aggregate strength depended on water suction and differences in tillage treatments.

Key Words: aggregation, aggregate peeling, chemical disequilibrium, microbial activity, water repellency

2 Introduction

The determination of physico-chemical soil properties is usually carried out on homogenized soil samples. However, aggregate size distribution, inter- and intra-aggregate pore continuity and natural aggregate strength occur in small scale physico-chemical heterogeneities with respect to the accessibility of reactive surfaces and transformation processes (Horn, 1990; Horn *et al.*, 1995). In soils, which contain more than 120 g kg^{-1} clay (particle size < 2 µm) or even in pure sandy soils with some salts there is a tendency to form aggregates (Horn and Smucker, 2005).

The process of structural formation enhances with changes of water content. When the soil dries, shrinkage occurs and mineral particles are tied together by capillary forces, which increase the number of points of contact and result in the formation of inter- and intra-aggregate pores (Horn and Dexter, 1989).

The higher bulk density of aggregates causes reduced access to chemical exchange places. It also diminishes interactions between microbial communities and their activity and influences physico-chemical properties of the decomposed organic components, such as hydrophobicity and leaching. Horn and Dexter (1989) described in detail the general processes of soil aggregate formation due to swelling and shrinkage as a function of water suction and frequency of wetting and drying. Taubner (1993), Hartmann *et al*. (1998) and Wilcke *et al*. (1999) analyzed the effects of aggregate formation on chemical disequilibrium and their interactions with hydraulic flux. Zausig *et al.* (1993) determined the effect of aggregate formation on gas exchange processes and found the aggregate type to be highly related to air entry values as well as structural dependent changes in redox potential with depth inside the aggregate. Furthermore, Horn *et al.* (1994) measured the N_2O emission out of single aggregates as a function of aggregate diameter and incubation time. The bigger the aggregate and the longer the incubation time, the higher was the N_2O release at a given pore water pressure under lab conditions.

Horn *et al.* (1995) also analyzed increased mechanical aggregate strength due to swelling and shrinkage and assumed that the mechanical strength of the aggregates is affected by pore heterogeneity and diameter of the aggregates. Horn (1990) suggested that during the formation of aggregates, many components of the soil are redistributed within the structural unit, developing gradients within individual soil aggregates. Shrinking and swelling processes result not only in the accumulation of fine textured particles on an aggregate surface but also in variations of chemical and physical properties within each aggregate. Horn *et al.* (1994) also demonstrated that external surface layers of aggregates contain more microorganisms than internal regions and that these layers vary in their chemical and physical properties. Santos *et al.* (1997) visualized the spatial distribution of organic components inside single aggregates and found greater differences in the gradients for Ca and Mg-concentration, which exist between external and internal regions of the aggregates.

Organic matter, and its mineralization through microbial activity, influence physical properties in soils, such as water transport and water retention. Microbial biomass and exudates in soils can cause reduced wetting also defined as water repellency. In most soils low levels of water repellency have been observed and described as subcritical water repellency (Tillman *et al.*, 1989; Hallett and Young, 1999). The slight reduction in infiltration rates through water repellency can cause an increase in soil aggregate stability, and results in the heterogeneity of overland flow and water infiltration at the field scale (Hallett *et al.*, 2004). However, it is still unclear to what extent these various processes affect the sequestration of organic matter in the soil. Little is also known about how mineralized components of organic matter change soil properties, such as wettability, gas, water flux patterns at various positions of the aggregates and mechanical strength.

The combined effects of these properties were analyzed in the present study at various scales of soils with different textural and structural properties. Thus, our investigations focused on: i) the analyses of the chemical, microbiological and physical differences within soil aggregates from different sites; ii) the effect of soil depth and vegetation type on wettability and aggregate strength; and iii) the effect of mechanical soil strength on gas fluxes and microbial activity.

3 Materials and methods

3.1 Study sites and soil sampling

Soil samples were collected in November 2002 from the experimental field of Rotthalmünster in southern Germany from two soils of different soil type, cultivation system and vegetation: Hortic Anthrosol under conventional tillage since 1979 with maize vegetation and Haplic Luvisol under conservation tillage since 1969 with wheat vegetation. The samples were taken from three depths corresponding to soil horizons: Ap1/Ap, 0--30 cm; Ap2/rAp, 30--36 cm; Sw-M/Bt, 36--43 cm. In addition, the aggregate analyses were conducted on two other sites: an Sw-Al horizon from a Stagnic Luvisol at forest site in Bucken and an Ap horizon of Cambisol from an agricultural site in Ritzerau, both in northern Germany. The detailed description of soil types and horizons are presented in Table III-1. Soil aggregates in diameter 15--18 mm were separated from the bulk soil by manually breaking the bigger blocks along planes of weakness in field moisture conditions.

Table III—1 *General properties of analyzed soils*

Site	Soil type	Use	Horizon	Soil depth [cm]	Texture clay	 silt g/kg	 sand	C_{org}	pH [-]
Rotthal-münster	Hortic Anthrosol	maize	Ap1	0 – 30	221	679	100	13.4	6.4
			Ap2	30 – 35	210	691	99	11.6	6.3
			Sw-M	35 – 45	214	721	65	6.3	6.2
	Haplic Luvisol	wheat	Ap	0 – 30	229	678	93	13.2	6.4
			rAp	30 – 39	257	655	88	5.9	6.2
			Bt	39 – 45	278	649	73	5.0	6.0
Ritzerau	Cambisol		Ap	0 – 30	55	200	745	12.7	6.1
Bucken	Stagnic Luvisol	Larch (Forest)	Sw Al	12 - 24	55	215	730	4.4	3.4

3.2 Aggregate peeling

Abrasion techniques started from the assumption that a single aggregate could be separated in concentric layers with different properties. Any gradient of elements or surface functions along these hypothetical layers could be a hint of such a simple geometric structure. However, the absence of a gradient was not sufficient evidence of no functional soil structure.

Thus, soil aggregates were separated mechanically by rolling single aggregates end-over end in a tea strainer enclosed in a sealed box. The aggregates were generally abraded as air-dried, but some soil aggregates for microbiological analyses were abraded in a frozen condition at -5 °C.

3.3 Chemical, physical and biological measurements

The general analysis of the physical and chemical soil properties were carried out according to Schlichtling *et al.* (1995) and Hartge and Horn (1992) with the more specific measurement techniques described below. Soil samples and methods used at different scales are listed in Table III-2.

Table III—2 *Methods and investigated soil samples at different scales*

method	Scale[a)]	Horizon[b)]	comments and further measurements
peeling	A	SwAl (Bc)	C_{org}
	A	Ap2 (M) (Rm)	chemical analysis; biological activity
water repellency	A	Ap-rAp-Bt (W) (Rm)	inside – outside; pre-desiccation (-6, -15, -30, -50kPa, air dry) for Ap-Bt
	A	Ap1-Ap2-SwM (M) (Rm)	inside – outside; pre-desiccation (-6,-15,-30,-50kPa, air dry) for Ap-SwM
	A	SwAl (Bc)	inside – outside (air dry)
	A	Ap (Rz)	time series
contact angle	H	Ap-rAp-Bt/SwM (M)(W) (Rm)	
water sorptivity	A	SwAl (Bc)	5 layers from outside
mechanical stability	A	Ap1/2-SwM/Bt (M) (W)(Rm)	crushing test
	B	Ap1/2 (M) (Rm)	oedometer test
CO_2-efflux kinetics	B	Ap2 (M) (Rm)	pre-desiccation: -6, -10, -30 kPa

a)Scale: A - aggregate, H - homogenized sample, B - bulk soil.
b)Sites: Rm - Rotthalmünster; Rz - Rizerau; Bc – Bucken
Vegetation: M – maize, W - wheat

Total element contents of potassium (K), sodium (Na), iron (Fe), aluminum (Al), and manganese (Mn) were determined by atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES), after wet digestion with nitric and perchloric acid. The phospholipid fatty acid (PLFA) content was estimated and classified according to Frostegard et al. (1993).

3.4 Water repellency

Water repellency based on the sorptivity rate of water and ethanol was measured using the method developed by Hallett and Young (1999). Sorptivity rates of those two different liquids were determined on the surface and the

interior of the air-dry aggregates and also on the surface of abraded aggregates (using a different set of aggregates). The test was also conducted on the exterior layer of aggregates with different pore water pressures. The single aggregates were placed on ceramic plates and desiccated to pore water pressures of -6, -15, -30, and -50 kPa, and at each pore water pressure value the sorptivity test was completed. In addition, water repellency was measured on air-dry aggregates sampled repeatedly from the field throughout the year.
Sorptivity measurements were also performed on homogenized material using a contact angle determination device (Tensiometer K100, Krüss). Soil material was taken from the same depths and the same vegetation types like aggregates, homogenized (sieved to < 2 mm), placed in glass tubes, and compacted to a bulk density of 1.4 g cm^{-3}.

3.5 Aggregate tensile strength

The aggregate strength was determined using crushing test method on samples from Rotthalmünster after desiccation under water tension -6, -15, -30, -50 kPa and air-dry (Table III-2). For calculation of aggregate tensile strength following equations were used (Dexter and Kroesbergen, 1985):

$$T_s = 0.567 \frac{F}{d^2} \qquad \textit{Eq. III-1}$$

T_S - tensile strength of the aggregate (kPa)

F - the applied force at failure (N)

d_a - equivalent diameter of an irregular aggregate (m) defined by

$$d_a = \left[\frac{6m}{\Pi \cdot d_B} \right]^{1/3} \qquad \textit{Eq. III-2}$$

m is the mass (g) of the aggregate and d_B its bulk density (g/cm^3).
This equation gives the equivalent diameter of a sphere having the same mass and density as the test aggregates.

3.6 Analysis of mechanical soil strength and its effects on gas fluxes and microbial activity

The rate of mineralization of C due to formation or destruction of soil structure were investigated using a gas flow-compaction-device (GAFLOCOD), which allowed the measurement of continuous gas flow and the production of CO_2 while the soil sample changed its pore size distribution by strain due to applied stress. In order to compact the soil sample under gas sealed conditions, it was placed in a bellows, connected, and sealed to a bottom and top plate, both being separated into outer and inner ring (Fig. 1). The outer ring consisted of a porous membrane for gas flow; the inner ring consisted of a ceramic plate for measurements or control of the water potential in the soil.

The soil samples had a diameter of 10 cm and an initial height of 6 cm. The stresses and strains onto the GAFLOCOD were applied by a loading frame (INSTRON 5569), and the concentration of CO_2 was measured by an infrared gas analyzer (ADC 2250, BioScientiffic Ltd., UK). The soil samples were percolated continuously with air. Prior to each measurement, the air percolation was interrupted for 10 minutes. Thereafter, percolation was started again, and the change of the CO_2-concentration was measured until changes in concentration became small (about 30 minutes). This procedure was carried out with three replicates before and after each step of the strain-controlled test. The strain was applied in four 1-mm steps; the time between each strain step was approximately 1 day.

The results of the gas flow measurements were analyzed by modeling the CO_2-efflux (A_t) using a two-component 1st order decay function:

$$A_t = a_1\left(1-e^{-k_1 t}\right)+a_2\left(1-e^{-k_2 t}\right) \tag{3}$$

where a_1 and a_2 describe the amount of CO_2, which is released in a period of time and the coefficients k_1 and k_2 indicate the rate of release. The a_1 and k_1 coefficients (fast mobilization of C by microbial processes) as well as the a_2 and k_2 coefficients (slow mobilization of C by microbial processes) defined different two C-pools, which could be exploited and could explain the kinetics of the release of CO_2 as a characteristic of these pools. From each test the a and k coefficients for Eq. 3 were derived. Then, the three replicates of each set of tests before and after each additional strain step were averaged. For calculation of correlation coefficient R^2 the Pearson test was used.

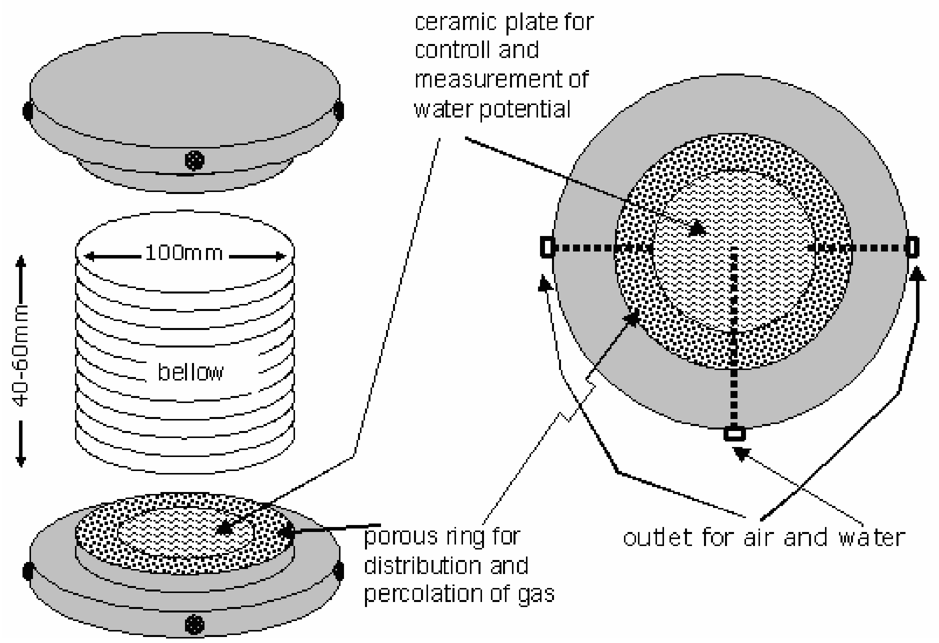

Figure III-1 *Sketch of the experimental setup of GAFLOCOD for the in situ determination of gas flow during compaction*

3.7 Calculations

Statistical calculation of the data was based on the arithmetic means and standard error of the mean considering the aggregates from soil depth and management system or replications of the bulk or homogenized soil. The calculations of analyses from peeled material were based on the replications (n=5) from exterior, transitional, and interior regions of aggregates of the same size. To evaluate the significance of observed differences the comparison tests were conducted using a one-way (no blocking) ANOVA statistical analyses with Tukey's HSD test at 5% level of significance.

4 Results

4.1 General description of the investigated sites

At the Rotthalmünster site, the silt fraction dominates by 649-721 g kg^{-1}, while clay and sand range at about 210-278 g kg^{-1} and 65-100 g kg^{-1} respectively (Table III-1). The soil was strongly structured and consisted of about 1-2 cm polyhedral aggregates. The organic carbon content distribution in different soil depths varied between 13 and 5 g kg^{-1} in the Ap and Sw-M/Bt horizons. The grain size distribution from the Ritzerau and Bucken sites showed a dominance of sand (730-745 g kg^{-1}) with 200-215 g kg^{-1} of silt and 55 g kg^{-1} of clay.

4.2 Chemical, physical and biological properties on different scales

Chemical aspects

Element concentrations in aggregate layers taken from the Rotthalmünster site differed intensely in their characteristic sequences (Fig. III-2a and b). Besides the absence of a gradient for organic carbon and a slight decrease of total manganese from the exterior to the interior layer of the aggregate, a sharp decline of total sodium concentration (exterior to the interior layer) can be seen. Meanwhile, the total concentration of potassium (K), aluminum (Al), and iron (Fe) increased from the exterior to the interior layer of the aggregates. All aggregates show an increase or decrease of chemical element concentration only in the exterior layers. Thus, about 60% of the total inner aggregate space reflected no further variation in chemical composition.

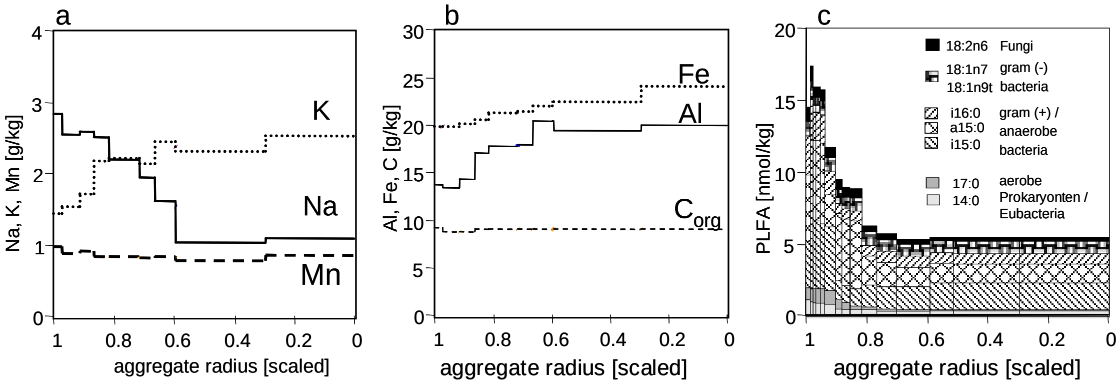

Figure III-2 *Gradients of total element concentrations (a, b) and phospholipids fatty acid (PLFA) as a markers for living organisms(c), along scaled aggregate radius for a Ap2-horizon from maize (site Rotthalmünster) under permanent maize production*

Another example of the existence of gradients along aggregate layers can be shown for aggregates from a Sw-Al horizon (Bucken site) under a larch (*Larix*) forest (Figure III-3). An organic carbon gradient was detected for nearly all investigated aggregates (*n* = 12). The largest two showed a decreasing carbon (C) content from external to internal regions, while the others could be characterized with increasing C content from the outer layers to the inner part of the aggregate.

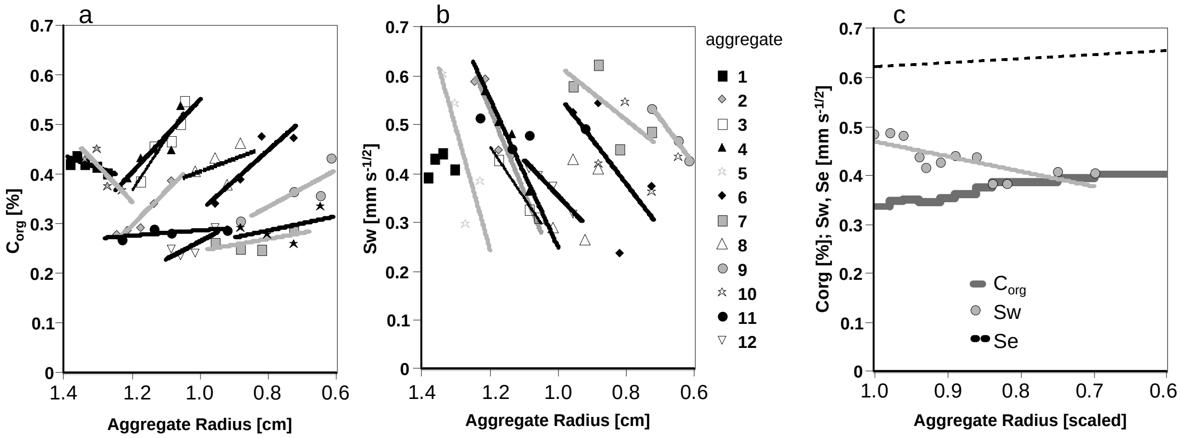

***Figure III-3** Gradients of organic carbon (C_{org}) (a) and sorptivity of water (S_w) and ethanol (S_e) (b,c) along 12 single aggregates and calculated mean values (scaled aggregate radius) (SwAl-horizon, site Bucken)*

Microbiological activity

The total amount of investigated phospholipid fatty acid (PLFA), as a marker for living organisms, shows a pronounced accumulation in the thin external skins of the aggregates. As a consequence of the depletion of total PLFA, a decrease of typical PLFA's for fungi, gram (+) bacteria or anaerobic bacteria and aerobic bacteria or Eubacteria was found (Figure III-2c).

4.3 Physical aspects

Water repellency

Measurements of the wettability (Fig. III-4) conducted on homogenized material show the values of contact angle between 73° to 77°, which means that the soil was a subcritical water repellent (Tillman *et al.*, 1989). The soil material from maize soil has higher values of the contact angle in comparison to the wheat soil, but the differences are not statistically significant. There is also slight (but not significant) tendency of higher water repellency in the topsoil horizons than in the subsoil.

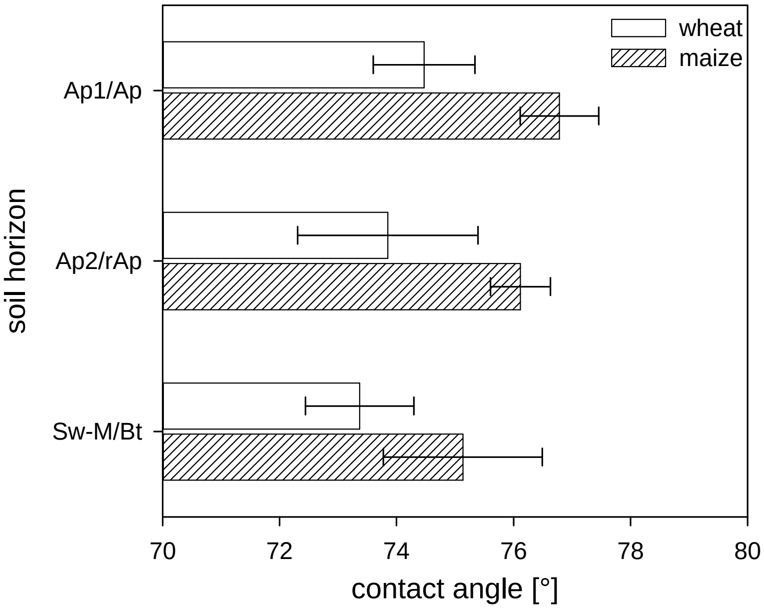

Figure III-4 *Contact angle values of homogenized soil material at different depths and vegetation types from site Rotthalmünster.*
Bars represent standard errors (n=6).

Single aggregates

The aggregates from the Rotthalmünster site show water repellency values slightly greater or smaller than 1.95 which can be identified as non repellent or subcritical water repellent (Tillman *et al.*, 1989; Hallett and Young, 1999). Water repellency measured on air-dry aggregates showed significant differences ($P < 0.05$) between the outer and inner surface in 4 of 6 tested aggregate sets (n=24). In the maize-cultivated Ap horizon the interior regions of aggregates were wettable at all depths, while the outer surfaces of the same aggregates were subcritical water repellent with repellency declining as soil depth increased (Fig. III-5). Analyzing the water repellency index in the wheat-cultivated soil it can be seen that in the Ap horizon only the outside surface of aggregates was repellent, but repellency declined towards non-repellent conditions with soil depth. Thus, the water repellency index of the aggregate interior increased with soil depth.

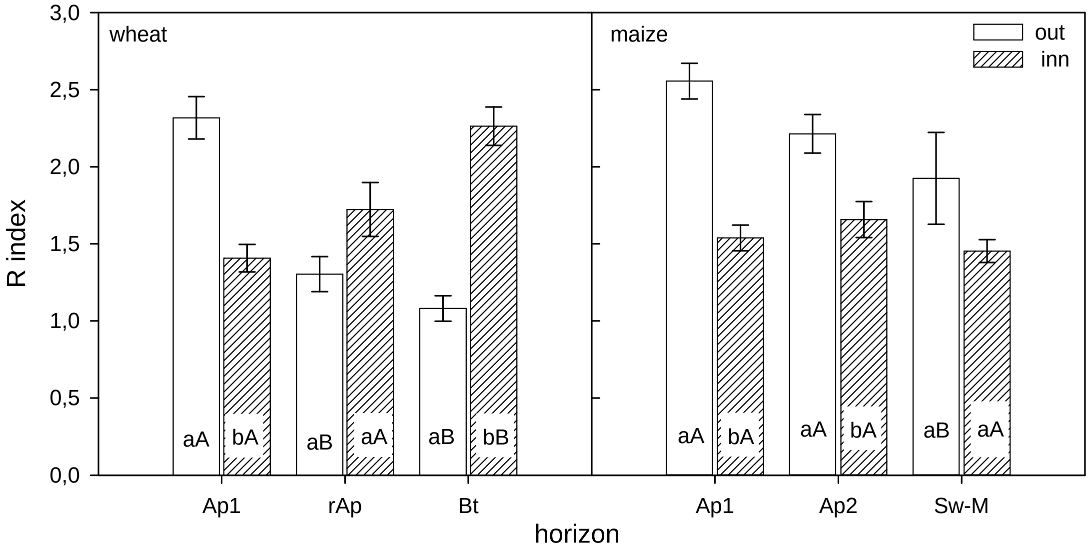

Figure III-5 *Water repellency index (R index) of external/internal region of aggregates at different depths and vegetation types*
Bars represent standard errors n=24. Small letters (abc) identify the significant differences of R index between exterior and the interior of the aggregate. Capital letters (ABC) identify the significance of R index between soil horizons

The water sorptivity measured on peeled aggregates from Sw-Al (Bucken site) (Fig. III-3b and c) declined towards the inside of the aggregate and could be related to increasing content of organic carbon (Fig. III-3a). Under the proven assumption of a more or less constant ethanol sorptivity (on the independent aggregate set) the content of hydrophobic substances increased.

The results of water repellency measurements achieved on aggregates at different pore water pressures, except for Ap wheat at water tension -30 kPa and Bt wheat air-dry, showed no significant effect of pore water pressure on water repellency (Table III-3).

Table III—3 *Water repellency index (R) of soil aggregates from site Rotthalmünster by increasing water tension. +/- are the standard errors of the mean; a,b identify the significant differences between aggregates at different water tension form the same horizon and vegetation (p=0.05)*

water tension (kPa)	pF	wheat						maize					
		Ap			Bt			Ap			Sw-M		
		R	+/-		R	+/-		R	+/-		R	+/-	
-6	1.8	1.72	0.18	a	1.84	0.47	a	2.69	0.66	a	1.72	0.18	a
-15	2.2	2.00	0.11	a	2.11	0.26	a	2.49	0.54	a	1.76	0.26	a
-30	2.5	3.26	0.51	b	2.08	0.29	a	2.37	0.21	a	2.02	0.55	a
-50	2.7	2.07	0.16	a	2.60	0.32	a	1.53	0.12	a	1.79	0.34	a
air dry	6.0	2.32	0.15	a	1.08	0.09	b	2.56	0.13	a	2.16	0.37	a

Seasonal changes of the wettability

The measurements of water repellency conducted on soil material collected repeatedly throughout the year from the Ritzerau site showed that the repellency of the upper soil horizon (Ap horizon) changed during the year (Figure III-6). The soil was moderately subcritical water repellent. The water repellency increased when there was no precipitation for a longer time (in August), but the original wetness of the soil was not the only factor controlling repellency while relatively high values of repellency occurred also after precipitation (in May).

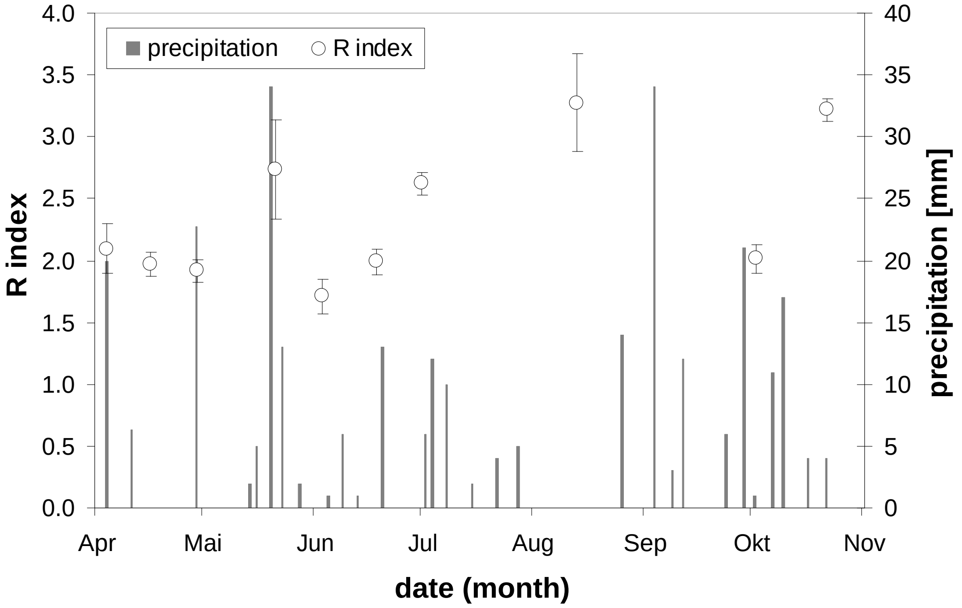

Figure III-6 *Water repellency (R) in Ap-horizon during the vegetation period 2003 (site Ritzerau).*
The bulks are standard error of the mean for n=20

4.4 Aggregates tensile strength

The results of the crushing test showed that air-dry aggregates had very high tensile strength. However, an increase in water potential decreased the stability (Figure III-7). The strength of air-dry aggregates is slightly dependent on land use and management, and soil aggregates from maize soil with conventional tillage have lower values of tensile strength in comparison to ones from wheat soil with the conservation tillage, although the differences are not statistically significant.

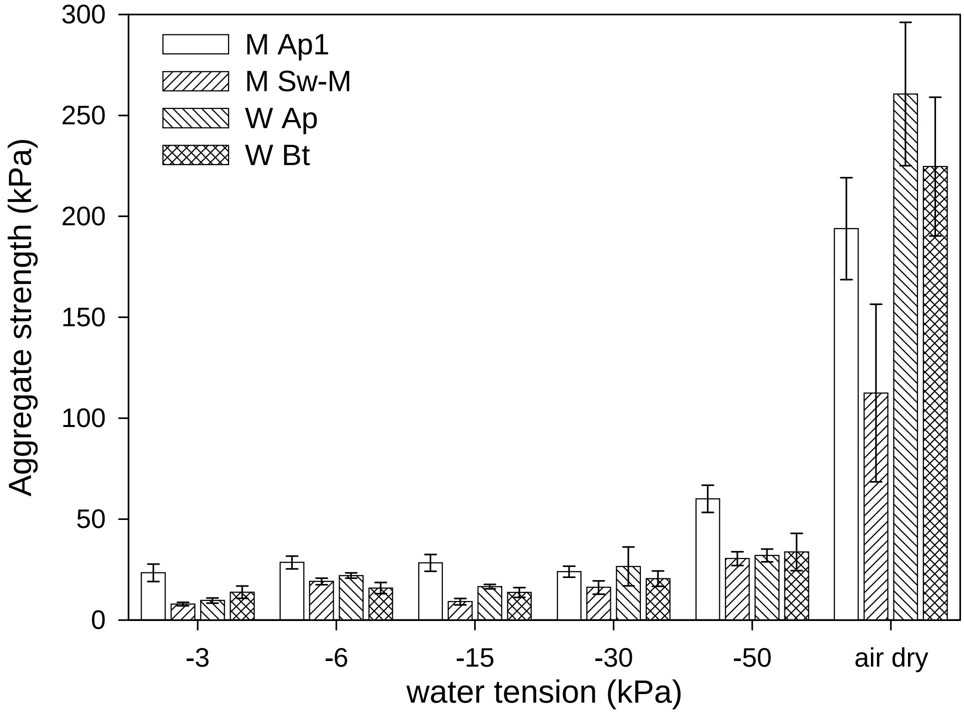

Figure III-7 *Aggregate strength at different water tension values*
Bars represent standard errors (n=10).

4.5 Gas fluxes

The measured data fit the model in Eq. (3) very well. A summary of all the *a* and *k* coefficients are given in Table III-4 along with R^2 for fits. The coefficients $a_1$and a_2 as well as k_1 and k_2 define different kinds of C-pools, which can be exploited and refer to fast and slow mobilization of C by microbial processes. For all tests fast mobilization (a_1 and k_1 coefficients) dominated over the pool with slow release of CO_2 (a_2 and k_2 coefficients). The a_2 values were constant with increasing strain for the tests “-6 kPa” and “-10 kPa” and decreased slightly with higher strains in test “-30 kPa”. The kinetics of the release, which were defined by the *k* coefficients, showed a distinct increase with strain in the fast pool and more or less constant values for the slow pool.

***Table III—4** Fitted parameters of the two component 1st order decay function (eq.III-1) for site Rotthalmünster (depth 90-150 mm) at 5 levels of compaction and three intensities of desiccation (-6, -10, -30kPa).*

	strain [mm]				
desiccation	0	1	2	3	4
-6 kPa					
a1	0.370	0.445	0.399	0.303	0.290
a2	0.194	0.173	0.119	0.127	0.171
k1	54	48	45	51	101
k2	10.3	9.0	9.0	7.5	9.3
R^2	0.962	0.994	0.986	0.954	0.926
-10 kPa					
a1	0.247	0.238	0.263	0.311	0.279
a2	0.101	0.107	0.116	0.112	0.115
k1	62	72	86	88	84
k2	7.9	9	7.8	8.2	8.4
R^2	0.997	0.998	0.993	0.998	0.999
-30 kPa					
a1	0.182	0.157	0.134	0.141	0.187
a2	0.120	0.114	0.090	0.087	0.080
k1	42	61	71	74	85
k2	4.4	6.5	6.9	6.0	6.3
R^2	0.980	0.989	0.980	0.990	0.995

Dimension: a-values [mg/m^2]; k-values [t^{-1}]
R^2 : coefficient of correlations of 6 measurements

Figure III-8 compares the total released CO_2 (*i.e.,* the sum of a_1 and a_2) of each strain step. It showed that the moister the soil sample (lower water tension) was (between the lower and higher limit of field capacity), the higher the CO_2 was produced. The compaction of the soil under -6kPa caused a decrease of the CO_2 concentration in contrast to the other two samples (-10 and -30kPa) where the concentration increased slightly or was not influenced by the compaction.

Each step of strain not only changed the kinetics before and after settlement, it also changed the CO_2-efflux when stress was applied to achieve additional strain (Fig. 9). During the state of re-compression, *i.e.*, stress application with only minor reduction in volume, constant CO_2-efflux-rates were determined. After exceeding the pre-consolidation value of each strain step, volume was decreased and the CO_2-efflux became less. When exceeding the pre-compression stress value of the total soil sample (in test “-6 kPa” this value equaled 31 kPa), *i.e.,* after destruction of aggregates at a strain of 3 mm (Figure III-8), the same pattern was found, however, on a higher CO_2-efflux level.

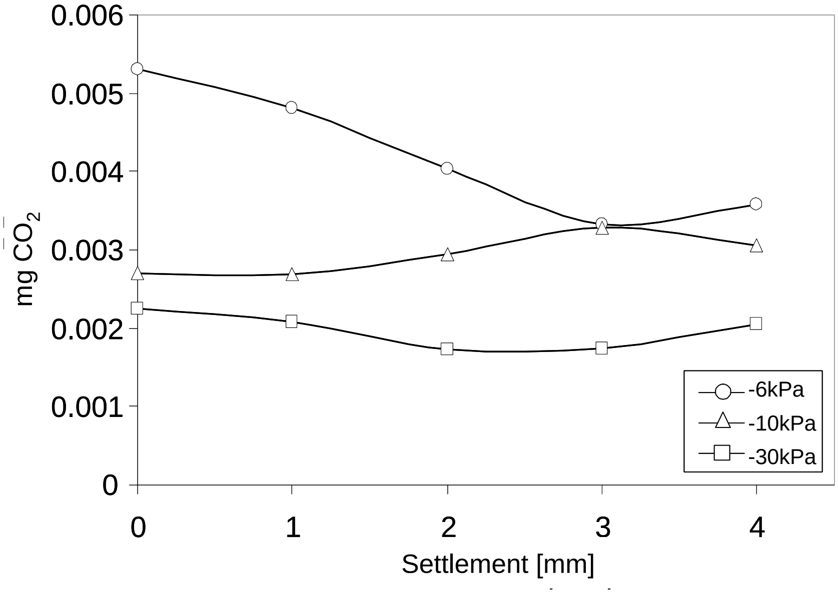

Figure III-8 *Release of CO_2 at different stages of compaction and different intensities of pre-desiccation*

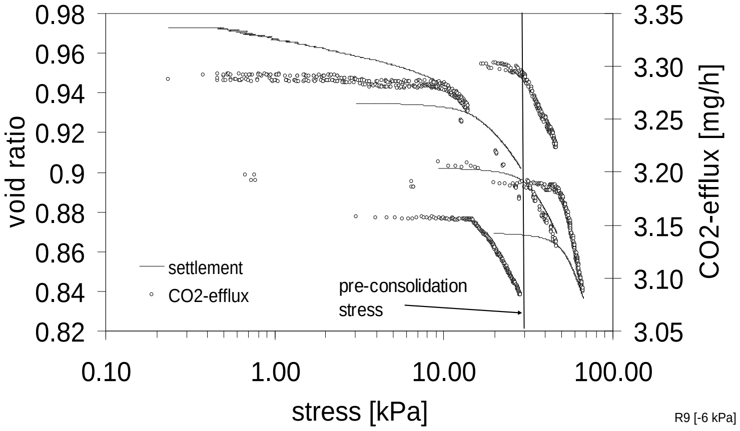

Figure III-9 *Change of CO_2-efflux with compaction and increase of CO_2-concentration after exceeding the pre-consolidation stress*

5 Discussion

Each soil tends to form aggregates, which partly reach a final dynamic equilibrium but are altered or destroyed during the following plowing and reseeding of the sites. Therefore, the more often and the more intense these aggregates are wetted and dried, the smaller the aggregates will be. Also, the physical and chemical properties as well as the microbial activity will change during these processes. Aggregates can be assigned to different hierarchical levels, *i.e.* a large aggregate consists of a number of small aggregates formed under different conditions. Aggregates of different hierarchical levels inherit a specific strength, which is dependent on the potential to mobilize water, the water potential, and hence on the water retention curve. The aggregates of the Rotthalmünster site showed very high values in tensile strength when dry, but deformed relatively easily when moist. Dexter *et al*. (1988) suggested that when soil dries the tension in the retreating menisci can generate sufficient force to displace the intervening water molecules and so produce much closer mineral-mineral contact, which results in very high strength of air-dry aggregates.

The mechanical stabilization of aggregates can be further increased by biotic activity (Tisdall and Oades, 1982), by organic matter (Zhang, 1991), or by humus composition (Hempfling *et al*., 1990). Changes of this state may either be caused by a change in land use and alteration (desorption) of bound soil organic matter or by input of mechanical energy, which may destroy the aggregates. The destruction of aggregates creates new surfaces, resulting in an increase of the coarse pores and also in better accessibility of soil organic matter for mineralization. The presence of secondary coarse pores increases the flow rate of the soil solution, which may lead to a differentiation in the chemical composition of soil material, but also results in a permanent disequilibrium between the solid, liquid, or gas phase, according to the higher flow rate and the composition change. Under forest decline aspects Kaupenjohann (1989) has shown that the disequilibrium between the outer and the inner part of aggregates or the outer to the inner pore walls results in a more pronounced decline phenomena. Such continuous disequilibrium may finally lead to an accumulation or to a depletion process on the aggregate surface and result in a diminution of the total accessible cation exchange places. In addition, the aggregates show a heterogeneous distribution of chemicals at various positions (Horn, 1989; Taubner, 1993; Hartmann *et al.*, 1998).

The depletion of aluminum, potassium, and iron in the outer layer, as found for the Ap2 horizon (Figure III-2), are a typical phenomenon of temperate soil horizons with eluviation properties and support the findings of Wilcke and Kaupenjohann (1997). If the aggregates are weakened or destroyed by plowing, such depletion zones in the Ap horizon can be found. However, the sharp decline of living organisms (PLFA's) at the investigated site in Rotthalmünster and existing gradients for total element concentrations are a hint for well-established aggregates that were not destroyed during plowing. These nutrient gradients can furthermore be formed by root induced acidification and selective element uptake (Jungk *et al.*, 1982; Jungk and Claassen, 1986; Gerke, 1997). Additionally, the microorganisms accumulated in the outer layer of the aggregates could influence the inorganic element gradient. A high microbial activity leads to higher mineralization rates and follows the spatial acidification in the outer spheres of the aggregates (Taubner, 1993). The formation or destruction of soil structure changes not only the pore size distribution and pore continuity, but also the accessibility of surfaces for microorganisms and the rate of C mineralization. Particularly if some of the pore spaces in soil aggregates serve as protective microhabitats for soil bacteria against predation by protozoa, such disequilibrium situations can persist (Hattori, 1988; van Overbeek and van Elsas, 1997). Predation is one of the driving forces for higher turnover rates (mineralization).

At the same time this spatial gradient represents the interface between the interaggregate pore system, which is the main source for water, oxygen, nutrients, and the micropores inside the aggregate, which work like a buffer system in time and space. Such conditions are almost optimal for microorganism survival (microhabitat) and are moreover supported by the organic decomposition components serving as C-sources for microbes. Because the pores are in the micrometer or nanometer range, bacteria and fungi cannot penetrate inside the inner aggregate pores (Scow and Alexander, 1992; Nam and Alexander, 1998). Consequently, this leads to retarded mineralization of organic substances inside the aggregate and creates physical protection of the organic carbon pool (Chenu and Stotzky, 2002). Nevertheless, a gradient for organic carbon in the investigated small aggregates collected from Rotthalmünster was not detected, whereas such a gradient was detected in the aggregates from Bucken. As these aggregates differed in texture, structure, and pore size distribution, it could be assumed that the hydraulic conductivity (mass flow) and aggregate bulk density influenced the accessibility of organic matter. These ideas were supported by the water repellency measurements in this study, which have showed lower values for the inside compared to the outside of the aggregate.

In this research no relationship was found between the amount of organic carbon and the degree of water repellency. Thus, even minor differences in the inorganic composition of the solid phase were assumed to cause differences in water repellency (Hallett *et al*., 2001). In addition, the repellency may correspond more to the content of specific hydrophobic groups than to the total organic carbon in the soil (Capriel *et al.*, 1995). The gradient of organic carbon in soil aggregates from the Sw-Al horizon could be a result of the eluviation process where, together with washing out of colloidal particles, the organic carbon from aggregate surfaces is leached into deeper horizons. The depletion of organic carbon from aggregate surfaces corresponds in this soil with a decrease of water sorptivity, which suggested that the organic matter was better protected against leaching processes in aggregate interiors than in exteriors.

Soil aggregates from the Rotthalmünster site showed small values of water repellency, but hydrophobic surfaces were still available. As no radial gradient in the distribution of organic C could be detected it was concluded that the specific hydrophobic carbon groups were more responsible for water repellency than the total amount of organic carbon. Furthermore, higher biological activity on the aggregate surface will produce organic compounds (*i.e.* bio films), which may increase the hydrophobicity. (Czarnes *et al.*, 2000) A relationship to inorganic compounds is further proven by the hydrophobicity independence of the degree of drying. An increase in repellency with a decrease of water potential is usually caused by soil organic matter structure. von Wandruszka (1998) suggested that humic substances in soil form micellar structures with hydrophobic and hydrophilic functional groups, which can change orientation depending on the degree of hydration. If the hydrophobic groups are pointed outward, then hydrophobicity increases, and when they are oriented towards each other or the interior, the hydrophobicity can decrease. This effect can cause the changes of water repellency on soil aggregates from the Ritzerau after precipitation.

Finally, the higher aggregate strength also affects the CO_2-efflux from the bulk soil, which decreases when the soil is compacted, but only as long as the aggregates are not destroyed. This underlines the persistence of the secondary coarse pores between the aggregates. If due to external dynamic forces the aggregate strength is exceeded, then the aggregates are destroyed and new surfaces or pore spaces are accessible. This results not only in reduction of the chemical disequilibrium and in destruction of microbial niches, but also affects CO_2-efflux from the soil (Reicosky *et al*., 1997). However, under the present conditions even the depletion of the (fast and slow) pools, *i.e*. the kinetic response, requires time and energy, which has to be further investigated.

6 Conclusions

Soil aggregation resulted in a chemical disequilibrium between the inner and outer layers of aggregates, while the distribution of organic compounds (difference between inner and outer layers) seemed to correlate with soil texture and bulk density. Microbial biomass was a good indicator for chemical and physical disequilibrium situations. The water repellency differed between inside and outside the single aggregates and underlined the sensitivity of the repellency method. The aggregate and the bulk soil strength clearly showed the close interrelation between gas transport, hydraulic conductivity, and microbial activity and underlined the fact that soil structure must be discussed as a very sensitive parameter to determine soil sustainability.

Acknowledgments

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IV Spatial distribution of hydrophilic and hydrophobic compounds and water repellency in soil aggregates from different tillage systems

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Geoderma (submitted)

1 Abstract

Water repellency in soils has high potential for stabilizing soil structure and protecting organic matter against mineralization. The heterogenic distribution of water repellency might be a consequence of different amounts of organic compounds present at various scales. The spatial distribution of hydrophobic and hydrophilic carbon groups at different aggregate scale in relation to water repellency were the objective of this study. Measurements were conducted on both homogenized soil and soil aggregates from silty loam Anthrosol under pasture and conservation tillage and Luvisol under conventional tillage, sampled from three soil horizons. The aggregates were fractionated into seven size classes by dry sieving; in addition single aggregates were also separated into exterior, transitional and interior regions using a soil aggregate erosion chamber (SAE). The material from different aggregate size classes or aggregate layer was used for carbon and nitrogen content measurements and for DRIFT spectrometric analyses of functional hydrophobic and hydrophilic groups. Water repellency was identified on the surface of different size class aggregates quantified using the sorptivity method.

The results showed strong variability of total organic carbon content within individual aggregates and size classes, considerably influenced by soil depth and management practices. Microaggregates had higher contents of total organic carbon than macroaggregates. Outer surface of aggregates from no tilled soils had the higher carbon content as well as the intensity of absorption of hydrophobic C-H and hydrophilic C=O groups.

Differences in subcritical water repellency for all soil aggregates were found between aggregate sizes and they were also affected by the type of vegetation and soil depth.

Very poor correlation was found between repellency in soil aggregates and total organic carbon, hydrophobic or hydrophilic groups content.

Keywords: aggregates, water repellency, soil organic carbon, hydrophobic and hydrophilic groups

2 Introduction

Spatial heterogeneity of differing components or properties of soil at various scales is defined as soil structure (Dexter, 1988). Such variation is ubiquitous in the pore size distribution, where secondary large inter-aggregate pores (coarse pores >50 µm), and small intra-aggregate pores affect transport phenomena and lead to preferential flow (Horn, 1994). Spatial heterogeneity in soils also occurs as a consequence of a nonhomogeneous distribution of microbial populations and organic substances. Several authors describe an accumulation of organic substances at the surface of soil aggregates due to the fluxes of dissolved organic carbon in the coarse pores, root growth and subsequent decay, and the excretion of organic material by soil animals (Allison, 1968; Hattori, 1988; Christensen et al., 1990; Augusitin et al., 1995). The combination of preferential flow of soil solutions and gaseous exchange, drive microbial colonization, in turn enhancing biological, chemical and physical gradients from the exterior to the interior regions of soil aggregates (Horn, 1990; Horn *et al.*, 1994a).

These processes increase soil stabilization, the proportion of fine pores tends to be higher near the surface of soil aggregates than in the centre (Horn, 1987). Gerke and Kohne (2002) showed how this impacts upon the hydraulic properties of the interior and exterior of soil aggregates. They found a significant reduction of water absorption rates in the exterior aggregate layer as a result of fewer coarse pores and clay eluviation. Other chemical and biological properties may vary from the external surface to the centre of soil aggregates thus influencing porosity and water flow. Horn *et al.* (1994a) demonstrated that the external surface layers of aggregates contain more microorganisms than internal region. Whilst Santos *et al.* (1997) reported significant differences in Ca and Mg concentration gradients between exterior and interior regions of aggregates. Land management may also affect aggregate structure, Park and

Smucker (2005a) reported higher porosities in exterior layers of soil aggregates from different managements and lowest intra-aggregate porosities in the central regions of conventionally tilled aggregates.

The flow of soil solution in aggregated soils is not only influenced by porosity but also by the heterogenic distribution of microbial exudates and organic matter which can reduce the wettability of soils. Water repellency has been observed in many soils around the world and can vary from very severe to hardly detectable. Tillman *et al.* (1989) suggested that soils expressing low levels of water repellency is a widespread condition occurring when hydrophobic surface coverage is less abundant and is referred as subcritical water repellency. Hydrophobicity influences many physical processes in the vadose zone, including infiltration, preferential flow and the distribution and dynamics of soil moisture (Dekker and Ritsema, 1994; Bauters *et al.,* 1998; DeBano, 2000). Such processes have negative effects on soil like erosion or surface runoff (Clothier *et al.*, 2000). Subcritical water repellency can however have beneficial impacts upon the environment and agriculture. A reduction in infiltration rates through hydrophobicity can increase soil aggregates stability (Zhang and Hartge, 1992; Hallett and Young, 1999) and also the stability of soil organic matter against microbial decomposition (Piccolo and Mbagwu, 1999).

Repellency has been shown to have a biological origin and can be affected by microorganism type (White *et al.,* 2000), nutrient levels (Hallett and Young, 1999), and exudate chemistry (Czarnes *et al.,* 2000).

The chemical origin of hydrophobicity has been investigated by several studies showing a correlation between carbon content and soil hydrophobicity (Chenu *et al.*, 2000; Mataix-Solera and Doerr, 2004). However this has been refuted by studies on other soils (Horne and McIntosh, 2003). Since not all carbon compounds are hydrophobic, it is proposed to consider the type of organic carbon present in the soil rather than simply the total amount of organic carbon (McKissock *et al.*, 2003). Long chain, aliphatic compounds have been linked to soil hydrophobicity, specifically long chain acids, alcohols, and wax esters with extensive polymethylene chains (Ma'shum *et al.,* 1988). In addition, fatty acids, alcohols, and esters, together with alkanes, phytols, phytol derivatives, and sterols, have all been isolated from water repellent soils and are associated with water repellency (Franco *et al.*, 2000).

To simplify the measurements of these compounds, Capriel *et al*. (1995) and Ma’shum *et al.* (1988) used reflectance Fourier transform infrared spectrometer (DRIFT) proposing the usefulness of this approach to quantify hydrophobicity. A linear relationship has been found between the amount of an aliphatic soil extract and the area of alkyl C-H peak at 3000-2800 cm^{-1}. The area of the peak is proportional to the concentration of aliphatic C (Capriel *et al.,* 1995). Using DRIFT, other types of functional groups present in soil can be also detected; for example the intensity of the absorption at 1720-1710 cm^{-1} and 1620-1600 cm^{-1} indicates carboxylic groups (C=O) (Celi et al.*,* 1997), which are proportional to the cation exchange capacity (CEC) of defined organic substances (Günzler and Böck, 1990).

Agricultural management clearly influences the number of aliphatic C-H units and implicitly the hydrophobicity of the soil organic matter (Capriel, 1997). Ellerbrock *et al.* (2005) used infrared spectroscopy to indicate the amount of hydrophobic and hydrophilic functional groups in relation to soil hydrophobicity and found that a higher ratio of hydrophobic to hydrophilic groups indicates higher water repellency. Doerr *et al.* (2005) conducted the DRIFT analyses on soils with different hydrophobicity and concluded that the amount of aliphatic C-H in soil material does not determine the water repellency of a soil.

Water repellency is a common feature of many soils and is thought to vary within aggregates from exterior surfaces to the centre. The origin of repellency is postulated to be due to microbial populations and the eluviated organic materials; however no study has determined directly how both repellency and the compounds that may be responsible for its development, vary within aggregates and across a range of aggregates sizes. The objectives of this study were to assess (I) if macropores which define the surfaces of soil aggregates contain more hydrophobic material than the bulk soil (II) if higher concentrations of hydrophobic materials induce higher levels of repellency on the surface of soils (III) the difference in carbon content and distribution of functional groups in aggregate exterior and interior; and (IV) the effect of arable soil management upon the distribution of hydrophobic compounds.

3 Materials and Methods

3.1 Soil preparation

Soil samples were collected from the experimental field of Rotthalmünster in southern Germany from a silty loam Anthrosol and Luvisol in spring 2004. The soil was sampled at four sites with different management systems and vegetation: (1) maize soil as monoculture since 1979 with conventional tillage; (2) wheat soil since 1969 with conservation tillage (since 1998) and two grassland soils (since 1961): (3) grassland A with acidic fertilization and (4) grassland B treated with alkaline fertilization. Samples were taken from three depths, which corresponded to soil horizons. A detailed description of the analyzed samples is presented in Table IV-1

Soil aggregates were separated from the bulk soil by manually breaking the bigger blocks along planes of weakness. Air-dried aggregates were gently sieved into the following seven size fractions: 15-12 mm; 12-8 mm; 8-5 mm; 5-2 mm; 2-1.25 mm; 1.25-0.63 mm; 0.63-0.125 mm diameter.

3.2 Separating aggregate layers

The separation of the aggregate regions was conducted using the soil aggregate erosion method (SAE) (Figure IV-1) (Park and Smucker, 2005b). Single air-dried aggregates, 8-5 mm diameter, were placed in SAE chamber and rotated in the rotary shaker (IKA KS 260 control) at 400 rpm to abrade the soil material from aggregate surfaces. The abraded soil fragments were separated by a screen and collected for further analyses.

Aggregates were separated into different regions from the surface to the core of the aggregate (Figure IV-2). The exterior aggregate region corresponded to 25% of abraded mass of the aggregate, 25-50% and 50-75% was the transitional region and the rest was the aggregate interior.

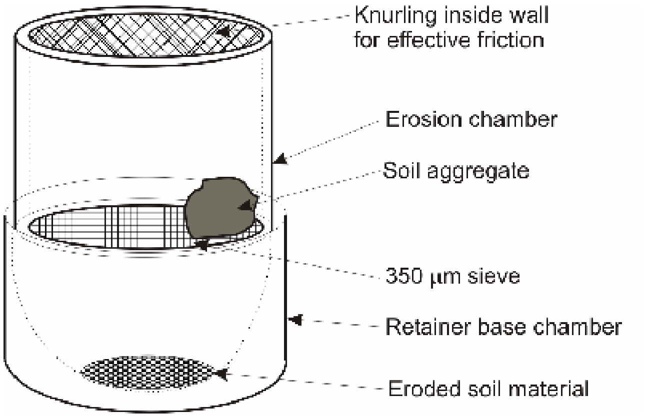

Figure IV-1 *Soil aggregate erosion chamber (SAE)*

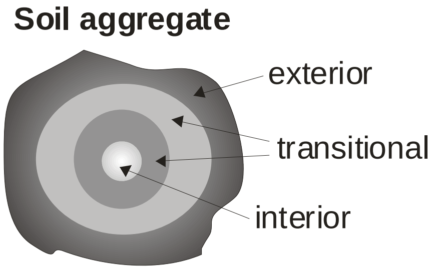

Figure IV-2 *Concentric layers of soil aggregate: exterior, transitional and interior**.***

3.3 Organic carbon and nitrogen determination

The organic carbon content (C_{org}) and nitrogen (N) were measured on the milled material from aggregates of different size and concentric layers using a continuous flow mass spectrophotometer consisting of an ANCA SL sample converter attached to a 20-20 IRMS (Europa Scientific, Crewe, UK).

3.4 DRIFT measurements

The spectroscopic analyses were conducted using a Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrometer (Brucker IFS 66) and OPUS software, using KBr as a background for the measurements. Soil material from the exterior, transitional and interior aggregate regions were placed in sample cups of 2.5 mm diameter and 2 mm depth and flattened by a spatula. Each sample was scanned 400 times at a frequency of 4 cm^{-1} and spectrum of 400-4000 cm^{-1}. A spectrum was recorded in absorbance mode and the amount of aliphatic C-H and carboxylic C=O groups was calculated by the peak area. Bands arising from C-H stretching of aliphatic compounds were taken as the 2800-3000 cm^{-1} region and for C=O carboxylic groups in 1740-1600cm^{-1}

(Capriel et al., 1995; Ellerbrock and Gerke, 2004; Doerr et al., 2005). An example of the IR spectra is presented in Figure IV-3 and the calculation of the peak area is shown in Figure IV-4.

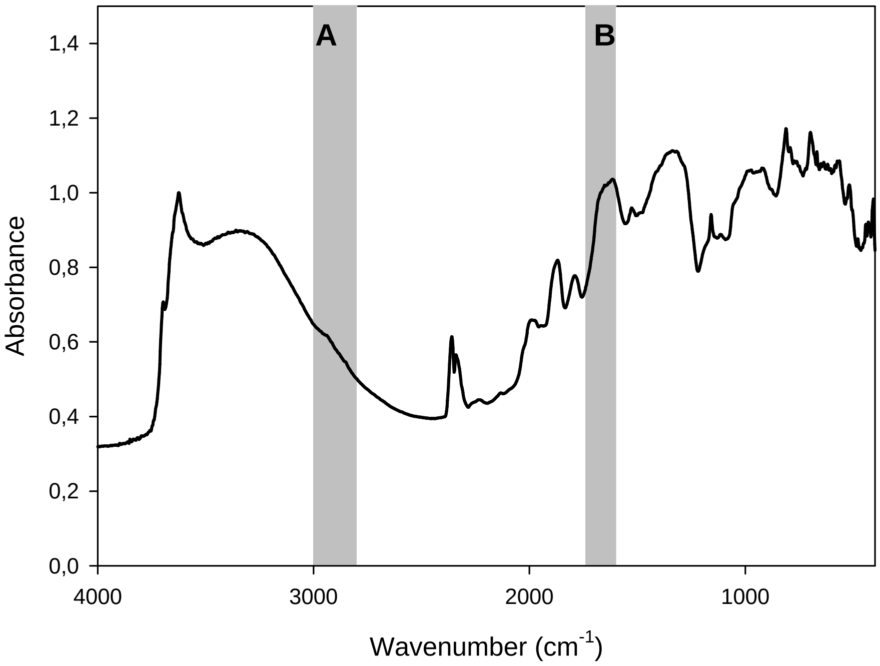

Figure IV-3 *An example of DRIFT spectrum with marked bands A for hydrophobic and B for hydrophilic groups*

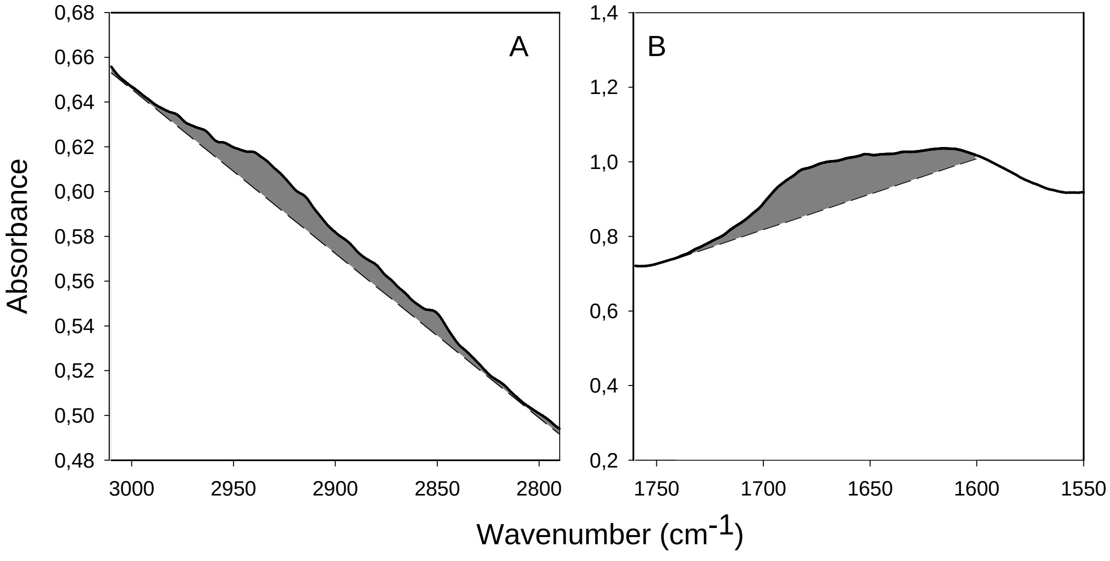

Figure IV-4 *Area under the peak for absorbance calculation at different frequency for (A) hydrophobic and (B) hydrophilic bands*

3.5 Water repellency measurements

Water repellency was measured on the surface of soil aggregates with the method described in Hallett and Young (1999). A water repellency index was calculated from the sorptivity of water S_w and ethanol S_e (Tillman *et al.*, 1989) using the relationship:

$$R = 1.95 \frac{S_e}{S_w} \qquad \text{Eq. IV-1}$$

where the value 1.95 accounts for the differences in surface tension (γ_e, γ_w) and viscosity (μ_e, μ_w) of these two liquids.

$$S_w = \left[\frac{\left(\mu_e / \gamma_e \right)^{1/2}}{\left(\mu_w / \gamma_w \right)^{1/2}} \right] S_e \qquad \text{Eq. IV-2}$$

The water repellency index (R) is a proportional representation of how much sorptivity is reduced by water repellency (Hallett *et al.*, 2001). $R > 1.95$ is defined (Tillman *et al.*, 1989) as subcritical water repellent, $R < 1.95$ identify nonrepallant soil.

3.6 Statistical analysis

Results were compared using arithmetic means (+/- standard error) of aggregates considering the size as well as different soil depth and the vegetation. Values for water repellency were established from 15 replicates, and determination of concentric layer properties on 5 replicates. Results were compared using confidence tests, applying a one-way (no blocking) ANOVA statistical analyses using Tukey's multivariate testat significance level of 95%.

4 Results

4.1 General description of analyzed soils

A detailed description of the analyzed soil from different management, vegetation and horizons is presented in the Table IV-1. The texture of the soil is silty loam with approximately 70% silt, 20% clay and 10% sand. The arable soils are slightly acidic (pH~6); grassland A (with acidic fertilization) is strongly acidic (pH 3.3-4.5), grassland B (with alkaline fertilization) is acidic (pH~5). Higher values of organic carbon and nitrogen content as well as a higher C/N ratio is found in Ap/Ah horizons and decreased in subsoil.

***Table IV—1** General description of analyzed soil*
CT - conventional tillage; CnT - conservation tillage

	soil type	soil tillage	soil depth	horizon	Texture (%)			pH	C_{org}	N	C/N
					Sand	Silt	Clay	($CaCl_2$)	(%)	(%)	
Maize (since 1979)	Hortic Anthrosol	CT	0-15	Ap1	10	68	22	6.4	1.4	0.14	10.1
			15-35	Ap2	10	69	21	6.2	1.3	0.14	9.6
			35-45	Sw-M	7	72	21	6.0	0.6	0.08	7.9
Wheat (since 1969)	Haplic Luvisol	CnT since 1998	0-20	Ap	9	68	23	6.4	1.4	0.15	9.1
			20-32	rAp	9	66	26	6.3	1.1	0.13	8.5
			32-45	Bt	7	65	28	6.2	0.5	0.07	7.5
Grassland A (since 1961)	Hortic Anthrosol		0-13	Ah	7	70	23	3.3	1.6	0.17	9.4
			13-28	rAp	9	71	21	3.8	0.8	0.11	7.9
			28-39	Sw-M	8	72	21	4.5	0.6	0.08	7.7
Grassland B (since 1961)	Hortic Anthrosol		0-16	Ah	8	70	22	5.6	2.7	0.28	9.7
			16-27	rAp	9	70	21	5.4	0.7	0.09	8.1
			27-38	Sw-M	8	70	22	5.2	0.7	0.09	8.1

4.2 Heterogeneity in organic carbon distribution

The distribution of organic carbon varied strongly in soil aggregates, depending on soil management, depth, size of the aggregate and location within aggregate. In all soils the highest organic carbon contents are in a topsoil horizons and decrease with soil depth.

In the topsoil of maize vegetation and grassland soils the aggregates of smaller size have significantly higher organic carbon contents than the larger ones (Figure IV-5, p=0.05, see also Appendix). In the soil from wheat vegetation and from the subsoil of maize vegetation and grassland soils only slight insignificant differences in the organic carbon content between aggregates of different sizes can be found.

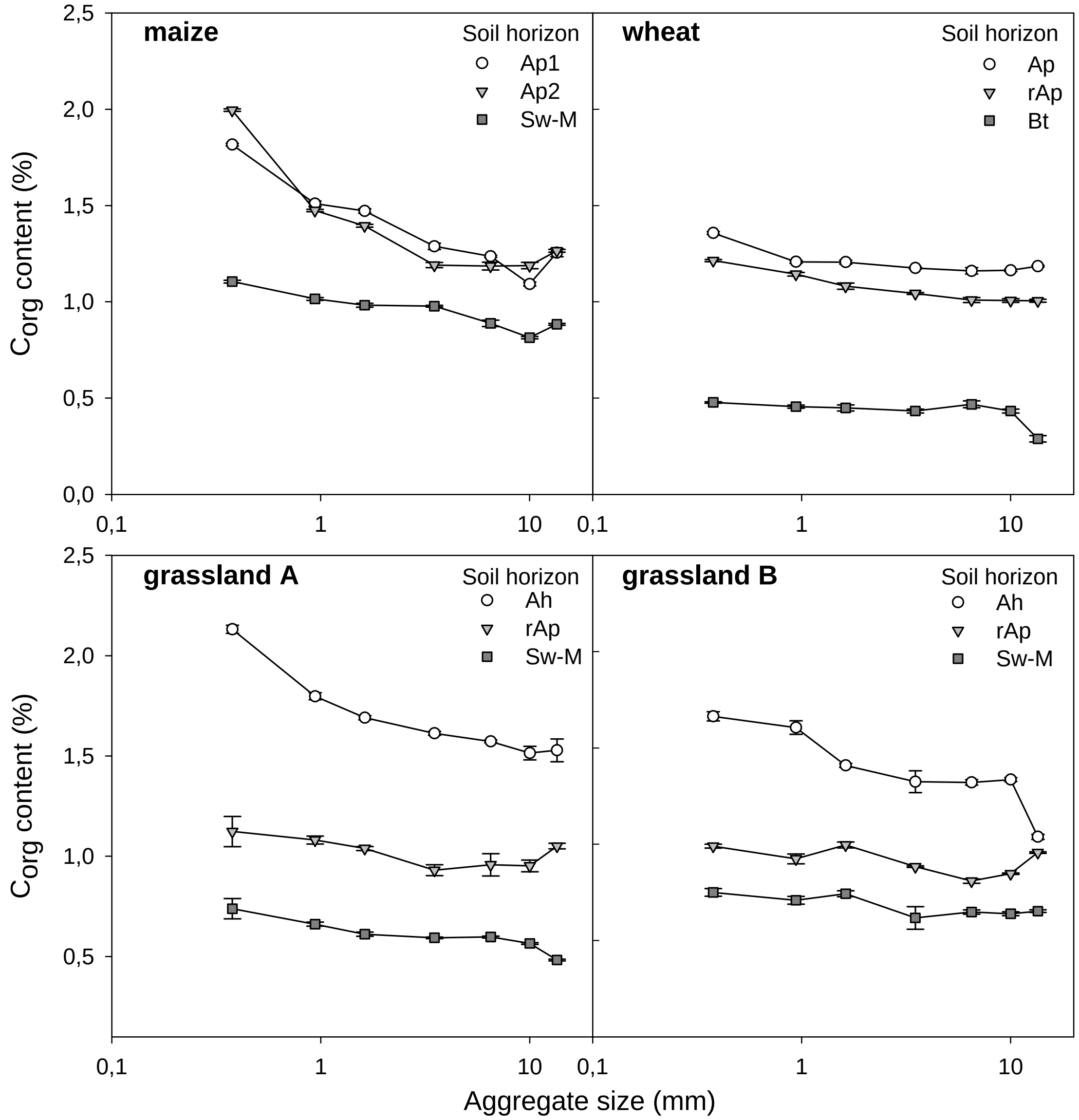

Figure IV-5 *Organic carbon content in different aggregate-size fractions Bars identify standard deviation.*

Analyses of the material from different concentric layers of the aggregates have shown in most samples (except the Ap horizons of maize and wheat vegetation) a tendency towards a higher content of C_{org} in the exterior region in comparison to the interior[*] (Figure IV-6, see also Appendix). This trend was especially pronounced in those soil horizons where aggregates were not disturbed by tillage. However, in the Ap horizon of wheat soil with conservation tillage, the decrease of carbon towards the interior starts from the transitional layer.

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[*] The differences are not statistically significant at p=0.05.

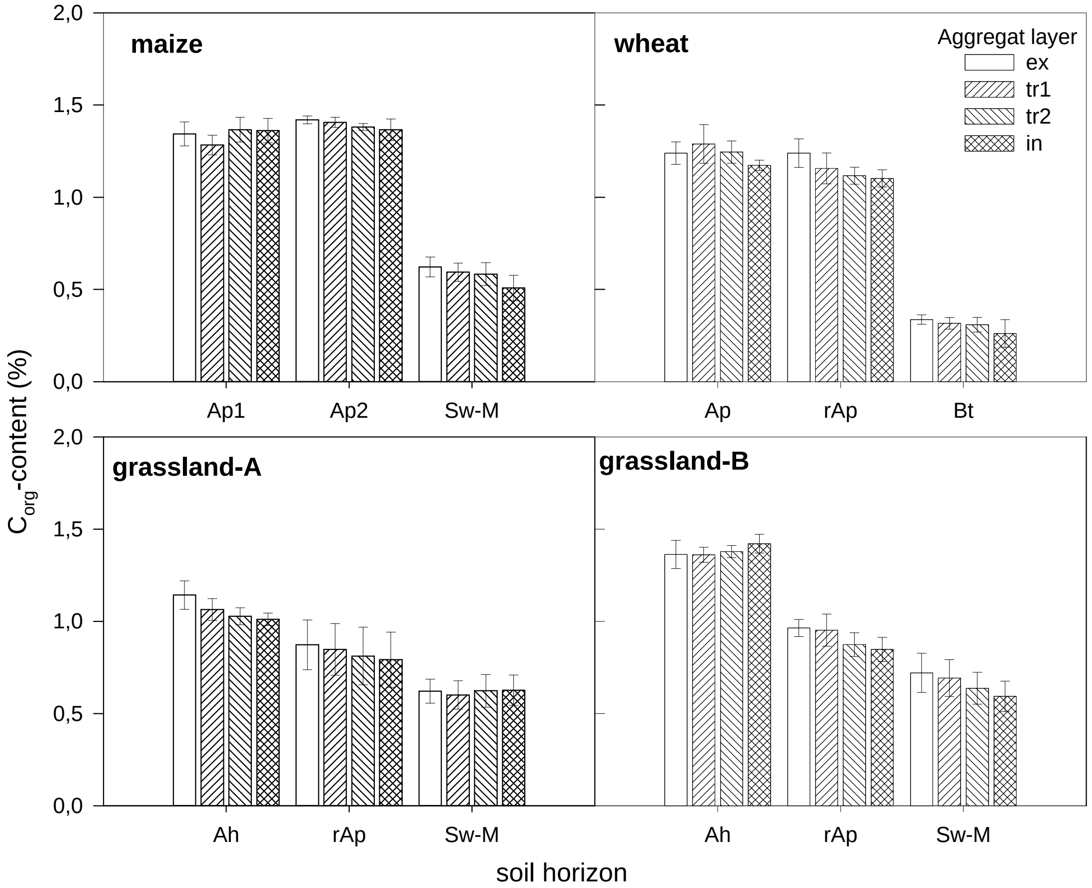

***Figure IV-6** Organic carbon content in external (ex), transitional (tr1, tr2) and interior (in) regions of single aggregates*
Bars indicate standard errors (n=5)

The distribution of the functional hydrophilic C=O and hydrophobic C-H carbon groups in the exterior and interior regions of single aggregates from different soil management and horizons is shown in the Figure IV-7 (see also Appendix). The intensity of absorbance caused by hydrophilic groups (C=O) is three times higher than the hydrophobic groups (C-H). Furthermore the values of hydrophilic groups vary not only among soil horizons, but also within single aggregates. More hydrophilic groups were present in the aggregate exterior than in the interior (except wheat-Ap).

The absorbance intensity of hydrophobic groups also varied among soil horizons, decreasing with soil depth and in subsoil the values were not detectable by DRIFT spectrometry. In addition it can be also recognize that exterior regions of the aggregates have more hydrophobic groups than the aggregate interior.

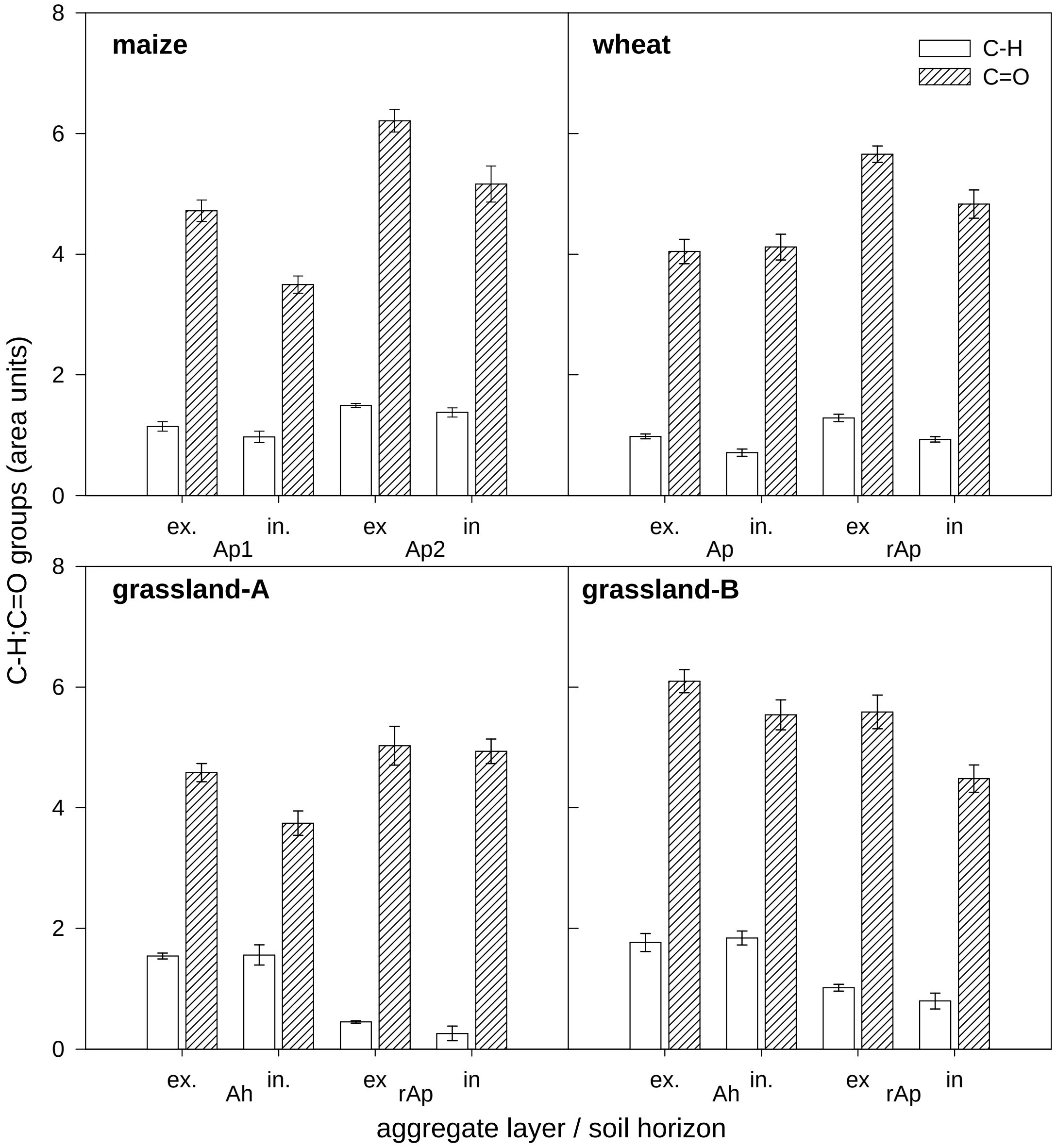

Figure IV-7 *C-H (hydrophobic) and C=O (hydrophilic) absorption band area in differently managed soils, horizons in aggregate exterior (ex) and interior (in) Bars indicate standard errors (n=5)*

The absorption intensity of hydrophobic groups correlated well with organic carbon content in soil (R^2=0.78) (Figure IV-8). Soil material rich in organic carbon contained more C-H groups, and in material with low carbon content the C-H groups were hardly detectable. Such a good correlation can not be found between the absorption intensity of the carboxylic groups and the organic carbon content (R^2=0.11).

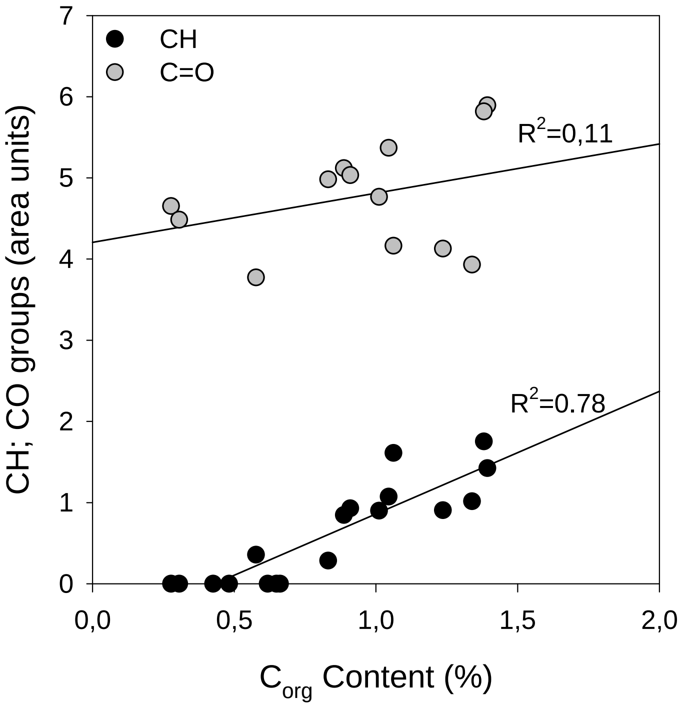

Figure IV-8 *Relation between C_{org} content and the absorbance of hydrophobic (C-H) $R^2=0.78$ and hydrophilic (C=O) groups $R^2=0.11$*

4.3 Water repellency in soil aggregates

The values of water repellency calculated from the sorptivity of water and ethanol showed subcritical water repellency (Figure IV-9, see also Appendix). In other words the reduced infiltration of water took place in all investigated aggregates and the repellency index values were higher than 1.95. Variation in repellency values was detected in soil with different vegetation and in aggregates of different size. The highest values of water repellency have been found in aggregates from maize vegetation, followed by the grassland soil. There were only a few significant differences among aggregates of the same size class but other horizons, although there was a slight tendency of higher water repellency values in topsoil than in subsoil (significant for 15-12 mm aggregate size of grassland-A soil, p=0.05). The most pronounced variation in repellency was observed between aggregates of different size-classes. In soil from maize vegetation the 8-5 mm aggregates had significantly higher values of repellency index than larger aggregates. Such a trend was also detected in soil from wheat vegetation in Ap, rAp and in grassland-A rAp, Sw-M horizons.

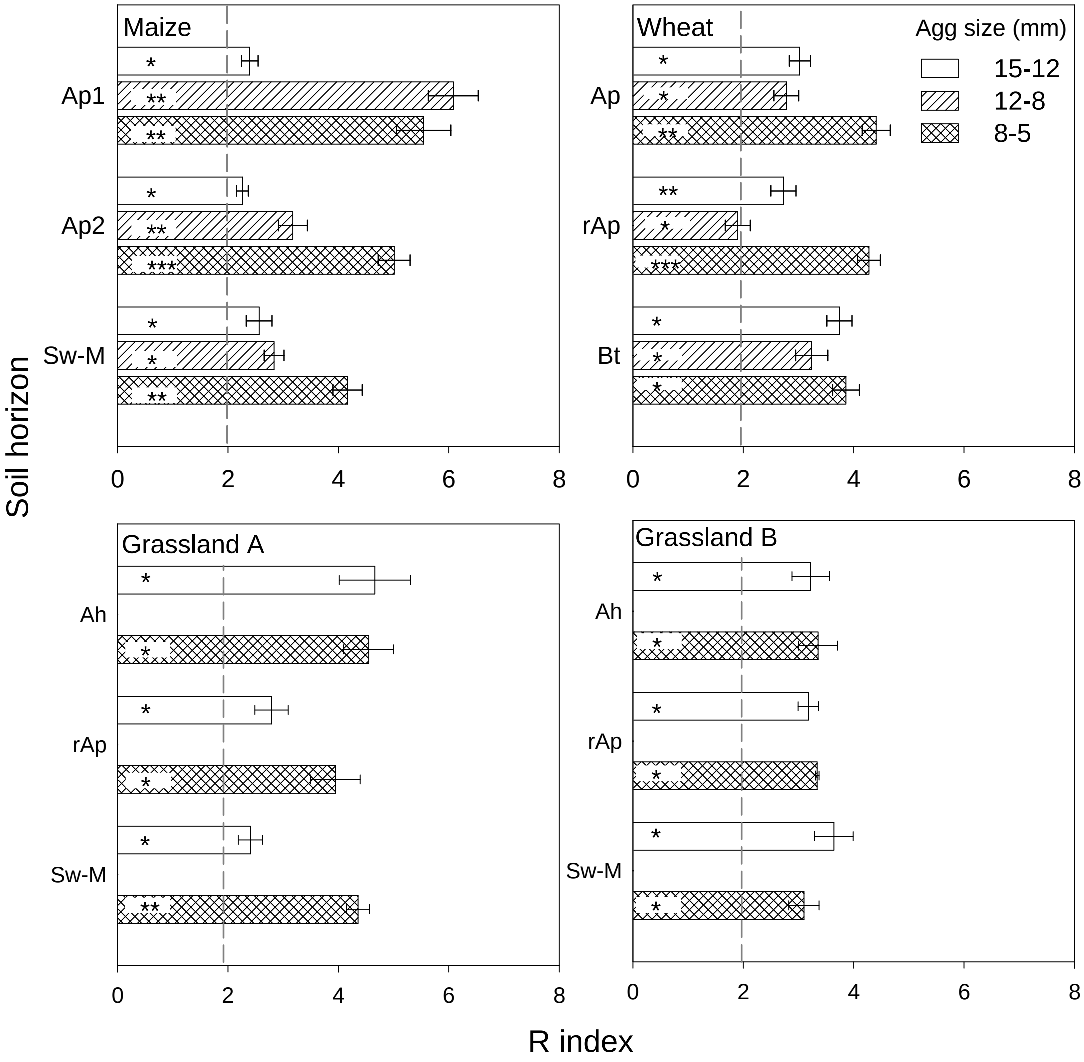

***Figure IV-9** Water repellency of soil aggregates of different size, horizon and soil management*
*Bars indicate standard errors (n=15). * ** *** identify significant differences between aggregate size classes (p=0.05).*

4.4 Water repellency and organic carbon content

The variability of water repellency in soil aggregates could depend on the content of organic carbon or hydrophobic and hydrophilic groups that attract or repel the water molecules. However, the results from organic carbon content measurements, absorption intensity of hydrophobic and hydrophilic functional groups as well as repellency showed no direct relationship between content or quality of organic carbon and repellency (Figure IV-10). There was also no correlation between the repellency and the absorption intensity of hydrophobic C-H groups.

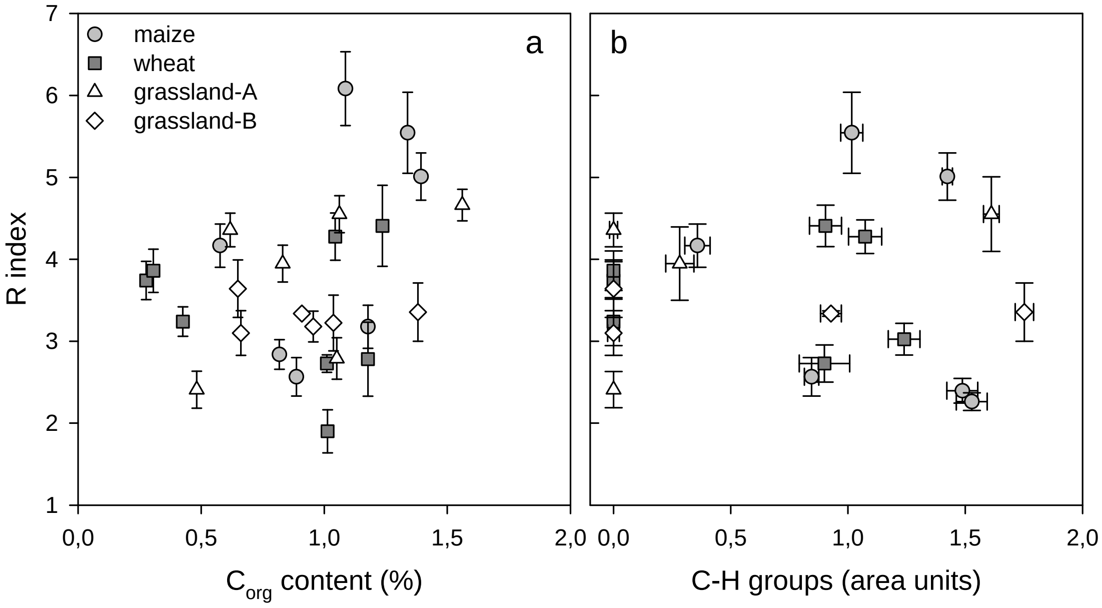

Figure IV-10 *Relationship between repellency index and organic carbon content (a) and absorption intensity of hydrophobic C-H groups (b)*
Bars identify standard errors of the mean (n=5).

5 Discussion

Soil management has a strong effect on soil organic matter (SOM) distribution and its decomposition (Angers and Chenu, 1997; Chan et al., 2002; Ding et al., 2002; West and Post, 2002) while tillage practices destroys the soil structure and the physical protection of SOM in soil aggregates. Beare et al. (1994) have shown that the SOM protection in aggregates is higher in no-till soils than in cultivated ones. Disruption of soil aggregates increase C mineralization in comparison to undisrupted aggregates (Elliott, 1986; Gupta and Germida, 1988). Several studies reported a decrease of organic matter in cultivates soils in comparison to pasture ones (Young and Ritz, 2000; Hallett et al., 2001) which corresponds to the results presented here; grassland soils contain more organic carbon than the cultivated soils. The variation of organic carbon content within soil management was also found according to different aggregate size classes. Some authors have shown that due to aggregate hierarchy the larger aggregates separated by wet sieving contain more organic carbon than the smaller ones (Elliott, 1986; Jastrow and Miller, 1998; Six et al., 2000) because larger macroaggregates contain extra organic carbon which works as a binding agent for smaller microaggregates. In contrast, in here presented results higher contents of organic carbon in smaller aggregate size classes were found than in larger ones which was probably due to the method of aggregate separation. Also Puget et al. (1995) reported that the aggregates separated by dry sieving contained more organic carbon in smaller aggregates than in larger ones and the aggregates separated by wet sieving have shown opposite trend.

The heterogenic carbon distribution in structured soils was also determined within single aggregates. Some scientists reported a higher concentration of carbon in the external layer of aggregates (Ellerbrock and Gerke, 2004; Park and Smucker, 2005b) while others did not found such tendency or it was not significant (Santos et al., 1997). In addition, Park and Smucker (2005b) reported that the aggregates from no-till or native vegetation had higher concentrations of organic carbon at the aggregate surface than those from conventional tillage. In reported results only slight and not significant tendency of higher carbon content in the exterior regions have been noticed probably due to the high heterogeneity among aggregates. Although results were not significant the tendency was most pronounced in aggregates from the horizons where no tillage was applied. Thus, it can be concluded that if soils structure remains undisturbed by machinery, microorganisms and roots as well as process of preferential flow will occur in secondary pores and the accumulation of organic matter on the aggregate surface will be more pronounced.

The variation in organic carbon distribution in different soil aggregates may influence the water infiltration into the soil since the reduced wettability can be caused by hydrophobic organic matter (Wallis and Horne, 1992) or hydrophobic surface films on soil particles (Carrillo et al., 1999).

Water repellent substances in SOM includes aliphatic elements (Capriel, 1997) and waxes (Franco et al., 2000) and the hydrophobic character of SOM determines the amount of hydrophilic C=O groups to that of hydrophobic C-H groups (Ellerbrock and Gerke, 2004). The determination of hydrophobic and hydrophilic groups in soil material using DRIFT analyses (Capriel et al., 1995) represents the hydrophobicity level. Presented results have shown that the amount of hydrophilic groups is higher than the hydrophobic groups and the difference is smaller in aggregate interior regions. Such results corresponds to findings of Ellerbrock and Gerke (2004) who also found more hydrophilic functional groups on the aggregate surface than in the center.

In addition a good correlation between the content of hydrophobic groups and total organic carbon was found but lack of such relation between numbers of hydrophilic groups and organic carbon content. Doerr et al. (2005) have also reported a good correlation between the amount of hydrophobic groups and the total organic carbon.

Following the reports of Capriel et al. (1995) the amount of hydrophobic groups in soil material represent the level of hydrophobicity, although the comparison of the results from sorptivity measurements and that of hydrophobic groups content did not show a good correlation. The measurements of water repellency using the sorptivity method have shown subcritical level of water repellency in all investigated aggregates. Higher water repellency found in soil aggregates under maize vegetation suggests that the exudates produced by maize roots are probably more hydrophobic than ones produced by other plants. In grassland soils and soil from wheat vegetation the repellency is lower and also the variation in repellency among horizons and aggregate size is lower. In cultivated soils from maize and wheat vegetation the variability of water repellency among aggregates from different size was very high; smaller aggregates had higher level of repellency than larger ones. Probably the crop type has a great influence on the repellency level and the cultivation practices cause variation in repellency between aggregates sizes and depths. Hallett et al. (2001) reported changes in water repellency of soil aggregates due to different soil management. They found in some soils higher repellency from plowed soils than in pasture ones, in others the higher repellency was in pasture soils. Hallett et al. (2004) investigated the spatial variability of reduced water infiltration of the soil and suggested it may be caused by submillimeter spatial variability of organic matter, organisms and the microbial environment in soil (Nunan et al., 2002). Not only organic carbon but also biological activity controlled by nutrient substrate levels contributed to water repellency (Capriel, 1997; Hallett and Young, 1999; Hallett et al., 2001). Many authors found a good correlation between repellency and organic carbon content (Chenu et al., 2000; Mataix-Solera and Doerr, 2004), but some others did not report such a link (Horne and McIntosh, 2003; Doerr et al., 2005). Horne and McIntosh (2003) and Roy and McGill (1998) suggested that not only the amount of organic compounds present in soil, but also its structural composition and arrangement influences water repellency. Von Wandruszka (1998) presented the specific formation of micellar structures by humic substances in soil, whereby molecules have hydrophobic (nonpolar) and hydrophilic (polar) parts. Hydrophobic bonding can cause humic molecules to associate in micelle-like aggregates. In some situations the hydrophobic groups orientate towards each other and the interior, and the hydrophilic functionalities are on the outside. Polar groups can be inside, and in such cases, interactions such as hydrogen bonding will decrease the hydrophilic character of the polar groups. The hydrophilic groups (inside or outside) in the micelle structures can interact through hydrogen bonding and dipole-dipole interactions with the solvent (water). Entropy increases as water structure is disrupted and decreases with micelle formation (Hayes and Clapp, 2001). The spatial arrangement of the functional groups at the molecular scale (carboxylic, aliphatic, hydroxylic groups) is responsible for chemical reactivity and sorptivity of SOM as well as hydrophobicity (Capriel et al., 1995; Ellerbrock and Gerke, 2004).

6 Conclusions

Soil aggregates from different tillage treatments, vegetation, and horizons showed a high heterogeneity in total organic carbon content, distribution of functional hydrophobic and hydrophilic carbon groups and water repellency. The variability was also pronounced in aggregates of different size classes as well as inside single aggregates. The highest organic carbon content was detected in small microaggregates in comparison to larger macroaagregates. Higher carbon contents as well as higher intensity of absorption of hydrophobic C-H and hydrophilic C=O groups were detected in the exterior regions of aggregates from those soil horizons which were not disturbed by tillage.

A good correlation existed between the content of hydrophobic groups and total organic carbon, but there was no relationship between the content of hydrophilic groups and organic carbon content.

All tested soil aggregates showed subcritical water repellency; higher values of repellency had smaller aggregates from cultivated soils. In addition it was found that probably the crop type has a great influence on the repellency level, however the cultivation practices cause variation in repellency between aggregates sizes and depths.

Very poor correlation exists between repellency in soil aggregates and total organic carbon, hydrophobic or hydrophilic groups content.

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V Tensile and erosive strength of soil macroaggregates from different soil management

1 Abstract

An aggregated well structured soil with high interaggregate and low intraaggregate strength is preferred as an arable site. The characterisation of soil aggregates concerns not only the heterogeneity of their properties according to their size and shape, but it has been also proposed that due to i.a. preferential flow of solutions concentric spatial gradients of physical, chemical and biological properties can be formed in soil aggregates.

The objectives of this study are to identify the erosive strength (E_s) of different concentric layers of aggregates; to compare the tensile and erosive strength of aggregates from different soil management and soil depths; and to find relationships between aggregate strength and other soil properties such as organic carbon and hydrophobic groups' content.

Soil aggregates from two size classes were abraded in soil aggregate erosion chambers (SAE) and separated into exterior, transitional and interior regions. The force needed to remove soil material from the aggregate was calculated as erosive strength (E_s) and compared with the tensile strength of the aggregates derived from crushing tests. The results showed an effect of soil tillage on lower erosive and tensile strength of soil aggregates in the topsoil horizons in comparison to the subsoil. Lower bulk density and erosive strength was found in the exterior regions of aggregates than in the interior ones. No correlation was found between the content of organic carbon, hydrophobic compounds and aggregate strength which suggesting that in dry soils organic carbon may loose its stabilizing properties. The positive relationship between the tensile strength and erosive strength of the aggregates suggest that the total strength of aggregate is controlled by the sum of strength of all concentric layers.

Keywords: tensile strength, erosive strength, exterior/interior aggregate region, aggregate, concentric layers

2 Introduction

Fertile and physically stable soils have to be able to withstand stresses induced by agricultural vehicles in order to maintain a structural state that permits the transport of water, gas and nutrients. At the same time, the overall strength should not be too high to inhibit root elongation. Therefore, an aggregated structure with high interaggregate and low intraaggregate strength is highly desirable (Horn, 1990). Studies on the effect of intensive soil tillage and field traffic on soil structure and its stability have shown their influence on infiltration, multidimensional water and ion movement, storage of water, aeration, erosion, plant root and microbiological activities and crop productivity (Tisdall, 1996). The structural stability is the ability of soil to preserve the arrangement of solid and void space when exposed to external stresses (Kay and Angers, 2000); in other words it can be defined as the minimum stress that will cause the body to fail (Hillel, 1998). Thus, the stability of soil structure depends on the strength of intraaggregate bonds, shape and size of the aggregates as well as on the type of applied stresses.

The structural configuration and distribution of possible failure zones in soils depend on the geometries of air filled pores, small cracks, strength of mineral-organic bonds, and other cementing agents between soil particles (Kay and Dexter, 1992). The distribution and resistance of these failure zones contribute to the dynamic physical characteristics controlling soil responses to cultivation, rain drop energies, root growth, and other applied stresses. One parameter to quantify aggregate strength is the tensile strength (T_s) of the soil, which can be considered as an indication of resistance in the weakest failure zones (Braunack *et al.*, 1979). The measurements of aggregate strength can be conducted on different sizes of aggregates as well as at different moisture conditions and it has been used to determine the T_s of aggregates from different soil types, management systems and soil depths to better understand the influence of different biological and chemical factors on the stability of soil.

Horn *et al.* (1995) found increased mechanical aggregate strength due to swelling and shrinkage and assumed that the mechanical strength of the aggregates is affected by pore heterogeneity and diameter of the aggregates.

The aggregate strength depends on capillary forces, intensity of shrinkage, number of swelling and shrinkage cycles, mineral particle mobility and binding energy between particles in or between aggregates or in the bulk soil (Horn, 1994). Dexter (1988) proposed the concept that larger aggregates are weaker than smaller ones, because they contain larger pores which are zones of weakness. Semmel *et al*. (1990) found that intensive drying of aggregates before irrigation results in lower tensile strength in comparison to those which were dried not that intense and for a longer time.

Dexter and Horn (1988) investigated the effect of land use on soil workability by determining the micro-relief of fracture surfaces and found that pasture soils are the most workable in comparison to forest and arable soils.

Causarno (1993) studied the effect of water content, organic matter and aggregate size on tensile strength. He found that in sandy loam soils with low content of organic matter the strength of aggregates is mainly affected by water content, while in clayey soils with a higher variability of organic matter (1-10%) the higher OM contents strengthened the aggregates if wet but weakened when they dried out.

Many studies have focussed on the relations between soil structural stability and organic material. Some of these studies reported positive effects of total organic matter (OM) (Tisdall and Oades, 1982) on structure stability, whereas others indicated that the composition of OM (especially the humified fractions) rather than the total amount per se is responsible for aggregate stabilization (Hamblin and Greenland, 1977; Dutarte *et al.*, 1993). The influence of organic on aggregate stability is mainly measured by wet sieving; aggregate tensile strength is relatively insensitive to differences in soil organic carbon. However, the variation of tensile strength within treatments is higher when organic carbon increases (Watts and Dexter, 1997).

Organic matter can decrease soil wettability and hydrophobic organic coating can prevent water from infiltrating into the aggregates or at least reduce their rates of wetting thereby contributing to their stability (Chenu et al., 2000). Haynes *et al.* (1991) reported that dried aggregates from a pasture soil rich in organic matter are more stable than field moist ones, and that it is the opposite for arable soils with low C content. The slower rewetting of pasture aggregates as compared to arable counterparts is ascribed to hydrophobic properties of

SOM. Capriel *et al*. (1990) reported good correlations between the hydrophobic aliphatic (C-H) fraction in soil and its aggregate stability. Piccolo and Mbagwu (1999) conducted studies on structural stability of soils with different SOM management practices. They showed that organic materials composed predominantly of hydrophobic constituents are more effective and long-lasting aggregate binding agents than those mainly made of hydrophilic compounds such as in root exudates or polysaccharides of plant tissues.

Santos *et al.* (1997), Ellerbrock and Gerke (2004) and Park and Smucker (2005a) reported the presence of concentric spatial gradients within soil aggregates. The variabilities in physical, chemical and biological characteristics within soil aggregates can be developed due to the existence of roots, preferential soil solution flow and wetting/drying cycles. Horn (1987) reported that the outer skin of aggregates contains more clay than the centre, and the latter has more coarse pores than the outer part. It has been also observed by Sextone *et al.* (1985) that in aggregate centres anaerobic conditions can be found as well as concentric gradients in O_2 profiles within large aggregates (R>10mm).

The variation of the aeration in aggregates causes differences in microorganisms presence: in exterior regions with more oxygen, nutrients and coarse pores more microorganisms can be found as compared to the aggregate interior (Hattori, 1988; Horn *et al.*, 1994b; Chenu *et al.*, 2001).

The separation of uniform concentric layers of aggregates using soil aggregate erosion chambers has been first proposed by Santos *et al*. (1997) and during the separation of the material the time of erosion was measured. They found that abrasion of soil aggregates varies in time. Thus, Park and Smucker (2005b) proposed the calculation of the erosive strength of single aggregates. They defined the erosive strength (E_S) as erosive forces required to remove 1 g of soil during 1 minute from the surface of a soil aggregate rotating along the abrasive wall within each SAE chamber. They investigated the aggregates from conventional, conservation tillage and forest soil from topsoil and found differences in erosion strength between them.

Thus, the objective of this study is to identify the erosive strength of different concentric layers of aggregates, to compare the tensile and erosion strength of aggregates from different soil management and soil depths, and to find a relationship between aggregate strength and other soil properties like organic carbon and hydrophobic group's content.

3 Material and methods

3.1 Soil preparation

Soil samples were collected from the experimental field of Rotthalmünster/Southern Germany from a silty loam Anthrosol and Luvisol at four sites with different management systems and vegetation at three soil depths representing different horizons. The undisturbed soil blocks after transportation were stored under cooled conditions (5° C) in order to minimize microbial transformations until further analysis could be carried out. These moist soil blocks were manually broken along planes of weakness and after air-drying gently manually sieved into different size fractions (15-12; 12-8; 8-5; 5-2; 2-1.25; 1.25-0.63; 0.63-0.125 mm diameter respectively) and determined the aggregate size distribution of each size class.

3.2 General description of analyzed soils

A detailed description of the analyzed soils with different treatments, vegetations and horizons is presented in the Table V-1. The texture of the soil is silty loam with about 70% silt, 20% clay and 10% sand. The pH values in arable soils are slightly acidic (pH~6); while in grassland-A due to an acidic fertilization pH is strongly acidic (pH 3.3 - 4.5). Grassland-B with alkaline fertilization has a slightly acidic pH (pH~5). The organic carbon and nitrogen content as well as the C/N ratio have higher values in Ap/Ah horizons and decrease with depth.

The aggregate size distribution of different sites and soil horizons (Table V-2) show the domination of 12-8mm and 8-5mm size class aggregates.

***Table V—1** General description of analyzed soil under various treatments. CT identify conventional tillage and CnT conservation tillage*

	soil type	soil tillage	soil depth	horizon	Texture (%)			pH	C_{org}	N	C/N
					Sand	Silt	Clay	($CaCl_2$)	(%)	(%)	
Maize (since 1979)	Hortic Anthrosol	CT	0-15	Ap1	10	68	22	6.4	1.4	0.14	10.1
			15-35	Ap2	10	69	21	6.2	1.3	0.14	9.6
			35-45	Sw-M	7	72	21	6.0	0.6	0.08	7.9
Wheat (since 1969)	Haplic Luvisol	CnT since 1998	0-20	Ap	9	68	23	6.4	1.4	0.15	9.1
			20-32	rAp	9	66	26	6.3	1.1	0.13	8.5
			32-45	Bt	7	65	28	6.2	0.5	0.07	7.5
Grassland A (since 1961)	Hortic Anthrosol		0-13	Ah	7	70	23	3.3	1.6	0.17	9.4
			13-28	rAp	9	71	21	3.8	0.8	0.11	7.9
			28-39	Sw-M	8	72	21	4.5	0.6	0.08	7.7
Grassland B (since 1961)	Hortic Anthrosol		0-16	Ah	8	70	22	5.6	2.7	0.28	9.7
			16-27	rAp	9	70	21	5.4	0.7	0.09	8.1
			27-38	Sw-M	8	70	22	5.2	0.7	0.09	8.1

***Table V—2** Aggregate size distribution of different sites and soil horizons (mass %)*

aggregate size (mm)	maize			wheat			grassland-A			grassland-B		
	Ap1	Ap2	Sw-M	Ap	rAp	Bt	Ah	rAp	Sw-M	Ah	rAp	Sw-M
15-12	26	42	22	20	52	9	33	44	41	27	37	35
12-8	20	18	41	29	19	52	24	25	31	35	22	26
8-5	12	13	16	21	12	19	17	13	15	16	14	12
5-2	17	15	13	18	11	13	15	12	10	15	15	16
2-1.25	8.5	4.8	3.8	4.4	3.1	3.1	4.9	2.9	1.8	3.1	4.2	4.5
1.25-0.63	7.1	3.6	2.2	3.1	1.9	1.9	3.1	1.6	1.0	1.8	2.9	2.8
0.63-0.125	6.3	2.9	1.2	2.4	1.2	1.3	2.5	1.2	0.8	1.2	2.2	2.1
<0.125	2.6	0.8	0.4	1.7	0.6	0.6	1.0	0.3	0.4	0.5	1.7	0.8

3.3 Aggregate peeling

Aggregates of the size class: 12-8 and 8-5mm were peeled off into exterior, transitional and interior regions using the soil aggregate erosion (SAE) method (Figure V-1). The single air-dried aggregates were placed in SAE chamber and rotated in a rotary shaker (IKA KS 260 control) at 400 rpm to abrade single particles from the aggregate surface. The abraded soil material was separated by a screen and collected for further analyses.

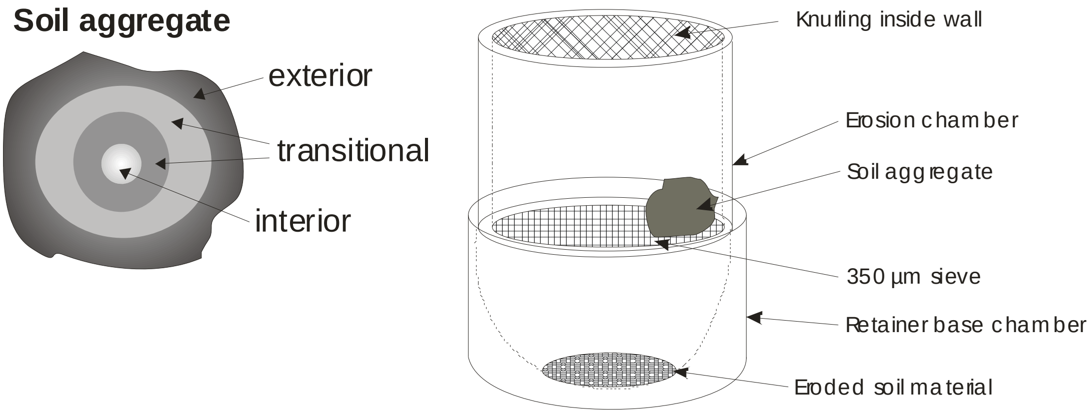

Figure V-1 *Concentric layers of soil aggregate: exterior, transitional and interior; soil aggregate erosion (SAE) chamber*

3.4 Determination of the C_{org} and hydrophobic groups distribution

The abraded material from exterior, transitional and interior regions of aggregates was analyzed for organic carbon content (C_{org}) and hydrophobic C-H groups. The organic carbon content (C_{org}) was measured using a continuous a flow mass spectrophotometer consisting of an ANCA SL sample converter attached to a 20-20 IRMS (Europa Scientific, Crewe, UK). The content of hydrophobic C-H groups was determined by a Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrometer (Brucker IFS 66 and OPUS software). Each sample was scanned 400 times at a frequency of 4 cm^{-1} and spectrum of 400-4000 cm^{-1}. A spectrum was recorded in absorbance mode and the amount of aliphatic C-H groups was calculated by peak area at the 2800-3000 cm^{-1} region (Capriel *et al.*, 1995; Ellerbrock and Gerke, 2004; Doerr *et al.*, 2005). KBr was used as a background for the measurements.

3.5 Bulk density measurements

The density of the bulk soil (d_B) was determined by measuring the mass and the volume of the soil in cylinders taken at the same depth as soil aggregates. The soil aggregates density was determined by coating the single aggregates with paraffin and measuring their volume in distilled water. The bulk density of the aggregates after abrasion was determined by measuring the mass and the diameter of the spherically shaped aggregates with calliper after defined abrasion time.

3.6 Aggregate tensile strength

Tensile strength of single aggregates was measured by crushing tests using a loading frame (Instron 5569, software Merlin). The minimal force applied on an aggregate which caused the breakage was taken as a crushing force. To calculate the aggregate tensile strength following equations were used (Dexter and Kroesbergen, 1985):

$$T_s = 0.567 \frac{F}{d^2} \qquad \text{Eq. V-1}$$

T_s - tensile strength of the aggregate (kPa)

F - the applied force at failure (N)

d_a - equivalent diameter of an irregular aggregate (m) defined by

$$d_a = \left[\frac{6 \cdot m}{\Pi \cdot d_B} \right]^{1/3} \qquad \text{Eq. V-2}$$

m is the mass (g) of the aggregate and d_B its bulk density (g/cm^3).

The equation gives the equivalent diameter of a sphere having the same mass and density as the tested aggregate.

3.7 Aggregate erosion strength (E_S) identification

Using the soil aggregate erosion (SAE) chamber the multiple concentric layers were removed from individual aggregates and the applied forces were determined to calculate the erosion strength of single aggregates.

In order to remove the soil material from the surface of each aggregate the external applied force must be higher than the internal resistant strength of the aggregate. The quantity of eroded soil material from each aggregate layer is proportional to the difference between external erosive forces and internal resistance or erosive strength (Park and Smucker, 2005b).

The natural soil aggregates after few minutes of rotation inside the SAE chambers get a spherical form and then the aggregate surface is in continuous contact with the knurled wall of the erosion chamber. The centrifugal force (C_F) applied on single aggregates by the rotary shaker was calculated as follows:

$$C_F = m(t)[R_{SK} + R_{SAE} - R_a(t)]\,\omega^2 \qquad \text{Eq. V-3}$$

where $m(t)$ is the mass (g) and $R_a(t)$ is the radius of each aggregate that changes with time t as each aggregate is eroded; R_{SK} is the radius of the rotary shaker movement; R_{SAE} is the radius of erosion chamber and ω is the angular velocity (*radian/sec*) determined by the rotational speed of rotary shaker (*rpm*) as follows:

$$\omega = 2\pi \times \frac{rpm}{60} \qquad \textit{Eq. V-4}$$

The rotation friction forces must exceed the natural cohesive and adhesive forces at the soil aggregate surface to remove soil particles from the surface of the rotating aggregate. The erosion rate is then proportional to the difference between external forces and the erosive strength at the aggregate surface.

The frictional force F is proportional to the centrifugal force C_F and frictional coefficient μ_f which is a function of the knurled wall roughness and the aggregate surface. The frictional force is defined as:

$$F = \mu_F C \qquad \textit{Eq. V-5}$$

The concentric layer erosive strength E_s (N·g/min) is equivalent to the erosive forces applied to the surface of each soil aggregate layer calculated from the frictional forces applied to the aggregate surface using the mass of soil removed during a given time of applied centrifugal force:

$$E_s = C_F \, / \left[\frac{m(t_n) - m(t_{n-1})}{t_n - t_{n-1}} \right] \qquad \textit{Eq. V-6}$$

where $m(t_n)$ and $m(t_{n-1})$ are the masses of the soil aggregate at time t_n and t_{n-1}, respectively. Therefore, these applied external energies could be established and used to compare erosive resistances of intraaggregate concentric layers among different aggregate size fractions for two soil types subjected to three different management treatments.

3.8 Statistical analysis

The statistical calculation of the data was based on the arithmetic means and standard error of the mean (+/-) considering the size of aggregates, soil depth and management system. The comparisons confidence test for the bulk density (n=10) and tensile strength (n=20) were conducted using one-way (no blocking)

ANOVA statistical analyses with Tukey’s multivariate test at the significance level of 95%. The calculations of the erosive strength for different aggregate regions were done on 5 replicates for each aggregate size. The regression analysis between E_S and % peeled mass was conducted on aggregates from the same size class, depth and vegetation. The best fit for this relation can be expressed by the equation:

$$E_S=a\ e^{bX} \qquad \text{Eq. V-7}$$

where x is % of peeled mass from the aggregate exterior to the interior (the location of the concentric layer within the aggregates), a and b are the regression constants of the exponential equation. The values of the erosive strength of exterior, transitional, interior region and the whole aggregate were calculated using the integration form of $E_S = \int ae^{bx}dx$.

4 Results

4.1 Bulk density and intraaggregate porosity

The measurements of density (d_B) of the bulk soil and the aggregates from different soil managements and soil depths show higher d_B values of aggregates in comparison to the bulk soil (Table V-3) and also increase with decreasing aggregate size. For example the d_B of the bulk soil from wheat Ap horizon is 10% lower than for the 12-8mm aggregates; the 5-2mm aggregates have 20% higher dB values than the 8-5mm aggregates. The bulk density for the whole soil as well as for different size aggregates show the lowest values in A horizons and increase with depth. The aggregate bulk density is not only affected by soil depth and aggregate size but also by tillage practices. Under conservation tillage (wheat) the bulk density of aggregates shows relatively higher values in comparison to conventionally tilled maize and grassland soil. The bulk density changes also within a single soil aggregate. The differences between the values of d_B for whole aggregates are relatively smaller than in the interior regions of aggregates.

Table V—3 *Density (d_B) (g/cm^3) of bulk soil, whole aggregates and the interior region in dependence on the soil management, horizon and aggregate size class*

		bulk	whole agg		agg interior		whole agg		agg interior		whole agg	
veget	H	soil	12-8	+/-	12-8	+/-	8-5	+/-	8-5	+/-	5-2	+/-
maize	Ap1	1.38	1.54	0.02	1.98	0.03	1.57	0.02	2.05	0.04	2.19	0.06
	Ap2	1.61	1.63	0.03	1.89	0.08	1.71	0.02	1.86	0.03	2.22	0.06
	Sw-M	1.54	1.67	0.01	1.87	0.06	1.71	0.00	1.88	0.01	2.09	0.08
wheat	Ap	1.49	1.66	0.04	2.13	0.09	1.72	0.02	2.20	0.21	2.19	0.11
	rAp	1.57	1.70	0.02	1.96	0.05	1.74	0.02	1.96	0.10	2.09	0.06
	Bt	1.50	1.77	0.03	2.00	0.04	1.75	0.03	2.00	0.06	2.32	0.05
grassland-A	Ah	n.d.	1.50	0.01	1.71	0.09	1.59	0.02	1.68	0.05	2.12	0.10
	rAp	n.d.	1.57	0.01	1.69	0.11	1.68	0.03	1.83	0.05	2.13	0.08
	Sw-M	n.d.	1.66	0.01	1.76	0.15	1.61	0.03	1.73	0.05	2.12	0.06
grassland-B	Ah	n.d.	1.58	0.05	1.71	0.05	1.72	0.05	1.69	0.17	2.03	0.19
	rAp	n.d.	1.57	0.03	1.90	0.09	1.62	0.04	1.87	0.09	2.36	0.05
	Sw-M	n.d.	1.65	0.03	1.84	0.05	1.83	0.07	1.89	0.10	2.17	0.10

4.2 Tensile strength of aggregates of different size

The tensile strength of air-dried soil aggregates presented in Figure V-2 (see also Appendix) ranges from 140 to 430 kPa for all soil horizons and management systems. Aggregates from A horizons have relatively lower tensile strength in comparison to the subsoil horizons and the difference is more pronounced in cultivated soils than in grassland soils. The tensile strength is also a function of aggregate size. Most of larger aggregates show lower values of T_S than smaller ones, but the difference is not statistically significant. Such a tendency can not be found in aggregates from grassland-A soil where the tensile strength has a low variability among different horizons and also aggregate sizes.

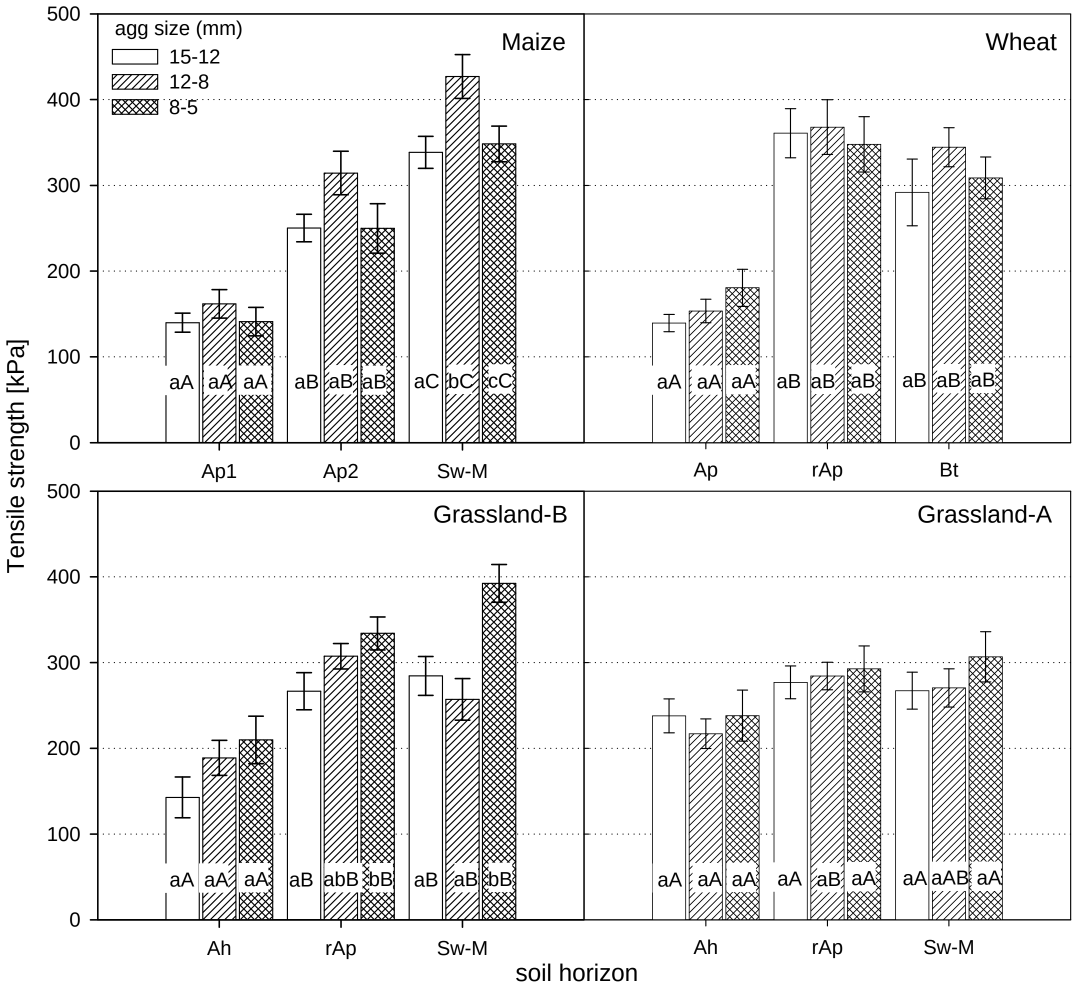

Figure V-2 *Tensile strength of soil aggregates of different size, from different vegetations and soil horizons*
Small letters (abc) identify significant differences among aggregate size classes (p=0.05), the capital letters (ABC) - among soil horizons (p=0.05)

4.3 Erosion time of aggregates

The time needed to erode soil material from the aggregate differs to a high extent (Figure V-3). Time required to abrade 75% of aggregate mass varies from 120 min (2 hours) till 1140 (19 hours) depending on the tillage system, horizon and size of the aggregates. Generally, the aggregates from the subsoil required more time for the abrasion than those from the topsoil. The shortest abrasion time were required for aggregates from the maize conventional tillage in comparison to the aggregates from the grassland and conservation tillage. The difference between abrasion time of larger and smaller aggregates is not significant. Because applied centrifugal forces change when the aggregate is peeled, the erosion time can be only used for quick estimation of aggregate strength and erosive strength values are more representative.

4.4 Erosive strength of single aggregates

The erosive strength of single aggregates correspond with the abrasion rates and show low values in the exterior regions which increase in the aggregate transitional and interior regions (Figure V-4). The empirical values of erosive strength for single aggregates are fitted with exponential curves and the parameters and correlation values are presented in the Table V-4.

The highest erosive strengths and at the same time the higher differences between aggregate exterior and interior regions have aggregates from the subsoil horizons (except maize 12-8mm and grassland-B 8-5mm) where the soil is not disturbed by tillage; weaker are aggregates from rAp horizons and aggregates from the topsoil. Between cultivated and grassland soils the difference in erosive strength can be recognized in the exterior regions where the erosive strength of aggregates from grassland soil is higher. In addition the aggregates from conservation tillage (wheat soil) show steeper exponential increase of erosive strength in transitional region than the aggregates from other treatments.

The erosive strength is also influenced by the size of aggregates; larger aggregates have higher E_s in A horizon, and smaller ones in the subsoil and rAp horizons of the grassland soil.

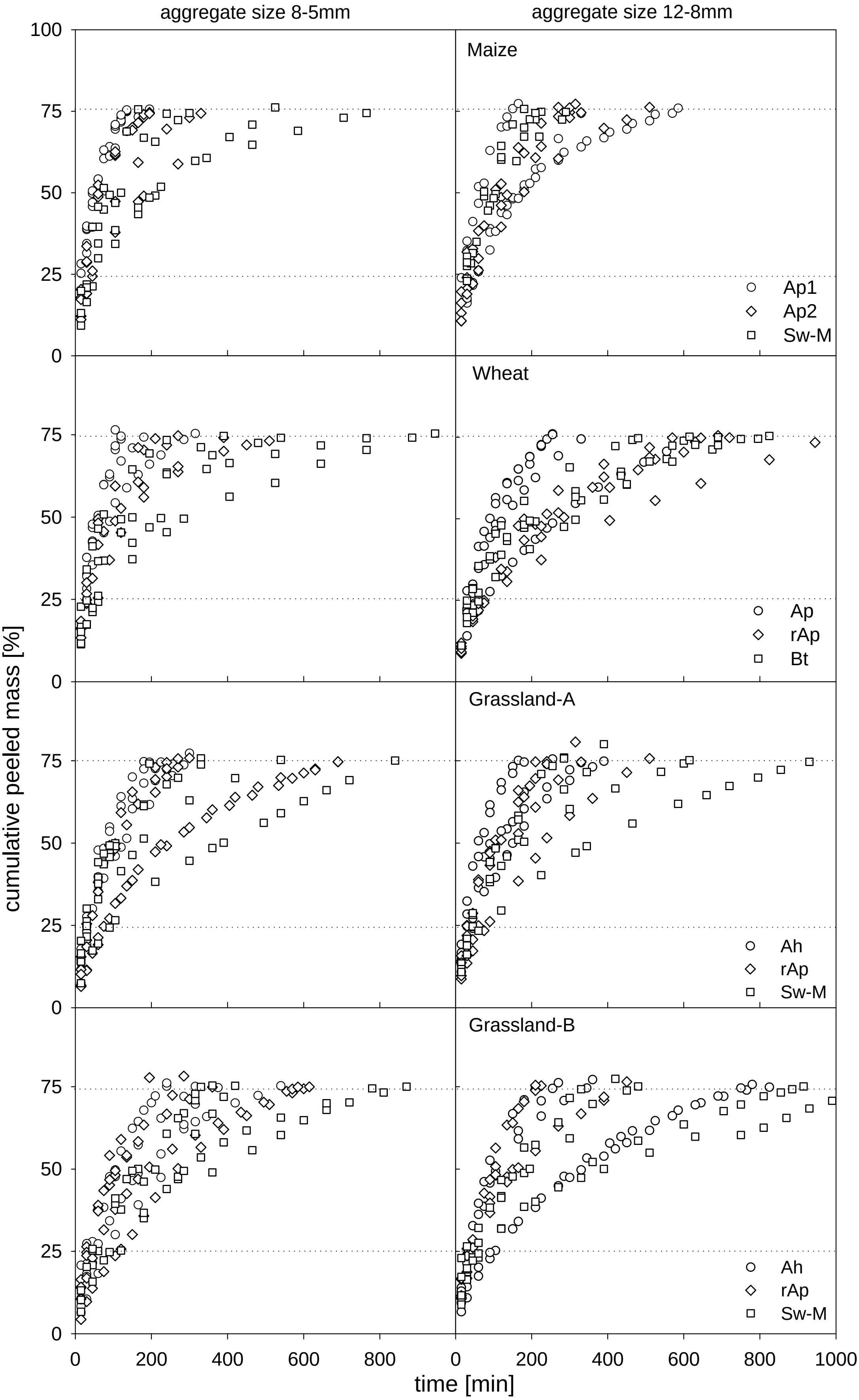

Figure V-3 *Abrasion time of soil aggregates from different vegetation and depths of two aggregate size classes*

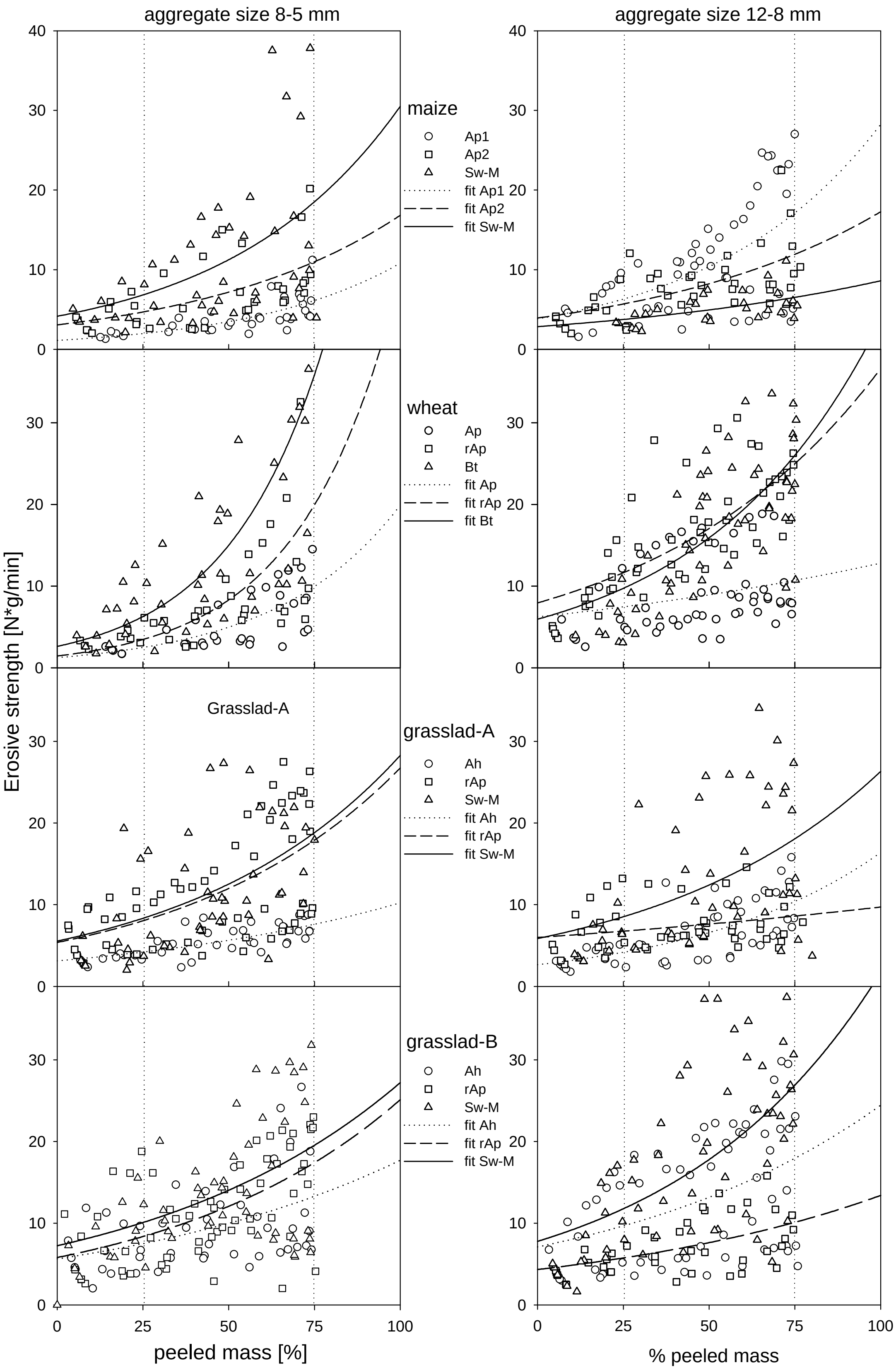

Figure V-4 *Erosion strength of single aggregates from different vegetation and depths of two aggregate size classes*

Table V—4 *Parameters a and b of the equation* $E_S=ae^{bx}$*, fitted relation between erosive strength (*E_S*) and peeled mass [%] for aggregates from different management, horizons and aggregate size classes*

land use	horizon	aggregate size 8-5mm			aggregate size 12-8mm		
		a	**b**	$\mathbf{R^2}$	**a**	**b**	$\mathbf{R^2}$
maize	Ap1	0.9	2.01	0.62 ***	2.54	1.82	0.25 ***
	Ap2	1.99	1.71	0.43 ***	2.36	1.7	0.52 ***
	Bv	2.62	1.89	0.3 ***	1.76	1.3	0.39 ***
wheat	Ap	1.36	2.44	0.53 ***	4.78	1.04	0.16 **
	rAp	2.16	2.52	0.57 ***	5.97	2.02	0.68 ***
	Bv	2.8	3.14	0.6 ***	3.58	2.73	0.62 ***
grassland-A	Ah	2.91	1.27	0.57 ***	2.36	1.89	0.51 ***
	rAp	4.93	1.63	0.38 ***	5.15	0.66	0.13 **
	Bv	3.61	2.22	0.39 ***	3.99	1.88	0.33 ***
grassland-B	Ah	5.15	1.1	0.23 **	6.02	1.57	0.31 ***
	rAp	5.1	1.49	0.27 ***	3.81	1.23	0.31 ***
	Bv	6.72	1.25	0.22 **	5.07	2.25	0.46 ***

*,**,*** means the significant level at <0.05, <0.01, <0.001 respectivly

4.5 Relationship between tensile and erosive strength, bulk density and organic carbon content

The erosive strength values (E_S) for the whole aggregates which were calculated from integration of single aggregate layers and tensile strengths (T_S) of aggregates from different soil horizons are positively correlated only between aggregates of the size class 8-5mm (Table V-5); while those of the size class 12-8mm correlate only for the wheat soil aggregates. In contrast to this, a negative correlation between T_S and E_S could be detected for the maize soil.

The bulk density influences the tensile strength of aggregates of different size, but in aggregates from grassland soil the correlation is relatively low.

Table V—5 *Pearson correlation coefficients between tensile strength (*T_S*) and the erosive strength (*E_S*), bulk density (*d_B*) of soil aggregates from different soil horizons; in different size-classes and vegetations.*

	aggregate size 12-8mm				aggregate size 8-5mm			
	maize	wheat	grassland-B	grassland-A	maize	wheat	grassland-B	grassland-A
E_S	-0.99	1.00	0.11	-0.21	0.99	0.64	0.97	0.97
dB	0.99	0.74	0.56	0.27	0.88	0.74	0.43	0.24

The distribution of organic carbon, which is not uniform within soil aggregates correlates negatively with the erosive strength of single concentric layers from aggregates from different management, soil horizons and sizes (Table V-6). The content of hydrophobic C-H groups also shows negative correlation with the erosive strength of single aggregate layer.

Table V—6 *Pearson correlation coefficients between erosive strength (E_S), the organic carbon (C_{org}) and hydrophobic C-H groups content in aggregates from different vegetations, horizons and aggregate size classes*

vegetation	horizon	C_{org}		C-H groups	
		12-8mm	8-5mm	12-8mm	8-5mm
maize	Ap1	-0.21	0.49	-0.66	-0.68
	Ap2	-0.96	-0.98	-1.00	-0.86
	Sw-M	-0.71	-0.98	-0.94	-0.31
wheat	Ap	-0.79	-0.24	-0.91	-0.93
	rAp	-0.98	-0.79	-1.00	-0.82
	Bt	-0.44	-0.15	-	-
grassland-A	Ah	-0.61	-0.81	0.37	-0.15
	rAp	-0.93	-0.91	-0.72	-0.97
	Sw-M	-0.93	-0.91	-0.72	-0.97
grassland-B	Ah	-0.98	0.93	0.81	0.19
	rAp	-0.99	-0.87	-0.96	-0.80
	Sw-M	-0.95	-0.87	-0.74	-0.70

5 Discussion

The strength of the bulk soil as well as soil aggregates has been reported to be mainly influenced by the arrangement of soil particles, geometries of air filled pores, strength of mineral-organic bonds and other cementing agents between soil particles (Kay and Dexter, 1992). Hartge and Horn (1984) considered two main reasons for soil strength: a high shear resistance per contact point and a high total number of contact points between single particles. An increased shear resistance results the soil particles are arranged in such way that even if the bulk density decreases the strength of aggregates is high (Horn and Dexter, 1989). On the other hand higher total number of contact points between single particles result in higher bulk density of aggregates and also in higher strength. Smaller aggregates have less coarse pores than larger ones and consequently their T_s is also higher which corresponds to hierarchical concept of aggregation (Dexter, 1988; Oades and Waters, 1991). Presented here results also show such tendency, the density of the bulk soil is much lower than one of soil aggregates and larger aggregates have lower density in comparison to smaller ones. The differences in aggregate tensile strength between aggregate size classes show slight tendency of higher strength of smaller aggregates, however the differences are more pronounced in those horizons where no mechanical disturbance of the soil take place. It can be only supposed that aggregates smaller than 5 mm are even stronger, but the chosen method of measurement did not allow determining tensile strength on smaller aggregates.

The high differences in soil strength were reported considering soil management and horizons. The most destructive for soil structure are the tillage practices which cause the breakage of natural arrangement of soil particles in aggregates (Hadas, 1990; Six *et al.*, 2000) and bring the subsurface soil to the surface and then expose it to wet-dry and freeze-thaw cycles or rain drop impact (Beare *et al.*, 1994; Paustian *et al.*, 1997). Such applied stresses cause disturbance in soil particles, especially clay particles which are displaced from their former equilibrium positions of low free energy and moved to a new position of higher free energy (Dexter *et al.*, 1988).

Due to these stresses in investigated soil aggregate strength in the A horizons is reduced. The aggregates from the topsoil are weaker than those from the deeper horizons; in addition aggregates from tilled horizons are less strong than those from grassland soil where no cultivation took place since several years. The relative higher strength of aggregates from rAp horizon from conservation tillage in comparison to the conventional tillage shows positive effects of reduced tillage on strength of soil aggregates. Dexter *et al.* (1988) reported that disturbed soil particles gradually rearrange their positions and orientations back towards a minimum free energy configuration which consequently increase the strength of soil.

The rearrangement of soil particles as well as growth of plant roots and preferential flow is reported to cause in some soil aggregates differences between the exterior and the interior regions of soil aggregates (Augusitin *et al.*, 1995; Park and Smucker, 2005a). Park and Smucker (2005a) identified higher porosities in exterior layers of soil aggregates from different treatments, with the lowest intra-aggregate porosities in the central regions of conventional tillage aggregates. Gerke and Kohne (2002) evaluated the hydraulic properties of the aggregate exterior and the interior and found that the external aggregate layer can significantly reduce water absorption rates, since the outer skin of aggregates contains more clay than the center and the latter has more coarse pores than the outer part. Thus, they did not only relate the hydraulic properties to their bulk density but also to the texture differences between the inner and outer region. Horn (1987) showed that the outer layer of soil aggregates contains more silt and clay and fewer sand particles than the interior of the aggregates. The soil aggregates from Rotthalmünster also show differences in porosity within single aggregates. Most of aggregates presented lower bulk density in the exterior region, and reduced into aggregate center which correlate with the erosive strength distribution. Higher bulk density means that less pore spaces are present between soil matrix and the aggregate centres are stronger. Higher bulk density affects also the availability of space for microorganisms; when the pore spaces are to small the microbes can not access those places and they concentrate on aggregate surfaces (Hattori, 1988). Erosive strength of aggregates is more representative for binding mechanisms of soil aggregates, but also the correlation between erosive and tensile strength mean that the tensile strength of the aggregate is controlled by the sum of the concentric layer strengths (Park and Smucker, 2005b).

Organic matter as well as specific hydrophobic C-H groups have been reported as important cementing agents for soil structure (Capriel *et al.*, 1990; Chenu *et al.*, 2000). On the other hand some scientists reported that in air dry conditions the content of organic carbon does not influence the strength of the aggregates. Perfect *et al.* (1995) reported that the organic matter can be positively related with the tensile strength of air-dry aggregates for some clayey soils, while it has no influence in intermediate texture. In soil aggregates with coarser texture the content of organic matter can have even a negative effect. Dexter *et al.* (1984), Guerif (1988) also have not found any correlation between carbon content and tensile strength.

Presented results also show that in air dry soil aggregates neither the organic carbon nor the hydrophobic groups’ content can influence the strength of soil aggregates. It can be although supposed that in dry conditions organic matter may loose their stabilizing effect. The strength of the dry soil might be more controlled by dispersible clay and silt which functions as cementing material (Kay and Angers, 2000). Dexter *et al.* (1988) underlined the importance of particle-particle bonds for soil strength and suggested that as the soil dries, the tension in the retreating menisci can generate sufficient force to displace the intervening water molecules and so produce much closer contact between mineral particles. Any ion or other species adjacent to such a contact is able to bond both involved particles. Where such double-bonding can occur the free energy will be lower than that for the same species adsorbed on a plane or convex surface. Consequently, these species tend to diffuse across the particle surfaces towards the regions of contact in response to the gradients of free energy. A wide range of ions, molecules, colloids and amorphous gels can diffuse in this way towards the regions of particle-particle contact where they can strengthen or cement the bonds.

6 Conclusions

The measurement of mechanical properties of soil aggregates from different soil managements and soil horizons show that the effect of environmental conditions plays a very important role in structure development and aggregate strength. The erosive and tensile strength of aggregates from the topsoil horizons are influenced by rapid changes in soil moisture and tillage processes.

Due to the wetting and drying processes the rearrangement of the particles take place which results in gradients of bulk density as well as erosive strength between exterior and interior regions of the aggregate. The increase of the erosive strength of the aggregates interior can be caused by higher number of the contact points and presence of finer intra-aggregate pores which effects in high resistance against the abrasion.

The results show that in dry soils organic carbon may loose their stabilizing properties and even contribute to formation of weakness zones in those places were organic matter is accumulated.

The hierarchical order of analysed aggregates results in higher bulk density and strength of smaller aggregates in comparison to the bigger ones. The positive relationship between the tensile strength and erosive strength of the aggregates suggest that the tensile strength of the aggregate is controlled by the sum of the concentric layer tensile strengths.

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VI Changes in soil organic matter, bulk density and tensile strength of aggregates after percolation in soils after conservation and conventional tillage

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1 Abstract

The type of tillage in arable soils affects porosity of the soil and in consequence the hydraulic conductivity. The accessibility and mobility of organic carbon in arable soils can differ depending on the type of tillage. The highest differences between conventional or conservation tillage are found in the topsoil layer of the A horizon in pore size distribution and organic matter content. Total porosity and pore continuity influence the hydraulic conductivity and also the exchange processes in structured soil. Percolation of soil can provide not only information on hydraulic conductivity of structured soil but also about the accessibility of fixed organic matter. The aim of this study was to find out how the type of the soil tillage influences the hydraulic conductivity and accessibility of organic carbon in the topsoil.

Soil samples from the topsoil layer under conventional and conservation tillage were percolated with distilled water and pyrophosphate solution. The differences in hydraulic conductivity between samples resulted in various amount of the organic carbon leached out. Organic carbon content (C_{org}), bulk density (d_B) and tensile strength (T_s) of soil aggregates after percolation have changed in comparison with the non-percolated soil and show in which aggregate fraction the organic carbon was easily available for leaching out. The highest C_{org} reduction was found in smaller aggregates in comparison with larger aggregates, which resulted in the tensile strength of macroaggregates being very little affected by percolation.

Keywords: percolation process, carbon distribution, aggregates strength

2 Introduction

Organic matter, its forms, distribution, and accessibility are very variable in structured soils and depend on other soil properties e.g. porosity, pore continuity, water relations. Soil pores and organic matter are often considered together while different forms of organic matter play an important role in the formation of pores as well as in stabilization of the structure when soils are exposed to different stresses (Kay and VandenBygaart, 2002).

In aggregated soils the movement of water is controlled by the presence of inter-aggregate pores where water flows faster than in intra-aggregate and mostly finer pores (Horn, 1990). The differences in hydraulic properties between the bulk soil and single aggregates results in a dominant flow in interaggregate pores which furthermore reduces the possibility of obtaining an equilibrated pore water pressure profile (Horn and Baumgartl, 2000). Pore continuity in macropores and a more tortuous pore system in single aggregates induce preferential flow especially near saturation (Beven and Germann, 1982). Youngs and Leeds-Harrison (1990) suggested that pore water pressure gradients cause water to flow preferentially in macropores with little flow within aggregates when both the macropores and micropores are saturated, which can be also derived from the Hagen Poiseuille Law. When saturated macropores surround unsaturated aggregates, solutes are transported by diffusion into the aggregates depending on the concentration gradient. If macropores inside the aggregates are filled with air they become isolated, severely reducing the possibility for redistribution of water and solutes in soil. Slower flow of soil solution gives more opportunities for chemical reactions within the entire microscopic pore structure owing to the relative importance of molecular diffusion compared with that of convection (Kutilek and Nielsen, 1994). Hartmann *et al.* (1998) have studied the influence of soil structure on cation exchange processes and found that the amount of exchangeable cations of water saturated structured soil samples is smaller compared with a homogenized sample of the same material. Hantschel *et al.* (1988) explained that the extract of homogenized soil contains more alkaline cations than the percolation soil extracts due to a larger accessible soil surface area of a homogenized sample and the differences are more pronounced with more intense aggregation and increasing amount of acids in the soil (Gradl *et al.*, 1987). In coarser pores the exchange processes are faster due to convective and diffusive ion transport, in fine intra-aggregate pore system the processes are slower while only diffusion allows the exchange processes (Becher, 1991). Higher tortuosity of the intra-aggregate pores decreases the accessibility of the intra-aggregate surfaces (Horn, 1987). Horn and Taubner (1989) found that the potassium release related to unit mass per unit time is smaller in bigger aggregates due to longer flow paths and smaller aggregate surface.

Organic matter in soils includes different organic compounds from easily-mineralizable plant residuals to more complex products from biotic and abiotic transformation processes or microbial biomass (Stevenson, 1994; Rethemeyer, 2004). The distribution of organic carbon in structured soil affects its availability for microorganisms and also for leaching into deeper horizons. The availability of organic carbon measured by respiration was found to correlate with water-extracted organic carbon (Burford and Bremner, 1975; Davidson *et al.*, 1987). Water and Na-pyrophosphate solution are often used for extraction of humic substances in soil (Swift, 1996), but mostly for homogenized material. The percolation of structured soils with water and pyrophosphate solution results in the extraction of only the easily-accessible organic matter. Davidson *et al*. (1987) stated that water-extracted organic carbon is "almost certainly available", and is the immediate substrate for microorganisms. However, Beauchamp *et al.* (1989) suggested that a significant proportion of water-extracted C was not available to denitrifying microorganisms. Zsolnay and Steindl (1991) found that 85% of water-extracted organic C was biodegradable. The processes of percolation which simulated the leaching of organic carbon from upper horizons to the subsoil conducted by e.g. Hartmann *et al.* (1998) have shown that the hydraulic conductivity and percolation time is primarily responsible for the accessibility of exchange surfaces. Percolation time for constant volumes increases with decreasing hydraulic conductivity and cause that also diffusion next to the fast exchange processes and mass flow determine the amount of exchanged cations.

Structured soils are characteristic for their heterogeneity in porosity and organic matter distribution. Because soil management may influence the pore system it has been reported that cultivation may change organic matter distribution and its accessibility. Some authors reported that the change from conventional to conservation tillage can result in accumulation of organic carbon in the topsoil together with a decrease of total porosity (Tebrügge and Düring, 1999; Yang and Kay, 2001).

The objectives of this study are to find out how far the conventional or conservation tillage influence the accessibility of organic carbon in structured undisturbed soil samples during percolation with water and pyrophosphate solution; to analyse the loss of organic carbon during the percolation processes affected by the distribution of organic carbon in aggregates from different size classes as well as in single aggregates and to quantify the effect of the altered organic carbon content due to percolation processes on the bulk density and tensile strength of single aggregates.

3 Material and methods

3.1 Soil material

Soil samples were collected in autumn 2002 from the experimental field of Rotthalmünster/Southern Germany from a silty loam Luvisol and Anthrosol at two sites with different cultivation systems and vegetation; soil with maize monoculture since 1979 with conventional tillage and soil with wheat monoculture since 1969 where soil tillage was changed into conservation system in 1998. The soil samples were taken at four different soil depths as undisturbed samples with 100 cm^3 cylinders.

3.2 Determination of pore size distribution in soil

In order to determine the distribution of pore sizes among conventional and conservation tilled soil and different soil horizons the samples were saturated and then adjusted to different matric suction of -3, -6, -15, -30, -1500 kPa. The pore size distribution was determined according to Sekera and Boodt (Scheffer and Schachtschabel, 2002).

3.3 Percolation with water and pyrophosphate solution

The percolation process was conducted on samples from 3-7cm depth from the conventional and conservation tilled soil. The samples were percolated with distilled water followed by 0,1M Natrium-dihydrogen-pyrophosphat ($Na_2H_2P_2O_7$) under saturated conditions (Swift, 1996). The soil cylinders were enclosed with ceramic plates from above and below, sealed from both sides and connected to the system presented in Figure VI-1. Above the soil cylinder a Plexiglas cylinder was installed in order to maintain constant pressure head of 2 cm. Below the soil cylinder there was a connection to a separating funnel to collect the soil percolate and another tube connected to the vacuum system. The process of percolation was conducted over more than 50 days with an uneven interruption periods (12, 24, 68 hours). At the beginning the samples were saturated and thereafter percolated with distilled water, followed by pyrophosphate solution and at the end again with water. The percolating solutions were leached through the soil sample and then every 20 ml of eluate was collected for further analyses. The percolation was conducted under a pressure of 20 hPa and each eluate was analyzed for dissolved organic carbon content with the Dima-TOC 100 (Dimatec).

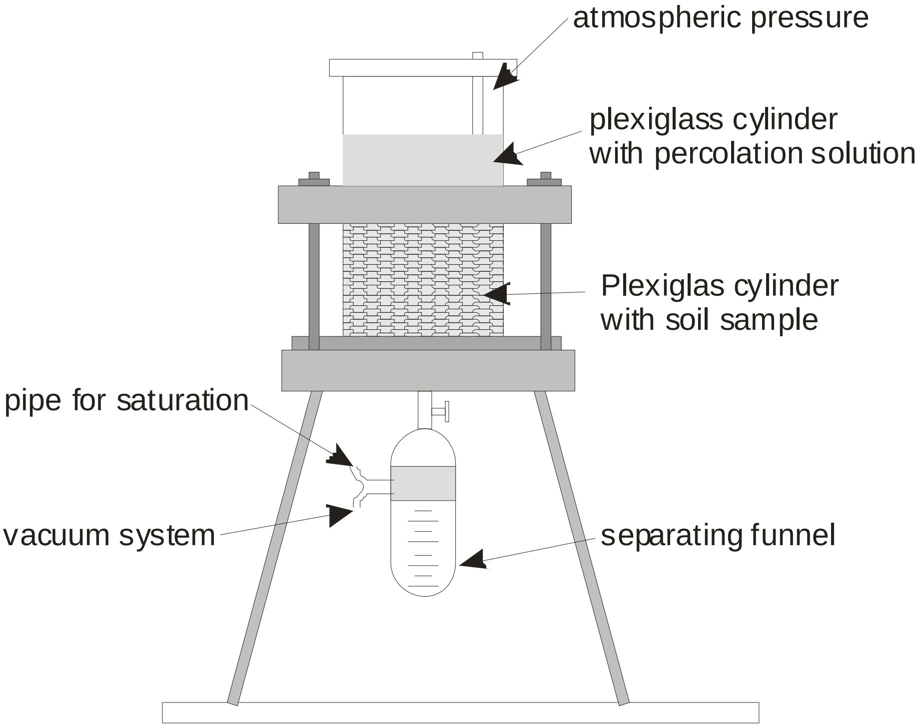

Figure VI-1 *Schema of percolation system under saturated conditions*

3.4 The determination of the C_{org} distribution in aggregates after percolation

After the finished percolation soil was removed from the cylinders and aggregates were separated by manually breaking the soil along the zones of weakness. The single aggregates were peeled in the soil aggregate erosion chamber (SAE) and the material from the exterior, transitional and interior region of the aggregates was collected for analyses of organic carbon. The organic carbon content (C_{org}) was measured on the milled material from aggregates of different size or concentric layers using a continuous flow mass spectrophotometer consisting of an ANCA SL sample converter attached to a 20-20 IRMS (Europa Scientific, Crewe, UK).

In order to find out the effect of percolation on soil aggregates the soil samples without percolation (control) were separated in the same way as percolated samples (numbers “I-V” represents percolated samples with increasing amounts of lost organic carbon according to Table IV-3).

3.5 Determination of bulk density and tensile strength of aggregates after percolation

The bulk density of air-dried soil aggregates was determined by coating the single aggregates with paraffin and measuring their volume in distilled water.

Tensile strength of single aggregates was measured by crushing tests using a loading frame (Instron 5569, software Merlin). The minimal force applied on an aggregate which caused the breakage was taken as crushing force. For calculation of aggregate tensile strength following equations were used (Dexter and Kroesbergen, 1985):

$$T_s = 0.567 \frac{F}{d^2} \qquad \textit{Eq. VI-1}$$

T_s - tensile strength of the aggregate

F - the applied force at failure

d_a - equivalent diameter of an irregular aggregate defined by

$$d_a = \left[\frac{6 \cdot m}{\Pi \cdot d_B} \right]^{1/3} \qquad \textit{Eq. VI-2}$$

m is the mass of the aggregate and d_B its bulk density.

The equation gives the equivalent diameter of a sphere having the same mass and density as the test aggregates.

3.6 Calculation and statistical analyses

The calculation of the results follows the presumption that soil samples from the same horizon and vegetation are replications and not percolated soil material is taken as a reference for samples after percolation. The calculation of pores size distribution was conducted on five replications from each horizon. The percolation process was conducted on five replications but due to the differences in hydraulic conductivity samples had to be calculated separately. The statistical calculation of the data was based on the arithmetic means and standard error of the mean (+/-) considering the management system, soil depth and size of aggregates. The comparisons confidence tests for organic carbon content, bulk density and tensile strength of aggregates were conducted using one-way (no blocking) ANOVA statistical analyses with Tukey’s multivariate test at the significance level of 95%.

4 Results

4.1 General description of analyzed soil

The general description of the analyzed soil is presented in Table VI-1. The texture of both soil types Anthrosol and Luvisol is silty loam with about 70% silt, 20% clay and 10% sand with the clay enrichment in the Bt horizon of the Luvisol. The pH values are slightly acidic (pH~6). The organic carbon, nitrogen content as well as C/N ratio have higher values in the Ap horizons and decrease in subsoil with an increase of organic carbon in conservative tilled wheat soil at the depth of 3-7cm.

Table VI—1 *General description of analyzed soil under conventional (CT) and conservative (CnT) tillage*

vegetation	soil type	soil tillage	horizon	soil depth	Texture			C_{org}	N	C/N	pH
					Sand	Silt	Clay				($CaCl_2$)
				[cm]	----------------		[g/kg]	----------------		[-]	[-]
Maize (since 1979)	Hortic Anthrosol	CT	Ap1	3-7	100	679	221	13.2	1.49	8.9	6.4
				11-15				13.4	1.51	8.9	
			Ap2	31-35	99	691	210	12.1	1.37	8.9	6.2
			Sw M	39-43	66	721	214	4.5	0.72	6.2	6.0
Wheat (since 1969)	Haplic Luvisol	CnT since 1998	Ap1	3-7	94	678	229	13.9	1.46	9.5	6.4
				11-15				12.3	1.35	9.1	
			rAp	31-35	88	655	257	7.2	0.88	8.1	6.3
			Bt	39-43	73	649	278	3.8	0.50	7.7	6.2

Water retention curves (Figure VI-2) as well as the derived pore size distribution (Table VI-2) from both soils under conventional (maize) and conservation (wheat) tillage show high differences. The Ap horizon under conventional tillage the total porosity is 10% higher than the soil from following horizons in contrast to small differences between the three horizons in the conservation tilled soil. Together with higher total porosity, the percentage of macropores in Ap horizons is also higher and finer pores lower than in the subsoil. In conservation tilled soil the differences in pore size distribution between soil horizons is less pronounced, however at a depth 3-7cm the percentage of macro- and mesopores is higher and fine pores – lower than in deeper horizons. At 11-15 cm and 31-35 cm depth the lowest total porosity with low content of macro- and mesopores was found.

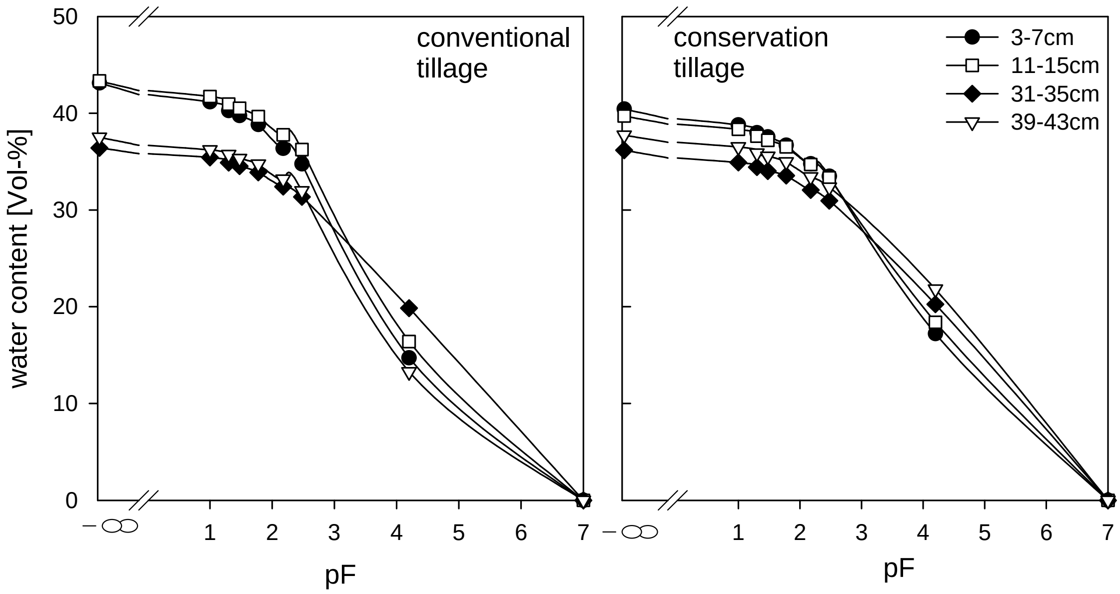

Figure VI-2 *Water retention curves of soil from conventional tillage (maize) and conservation tillage (wheat) from different soil depths*

Table VI—2 *Pore size distribution determined from the pF curves under conventional (CT) and conservation (CnT) tillage*

tillage system	horizon	soil depth (cm)	dB [g/cm^3]		total porosity	coarse macropores > 50 µm	narrow macropores 50-10 µm	mesopores 10-0.2 µm	fine pores <0.2µm
			mean	st dev	------------------------		[Vol%]	------------------------	
CT	Ap1	3-7	1.30	0.04	50.5	11.7	4.1	20.0	14.7
		11-15	1.39	0.05	47.1	7.4	3.4	19.8	16.4
	Ap2	31-35	1.57	0.04	40.4	6.5	2.5	11.5	19.9
	Sw-M	39-43	1.50	0.06	42.9	8.2	2.8	18.7	13.3
CnT	Ap	3-7	1.40	0.09	46.7	10.0	3.2	16.3	17.2
		11-15	1.51	0.04	42.7	6.2	3.2	14.9	18.4
	rAp	31-35	1.53	0.09	42.0	8.5	2.6	10.7	20.3
	Bt	39-43	1.46	0.06	44.5	9.6	2.6	10.5	21.8

4.2 Organic carbon content in percolated solution

The percolation of undisturbed soil samples with water and pyrophosphate solution resulted in leaching of soil organic carbon. The results from the measurement of carbon concentration in the eluate as a function of time (Figure VI-3) show the highest concentration of organic carbon at the beginning of the percolation process and decrease with time to a certain minimum level of about 15 mg/l (see also Appendix).

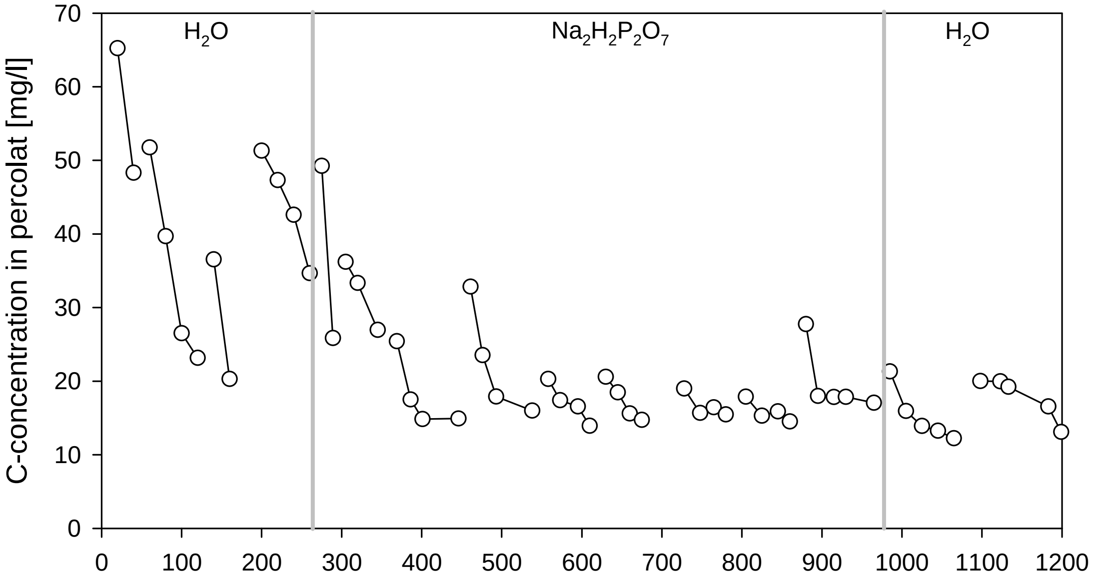

Figure VI-3 *An example of changes in carbon concentration in the eluate during percolation process with several interruption periods*

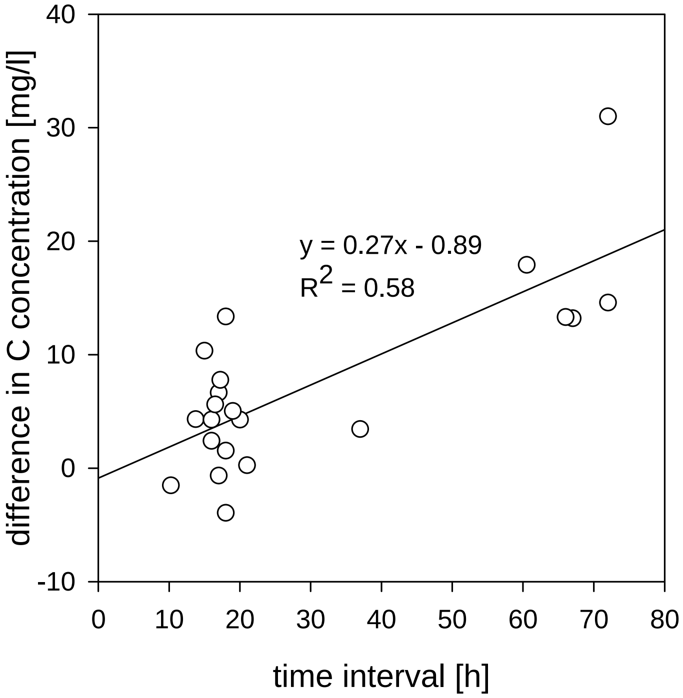

Figure VI-4 *Difference in C concentration in eluat before and after interruption of percolation process*

Interruption of percolation process caused an increase of carbon concentration at the beginning of the next percolating interval and decreases again when the process is continued. The duration of the interruption has an effect on the concentration of organic carbon (Figure VI-4); the longer the interruption time the higher is the increase in concentration.

Considering the equal duration of the percolation process the amount of the total percolated water and pyrophosphate solution was relatively higher in conventional tilled soil than in the conservation tilled ones which also reflected in lower cumulative mass of organic carbon leached off from the soil (Figure VI-5). Similar but less pronounced was the variation between replicates: each soil sample presented an individual amount of percolated solution and mass of lost organic carbon. In soil from conservation tillage four samples have shown similar amount of percolated solution and organic carbon lost with an exception of one sample. In soil samples from conventional tillage even that the volume of percolated solution in each replicate was different the total amount of lost organic carbon was similar. Figure VI-6 which presents the relation between the concentration of organic carbon in the solution and the hydraulic conductivity shows that a retarded flux results in more organic carbon leached off from the soil as compared to a faster flow.

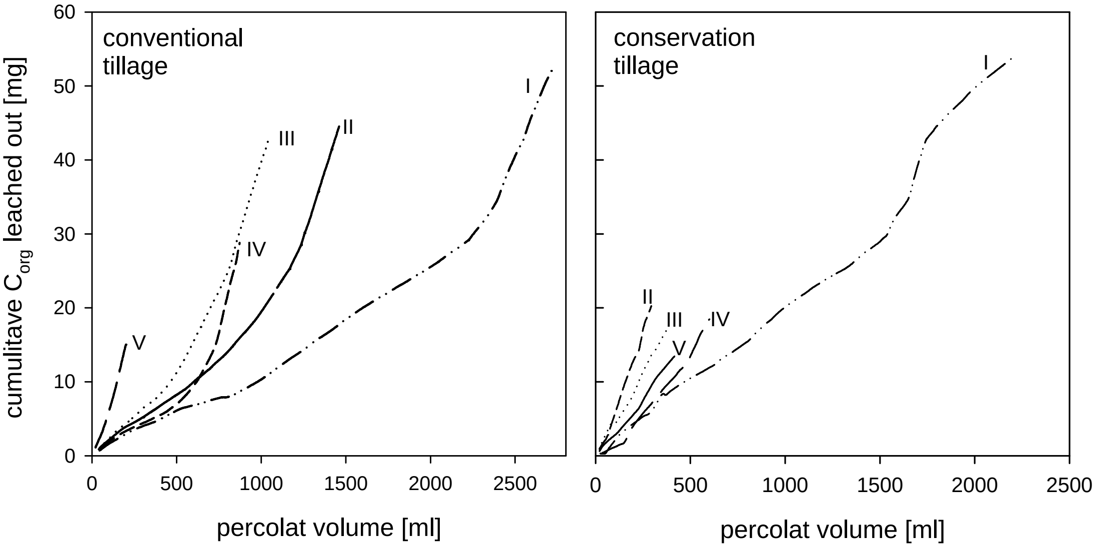

Figure VI-5 *Cumulative total organic carbon (TOC) measured in the percolation solution during the complete percolation process*

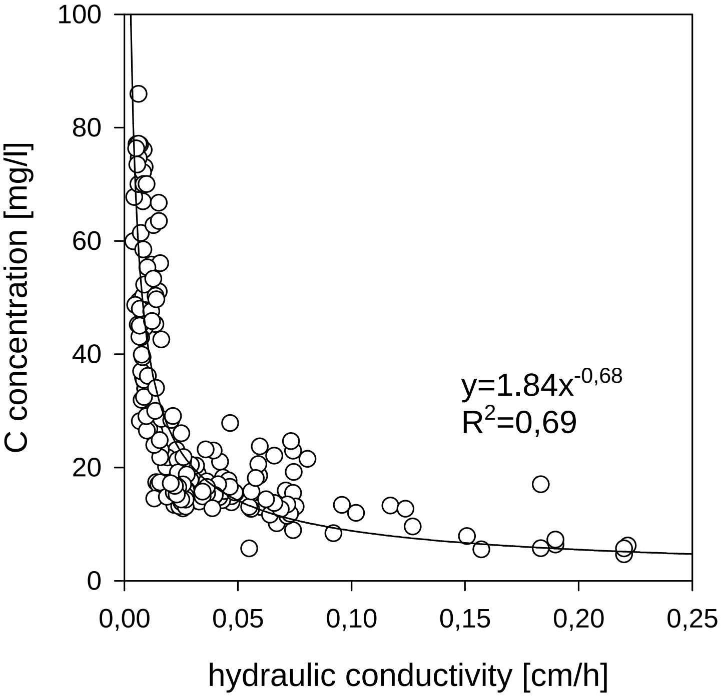

Figure VI-6 *Dependence of carbon concentration in eluat from hydraulic conductivity*

Table VI—3 *Volume of percolated solution and organic carbon lost in soil samples from 3-7cm depth under maize and wheat vegetation*

tillage system	sample nr	zylinder nr	percolated volume [dm^3]	C-lost [g]	tillage system	sample nr	zylinder nr	percolated volume [dm^3]	C-lost [g]
CT	I	R11	0.213	0.016	CnT	I	R51	0.416	0.013
	II	R34	0.873	0.029		II	R53	0.389	0.018
	III	R8	1.049	0.043		III	R55	0.601	0.018
	IV	R6	1.46	0.045		IV	R77	0.295	0.020
	V	R36	2.861	0.054		V	R81	2.194	0.054

4.3 Changes in organic carbon distribution after percolation

Percolation of soil with water and pyrophosphate solution caused some of organic matter to be leached out (Table VI-3). Comparison of the distribution of C_{org} in “control” soil and soil after percolation showed a reduction of organic carbon content in the latter, especially in aggregates from those samples where more volume of eluate was percolated (Figure VI-7).

In the “control” samples the organic carbon content was higher in smaller aggregates; a similar tendency was found only in few samples after percolation with very small amounts of organic carbon leached out. In contrast, in those samples in which higher amounts of C_{org} were lost the difference in C_{org} content between aggregates from different size classes was very slight.

Percolation of soil from conventional tillage resulted in very slight decrease of C_{org} in aggregates from 12-8mm size class (Figure VI-7), but high decrease in smaller aggregates. The highest differences were found in the aggregates <2mm, where “control” and “I” aggregates show significantly higher values than “IV” and “V”. In soil aggregates from conservation tillage the content of organic carbon decreased in all size classes after percolation except “III” soil sample.

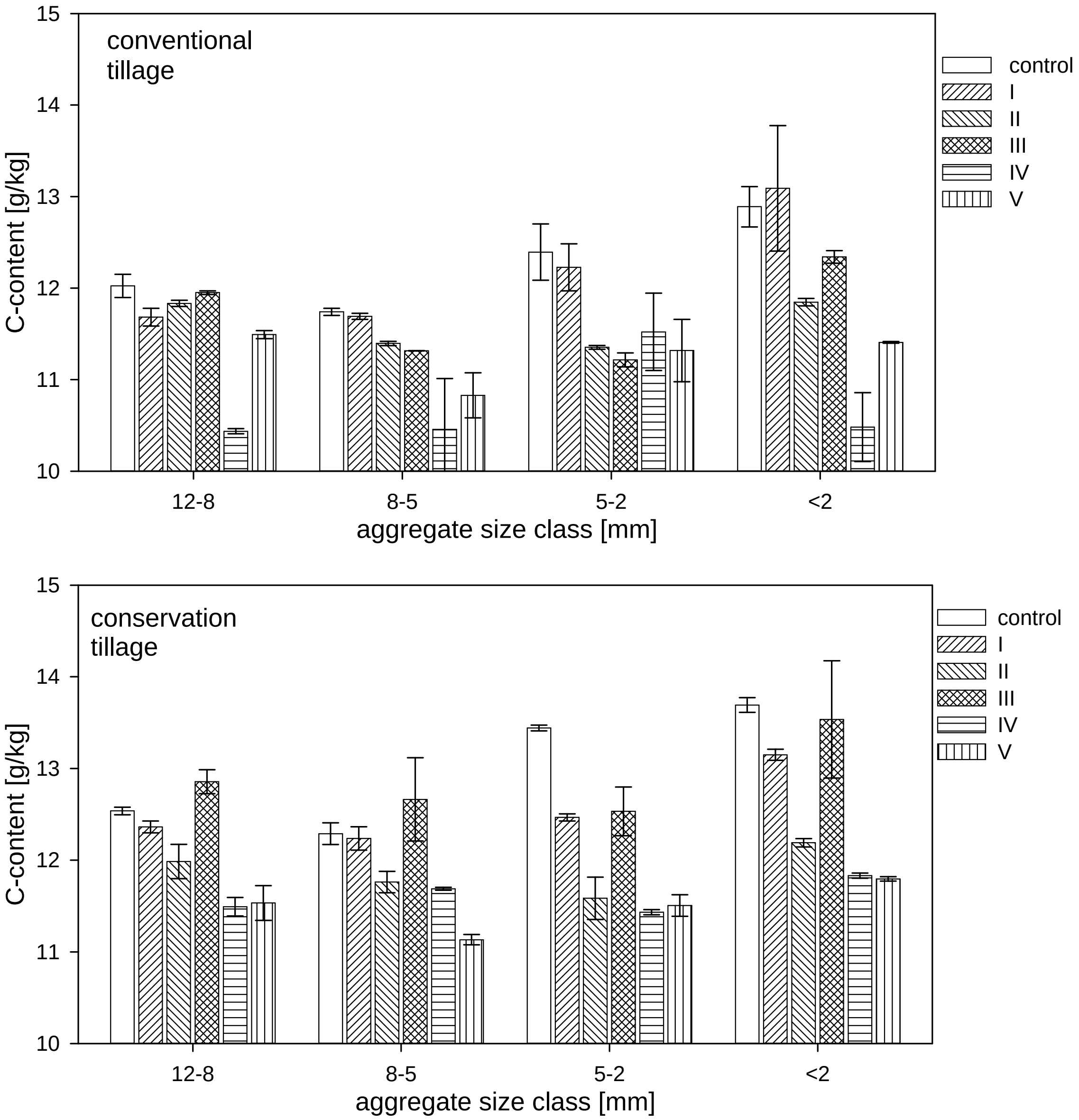

Figure VI-7 *Content of organic carbon (C-content) in soil aggregates from not percolated soil (control) and percolated soil with different amount of lost organic carbon; a) conventional tilled soil, b) conservation tilled soil*
I-V refer to sample no (see Table VI-3);

The analyses of organic carbon content in different aggregate layers showed very high variability between the exterior, transitional and the interior regions but the differences are insignificant (Figure VI-8). In some samples a higher content of organic carbon in the interior region can be seen, but in other ones the tendency is opposite. In addition, higher variations among aggregate regions expose the aggregates from the conventional tilled soil in contrast to one from conservation tilled, where the values are more similar.

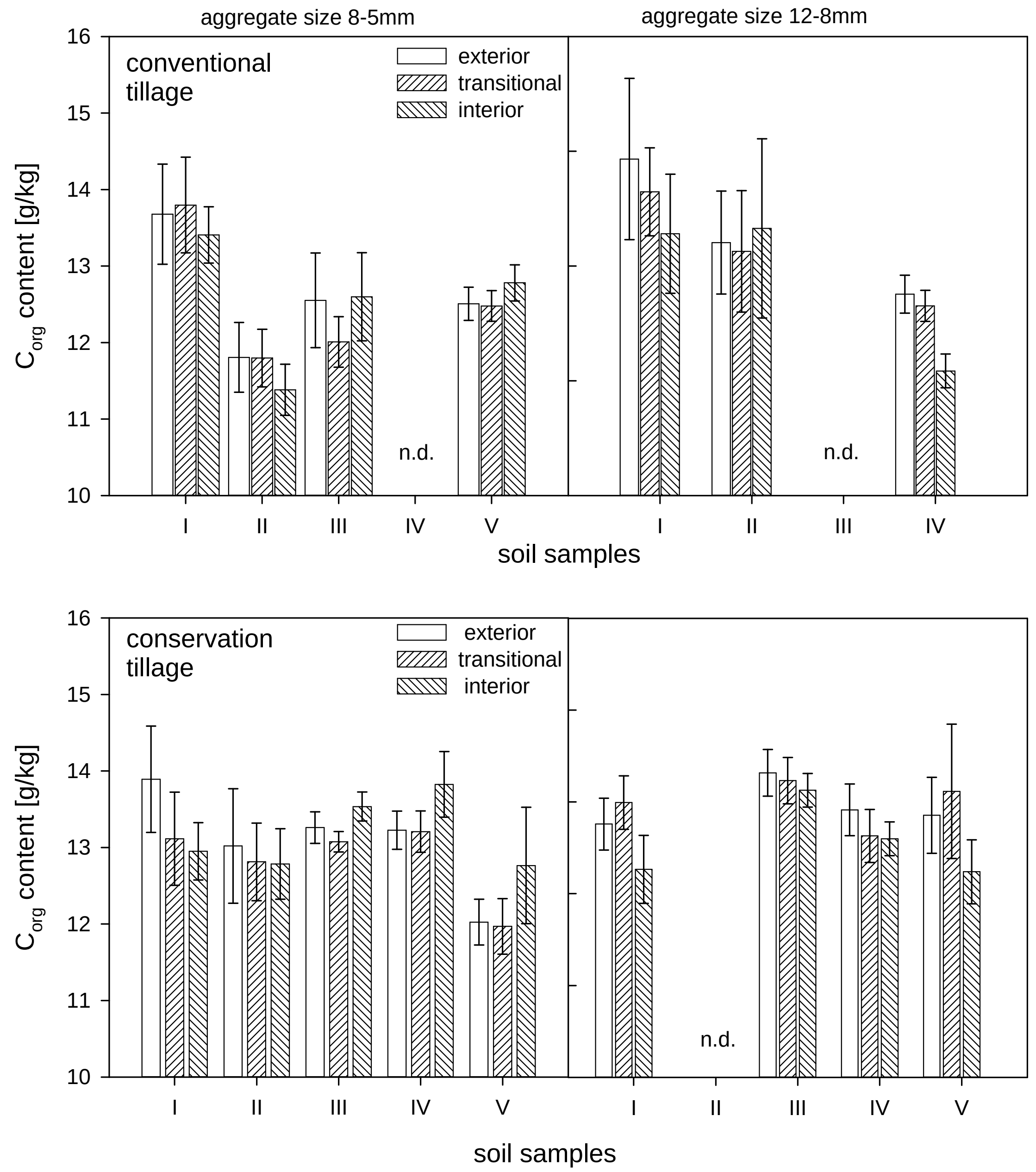

Figure VI-8 *Content of organic carbon (C-content) in soil aggregates from different aggregate regions in percolated soil with different amount of lost organic carbon; a) conventional tillage, b) conservation tillage*
I-V refer to sample no (see Table VI-3);

4.4 Changes in mechanical properties after percolation processes

The measurements of the mechanical properties of soil aggregates after percolation showed an increase of aggregate density from conventional tilled soil and insignificant changes in aggregates from conservation tilled soil. The tensile strength of aggregates show no significant differences between two size classes; only the “control” of wheat soil is significantly higher in 8-5mm than the aggregates from 12-8mm. Comparing tensile strength (T_s) of the control soil aggregates and those after percolation it could be seen that with increasing loss of carbon the T_s decreases, but such a tendency is not always statistically significant. In aggregates from conservation tillage the lost of organic carbon does not significantly change the T_s of 12-8mm aggregates and in aggregates from 8-5mm the difference is significant only between aggregates from “control” and “III” samples.

Table VI—4 *Bulk density and tensile strength of soil aggregates without and after percolation process with different amount of carbon lost*
abc letters identify significant differences between samples (p=0.05)

tillage system	sample nr	C-lost	bulk density [g/cm^3]				tensile strength [kPa]					
			12-8mm		8-5mm		12-8mm			8-5mm		
		[mg]	mean	st.err	mean	st.err	mean	st.err		mean	st.err	
CT	control	0.000	1.55	0.01	1.57	0.02	170	10	c	120	15	ab
	I	0.016	1.71	0.03	1.84	0.04	126	8	cb	189	26	b
	II	0.029	1.71	0.01	1.72	0.02	123	13	cb	129	15	ab
	III	0.043	1.67	0.02	1.96	0.12	83	13	ab	87	15	a
	IV	0.045	1.88	0.11	1.86	0.15	111	16	b	116	21	ab
	V	0.054	1.63	0.04	1.81	0.07	63	6	a	90	31	a
CnT	control	0.000	1.72	0.06	1.71	0.03	170	15	a	241	22	b
	I	0.013	1.76	0.02	1.86	0.04	229	23	a	166	25	ab
	II	0.018	1.74	0.02	1.74	0.01	234	34	a	195	24	ab
	III	0.018	1.84	0.05	1.80	0.02	188	22	a	140	10	a
	IV	0.020	1.80	0.03	1.78	0.04	181	9	a	178	21	ab
	V	0.054	1.79	0.04	1.92	0.06	173	9	a	176	17	ab

5 Discussion

The movement of water and soil solution in soils depends especially on the amount of the macropores (Beven and Germann, 1982; Schjønning and Rasmussen, 1989) and their continuity (Beven and Germann, 1982; White, 1985; Ball *et al.*, 1988). Changes of soil tillage system from conventional to conservation or no-tillage system usually results in reduced porosity of topsoil (Roseberg and McCoy, 1992; Bhattacharyya *et al.*, 2006) and affects the hydraulic conductivity and storage of water.

In analysed soils from different soil tillage systems, there were also some differences in topsoil porosity which influenced the progress of percolation. Higher total porosity of conventional tilled soil with high percentage of coarse pores resulted in higher hydraulic conductivity in comparison with the less porous soil from conservation tillage. Due to lower hydraulic conductivity and smaller amount of macropores the percolation process was much slower and less organic matter was leached off.

Percolation experiments on structured soils may give not only important information about the transport processes in soil but also on elements distribution and their accessibility by analyses of eluate. Taubner (1993) and Hartmann (1999) found differences between eluate from percolation of structured soil and extraction of homogenised material. Taubner (1993) conducted percolation experiments on soil samples with different soil structure and found that the differences in solution composition between the intraaggregate pore system and the bulk soil (mostly interaggregate) pore system were higher in stronger structured subangular blocks and in blocks than those with the weaker aggregated prisms. In addition Hartmann *et al*. (1998) found that the amount of available cations in structured soils is much lower than in homogenised material. Youngs and Leeds-Harrison (1990) described that when saturated macropores surround unsaturated aggregates, solutes will be transported by diffusion into the aggregates depending on the concentration gradient.

When the movement of the soil solution is stopped the exchange between fine and coarse pores takes place and causes an increase of organic carbon concentration in the solution.

The analyses of the eluate from percolated soil samples have shown similar tendency. Slower percolation resulted in higher concentration of organic carbon in the solution and the interruption of the process for several hours caused an increase of carbon concentration. Although, even that lower hydraulic conductivity induced higher exchange processes and C concentrations, the total amount of carbon loss was higher in those soil samples where more pyrophosphate solution was percolated.

All studies on percolation focus on the analyses of the extracted solution, but the examination of the remaining soil material may give additional information about accessibility and distribution of organic carbon in different sizes of aggregates as well as within single aggregates. Comparison of organic carbon content between non-percolated and percolated samples can explain in which places the organic matter was more-easily accessible and where it was better protected against leaching.

However, it has to be taken into consideration that the differences in carbon content in different aggregate sizes could also be due to spatial variation in soil samples. Small change in organic carbon content in larger aggregates suggests that in these pores the organic carbon was better protected than in small aggregates. The strong decrease of carbon content was found in aggregates <2 mm where probably most of fresh organic matter not associated with a mineral phase was accumulated. The close association of organic carbon with the mineral particles and aggregates, supposed to provide physical protection for organic matter and has been reported as one of the main mechanisms of carbon sequestration in soils (Oades *et al.*, 1988).

Examination of single aggregates and the distribution of organic carbon in the external, transitional and the internal regions has shown very high variation within aggregates but no significant trend. This suggests that during the percolation the exchange processes in some compartments were stronger than in other ones, but cannot be separated into the exterior and the interior aggregate regions.

Removal of soil organic matter by percolation affected the density and tensile strength of aggregates. Aggregate density increased after percolation which was probably caused not only by organic matter loss but also by the redistribution of clay and silt particles and consolidation of particles. Slight changes in tensile strength of macroaggregates after percolation confirm the small effect of C_{org} leaching from large aggregates, but also suggest that the tensile strength of air dry aggregates does not depend on the content of organic matter in the aggregates.

6 Conclusions

The chemical composition of percolated soil solutions gives information about hydraulic properties of structured soils and also helps to characterize the accessibility and distribution of organic matter. The changes in organic carbon concentration in percolated solution from soil samples from conventional and conservation tillage suggest that in conventionally-tilled soil where more coarse pores are present the accessibility of organic carbon for microorganisms and leaching into deeper horizons is higher than in conservation-tilled soil. The lower amounts of percolate volume also resulted in less organic carbon removed from the soil. The analyses of the organic carbon distribution in soil aggregates after the process of percolation suggest that the organic carbon associated with macroaggregates is better protected against mineralization and leaching than organic carbon not associated with the mineral phase or present in small aggregates. Slight changes in tensile strength of macroaggregates after percolation confirm the small effect of C_{org} leaching from large aggregates, and also suggest that the tensile strength of air-dry aggregates does not depend on the content of organic matter in the aggregates.

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VII Determination of organic carbon distribution in single aggregates using natural ^{13}C as a tracer

1 Abstract

Soil has a high capacity to sequestrate carbon in form of soil organic matter and well developed soil structure also contributes to protection of organic carbon against mineralization. However, the association of the fresh and old organic matter into soil matrix and soil aggregates is still not fully understood. The aim of the study was to identify organic carbon distribution in aggregates of different sizes and their concentric layers and to find out where the fresh organic matter is mostly accumulated. Soil aggregates were separated by dry sieving into different size classes. The aggregates of two size classes were thereafter also separated into the exterior, transitional and interior regions. In addition the maize plants (C_4) were grown on soil from previous wheat (C_3) vegetation and wheat plants on soil from previous C_4 vegetation under greenhouse conditions for six weeks. Using δ^{13}C isotopic signal the fresh associated carbon was determined in soil aggregates. The results have shown that even such a short period of time as six weeks can result in accumulation of about 12% of fresh carbon in smaller 8-5mm aggregates and about 7% in the larger 12-8mm ones. No significant trend was found in accumulation of organic carbon in the exterior aggregate regions in original aggregates as well as in those after greenhouse experiment. The higher contents of organic carbon and less negative isotopic signals of δ^{13}C was found only in aggregates <2mm in the original soil.

Keywords: organic carbon, natural δ^{13}C tracer, aggregates, C_4 and C_3 vegetation

2 Introduction

Soil has a high potential to sequestrate the organic carbon (C_{org}) in form of soil organic matter and to reduce or delay its migration to the atmosphere as CO_2. Soil organic matter (SOM) is defined as all dead material in or lying on the soil that contains carbon (Sollins *et al.*, 1996) and its mineralization is controlled by microorganisms and enzymes activity (Adu and Oades, 1978). Christensen (1996) proposed three main mechanisms of SOM stabilization: chemical, physical and biochemical protection. Chemical stabilisation is the result of the chemical or physicochemical binding between SOM and soil minerals; a good relationship exists between SOM fractions and clay or silt content (Hassink, 1997). Biochemical stabilization or protection of SOM occurs due to the complex chemical composition of the organic materials (Six *et al.*, 2002). The physical protection indicates a positive influence of aggregation on the accumulation of SOM (Tisdall and Oades, 1982; Jastrow *et al.*, 1996; Six *et al.*, 2000). It has been also proposed by Oades et al. (1988) that the sequestration of carbon in soil is controlled by chemical transformations of the carbon and its close association with the mineral phase, which provides physical protection. Six *et al.* (2002) underlined the importance of soil structure for the stabilization of SOM while in soil aggregates exist physical barriers between microbes and enzymes and their substrates which control the interaction and consequently microbial turnover (Elliott and Coleman, 1988). Positive influence of aggregation on the accumulation of SOM is reported by many studies (Cambardella and Elliott, 1993; Golchin, 1994; Puget *et al.*, 1995; Jastrow *et al.*, 1996; Angers and Chenu, 1997; Six *et al.*, 1998). Destroying soil structure brings negative effects on soil organic matter protection. One of destructive forces for soil structure is cultivation which causes a release of C by breaking up the aggregate structures, the C-rich macroaggregates are lost; the amount of C-depleted microaggregates increase which results in an increase in the availability of carbon (Elliott, 1986; Six *et al.*, 2000). The highest effects of cultivation is observed on macroaggregates, which decrease in C and N contents as well as in water stability, whereas microaggregates remain mostly unaffected (Oades, 1984; Elliott, 1986; Cambardella and Elliott, 1993). SOM in microaggregates is better protected against mineralization in cultivated soils while they are not so sensitive on management type as macroaggregates (Elliott, 1986; Beare *et al.*, 1994; Balesdent *et al.*, 2000). Jastrow (1996) show that nearly 90% of SOM is located within soil aggregates, in addition particulate organic matter (POM) in cultivated soils is located mostly within soil aggregates and free POM in the interaggregate pore space of the soil (Puget et al., 1996 cited by (Angers and Chenu, 1997).

Following the assumption of Augustin *et al.* (1995) that in soil aggregates exist different gradients it has been also investigated if organic matter distribution in soil aggregates also follow such role. Santos et al. (1997), Ellerbrock and Gerke (2004) and Park and Smucker (2005b) reported that in some soils higher contents of organic carbon are present in the exterior regions in comparison to the aggregate interiors. The higher abundance of microbes in the outer part of the aggregates (Hattori, 1988) means that the essential part of SOM in the center of the aggregates is not easily accessible substrate for microbes in aggregates.

Not only the distribution of total organic carbon but also its age and its origin are important to be understood by examination of the carbon sequestration. One of the effective methods to trace soil organic carbon inputs is the natural stable isotope composition ^{12}C and ^{13}C (Balesdent *et al.*, 1987). Carbon derived from a C_4 plant can be distinguished from that of C_3 plants by its isotopic composition (Smith and Epstein, 1971). The cropping of maize, a C_4 plant, on soils with previously C_3 vegetation provides a natural label of SOM, which can distinguish young SOM derived from the crop and older SOM from the previous C_3 crops (Puget *et al.*, 1995). Plants with the C_3 pathway of photosynthesis (almost all temperate species and trees) have $\delta^{13}C$ values ranging from approximately -32 ‰ PDB to -22 ‰ PDB, with a mean of -27 ‰ PDB and C_4 plants (most of tropical species) have $\delta^{13}C$ values ranging from approximately -17 ‰ PDB to -9 ‰ PDB, with a mean of -13 ‰ PDB (O'Leary, 1988; Boutton, 1991). PDB is the reference material used for isotopic determination with $\delta^{13}C = 0‰$.

Using ^{13}C abundance Puget *et al*. (1995) qualified the carbon derived from maize in silty soils after 23 and 6 years of maize cultivation and found that young carbon composed of decomposing plant residues and mineral-associated carbon tends to accumulate in larger aggregates acting as a binding agent. Balesdent *et al*. (1990) reported a 20% enrichment of C from maize in the Ap horizon after 17 years of maize cropping and Flessa *et al.* (2000) found 15% of maize derived carbon after 37 years of continuous maize cropping in sandy soils. Horn and Smucker (2005) suggested that due to the plant roots accumulation of C on surfaces of soil aggregates can be identified for periods as short as 6 weeks under greenhouse conditions, or 20 months in rotational field studies. The exterior, transitional and the interior aggregate material can be separated from each other using soil aggregate erosion (SAE) which mechanically remove the outer concentric layer from the aggregate (Santos *et al.*, 1997).

The aim of this study was to find out how organic carbon is distributed in aggregates of different sizes, as well as in different aggregate concentric layers of a silty loam Luvisol and Anthrosol from Ap horizon and to find out if after six weeks period of maize growth in soil previously grown with C_3 vegetation the accumulation of the fresh organic matter can be detected.

3 Material and methods

3.1 Soil material

Disturbed soil samples were collected in autumn 2002 from the experimental field of Rotthalmünster/Southern Germany from a silty loam Anthrosol and Luvisol at two sites with different cultivation systems and vegetation; conventionally tilled soil with maize monoculture since 1979 (previous cultivation was probably grassland until 1970, subsequently spring wheat and winter wheat) and continuous wheat plot since 1969 (Triticum aestivum L.) with NPK-fertilization on former grassland. Since 1998 the cultivation of wheat was changed into conservation tillage applying only chiselling after harvest. The soil samples after transportation were stored under cooled conditions (5° C) in order to minimize microbial transformations until further analysis could be carried out. General description of analyzed soil is presented in the Table VII-1. The texture of the soils is silty loam with 65-72% silt, 22-28% clay and 10-7% clay. In Bt horizon of haplic Luvisol the enrichment of clay content is detected together with the depletion of organic carbon.

***Table VII—1** General description of analysed soil (CT is the conventional soil tillage, CnT is the conservation tillage)*

vegetation	soil classification	soil tillage	soil depth (cm)	horizon	Texture (%)			pH ($CaCl_2$)	C_{org} (%)	N (%)	C/N
					Sand	Silt	Clay				
Maize (since 1979)	Hortic Anthrosol	CT	0-15	Ap1	10	68	22	6,4	1,4	0,14	10,1
			15-35	Ap2	10	69	21	6,2	1,3	0,14	9,6
			35-45	Sw M	7	72	21	6,0	0,6	0,08	7,9
Wheat (since 1969)	Haplic Luvisol	CnT since 1998	0-20	Ap1	9	68	23	6,4	1,4	0,15	9,1
			20-32	rAp	9	66	26	6,3	1,1	0,13	8,5
			32-45	Bt	7	65	28	6,2	0,5	0,07	7,5

3.2 Preparation of soil material

Soil aggregates from maize and wheat plots from three horizons (Ap1, Ap2, Sw-M of maize soil; Ap, rAp, Bt of wheat soil) were separated by manually breaking the bigger blocks along planes of weakness in field moist conditions. After drying at 40°C the aggregates were gently sieved into the following four size fractions: 12-8mm; 8-5mm; 5-2mm; <2mm diameter and the aggregate size distribution determined.

Soil aggregates from Ap1 (maize) and Ap (wheat) were filled in cylinders (diameter d=12cm and height h=15cm) closed by a net at the bottom. The proportion of aggregate size classes was the same as in the original soil, but due to loose packing of soil aggregates the final soil density in the cylinders was lower (1.4 ±0.1 g/cm^3) than bulk density of the undisturbed soil (0.96 ±0.03 g/cm^3). Eight cylinders were filled with aggregates and thereafter watered from the bottom. In four cylinders of the former wheat soil maize seed were planted and in other four cylinders with maize soil wheat seed was planted. The remaining eight cylinders were left without any plants. Filled soil cylinders were placed in the greenhouse, watered and the plant growth controlled. After six weeks, the plants were harvested and the soil aggregates removed from the cylinders. The upper layer of 0-2 cm and the lowest part from 12-15 cm were discarded and upper and lower parts of soil sample 2-6 cm and 7-12 cm were separated. For further analyses the aggregates were dried, roots were removed from the aggregate surface with forceps and the aggregates of two size classes 12-8mm and 8-5mm were chosen for further analyses. The aggregates from different soil samples were collected taking care to choose those aggregates where no roots penetrated the center of the aggregate. After drying at 40°C the aggregates were separated into different regions exterior, transitional and the interior region using SAE chambers.

3.3 Separation of aggregate layers

The separation of the aggregate regions was conducted using the soil aggregate erosion method (SAE) (Figure VII-1) (Park and Smucker, 2005b). Single air-dried aggregates, 12-8mm and 8-5 mm in diameter, were placed in each SAE chamber and rotated in the rotary shaker (IKA KS 260 control) at 400 rpm to abrade the soil material from aggregate surface. The abraded soil fragments were separated by a screen and collected for further analyses.

Aggregates were separated into different regions from the surface to the core of the aggregate (Figure VII-2). The exterior aggregate region corresponded to 50% of the abraded mass of the aggregate, 25-50% is the transitional region and the final 25% equals the aggregate interior.

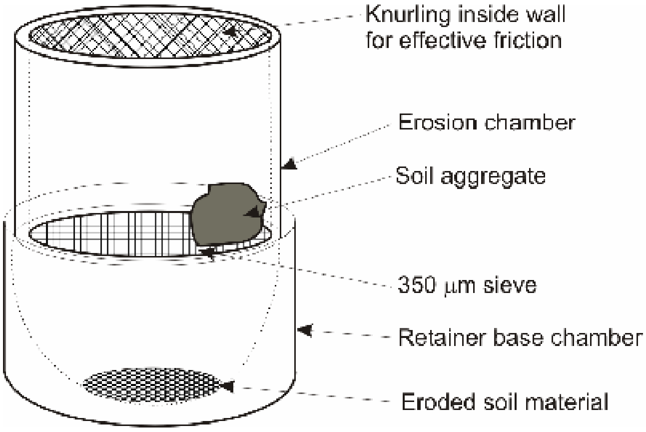

Figure VII-1 *Schematic graph of soil aggregate erosion chamber (SAE)*

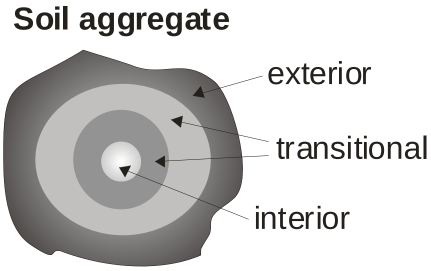

Figure VII-2 *Concentric layers of soil aggregate: exterior, transitional and interior.*

3.4 Measurements of organic carbon and ^{13}C isotope in soil

The organic carbon content and the ^{13}C isotope determination was conducted on soil material from each aggregate layer with help of an elemental analysis mass spectrometer unit (type 1108, Carlo Erba, Milan, Italy; Delta C, Thermo-Finnigan, Bremen, Germany).

3.5 Calculation and statistical analyses

The ^{13}C/^{12}C ratio denoted as δ^{13}C in ‰ PDB was calculated using following equation (Eq. VII-1):

$$\delta^{13}C\ (‰\ PDB) = [(^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{reference})-1] \cdot 1000 \qquad \text{Eq. VII-1}$$

where the reference material has δ^{13}C = 0 ‰ PDB.

The proportion of carbon derived from maize (*f*) in samples was calculated according to Balesdent and Mariotti (1996) (Eq. VII-2):

$$f = \frac{\delta_{sample} - \delta_{reference}}{\delta_{maize} - \delta_{reference.plant}} \qquad \text{Eq. VII-2}$$

where δ_{sample} is the measured δ^{13}C of the sample, $\delta_{reference}$ is δ^{13}C of reference sample from C_3 reference soil, and δ_{maize} and $\delta_{reference.plant}$ is the δ^{13}C values of maize and reference plant-wheat residuals (roots) collected on the experimental plots.

The δ^{13}C value was -26.8 ± 0.1‰ PDB for wheat and -12.7 ± 0.2‰ PDB for maize resulting in a difference of 14.1‰ PDB (John, 2003).

The statistical significance confidence comparisons between aggregate size classes and aggregate concentric layers were conducted applying one-way (no blocking) ANOVA analyses using Tukey's multivariance test at a significance level of 95%.

4 Results

4.1 Organic carbon and $\delta^{13}C$ distribution in aggregates in soil

Distribution of organic carbon in soil aggregates from maize and wheat soil have shown not only a difference between horizons (enrichment in the topsoil horizons, and decrease in the subsoil), but also between aggregate size classes

(Table VII-2). The highest C_{org} contents were detected in the aggregate size class <2mm and decreased in larger aggregates. The highest variation was found in Ap horizons and smaller differences were determined in deeper horizons where the total content of organic carbon was generally lower. The values of $\delta^{13}C$ in maize aggregates were lower in larger aggregates and decreased with aggregate size. Such increase was the most pronounced in Sw-M horizon where the value increased from -27.7‰ in aggregates from size class 12-8mm to -23.3‰ in aggregates <2mm. In wheat soil the $\delta^{13}C$ values did not significantly vary between all horizons and aggregate size classes.

Table VII—2 *C_{org} content and $\delta^{13}C$ values for aggregates of different size classes from different horizons of the maize and wheat soil.*
The standard errors are in the brackets. abc identify significant difference between aggregate size class from the same horizon (p=0.05)

	aggregate size class [mm]	Ap1		Ap2		Sw-M	
		C_{org} content	$\delta^{13}C$	C_{org} content	$\delta^{13}C$	C_{org} content	$\delta^{13}C$
maize	12-8	1,29 (0.13) a	-24,22 (0.67) a	1,50 (0.13) bc	-23,18 (0.94) ab	0,67 (0.05) a	-27,70 (0.59) a
	8-5	1,34 (0.13) ab	-24,45 (0.54) a	1,39 (0.07) ab	-23,88 (0.86) a	0,58 (0.12) a	-27,74 (0.53) a
	5-2	1,29 (0.14) a	n.d. -	1,19 (0.1) a	n.d. -	0,98 (0.1) b	n.d. -
	<2	1,55 (0.18) b	-21,51 (1.34) b	1,64 (0.27) c	-22,18 (1.39) b	1,00 (0.11) b	-23,28 (0.59) b

	aggregate size class [mm]	Ap		rAp		Bt	
		C_{org} content	$\delta^{13}C$	C_{org} content	$\delta^{13}C$	C_{org} content	$\delta^{13}C$
wheat	12-8	1,20 (0.07) a	-27,70 (0.41) a	1,04 (0.06) a	-27,14 (0.53) a	0,31 (0.08) a	-27,94 (0.87) a
	8-5	1,24 (0.13) a	-28,90 (0.84) b	1,15 (0.13) a	-27,17 (0.83) a	0,31 (0.1) a	-28,65 (0.93) a
	5-2	1,18 (0.1) a	n.d. -	1,04 (0.1) a	-27,58 (0.51) a	0,43 (0.08) a	n.d. -
	<2	1,28 (0.08) a	-27,09 (0.32) a	1,07 (0.1) a	-27,88 (0.15) a	0,45 (0.04) a	-27,01 (0.7) a

The organic carbon distribution within single aggregates from each horizon and aggregate size class slightly differed between exterior, transitional and interior regions of aggregates (Figure VII-3). In some aggregates a slight tendency of higher carbon content in the aggregate exterior than in the aggregate interior was detected, however such difference was statistically insignificant. As it was also true for the organic carbon content there was no statistically significant difference in $\delta^{13}C$ values between aggregate layers.

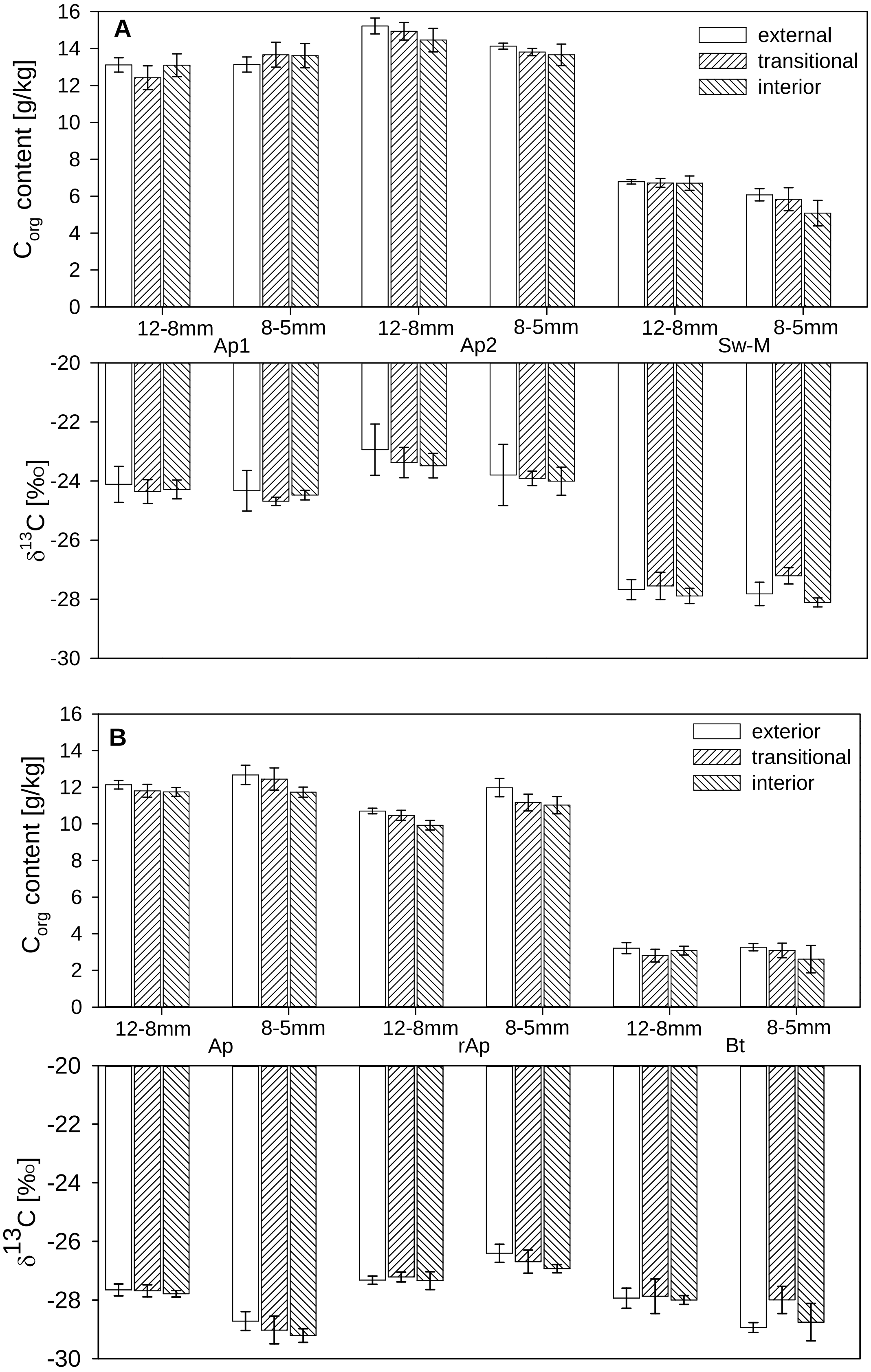

***Figure VII-3** C_{org} content and δ^{13}C in soil aggregates from exterior, transitional and interior layers in two aggregate size-classes from different horizons A) in maize soil; B) in wheat soil*

***Table VII—3** Maize derived carbon in soil aggregates from different soil horizons and aggregate layers.*
+/- identify standard error (n=5). Statistical differences are only between horizons (p=0.05)

aggregate size	aggregate layer	Ap1		Ap2		Sw-M	
		mean	+/-	mean	+/-	mean	+/-
12-8	exterior	0.28	0.014	0.36	0.028	0.02	0.009
	transitional	0.26	0.029	0.33	0.036	0.05	0.035
	interior	0.26	0.023	0.32	0.029	0.02	0.013
8-5	exterior	0.26	0.015	0.30	0.029	0.02	0.009
	transitional	0.23	0.010	0.29	0.015	0.06	0.019
	interior	0.25	0.012	0.28	0.030	0.01	0.005

4.2 Organic carbon and δ^{13}C distribution in soil aggregates after growing maize plants on wheat soil and wheat plants on maize soil

The growth of maize plants on wheat soil and wheat plants on maize soil for six weeks resulted in a slight increase of organic carbon content in soil aggregates. In soil where wheat plants were grown on maize soil (Figure VII-4a) the differences between the exterior and the interior of aggregates were higher in comparison to the original soil (Figure VII -3A) and the δ^{13}C values were lower in the interior region of aggregate. Neither between different aggregate size class (12-8; 8-5mm) nor in upper (2-6cm) and lower (7-12cm) part of the cylinder no significant difference in organic carbon distribution were found. In wheat soil aggregates where maize plants were grown (Figure VII-4B) the variation in carbon content between the exterior and the interior layer was much lower in comparison to the maize soil and also differences in δ^{13}C values between aggregate layers were not significantly different. The characteristic was although that the δ^{13}C values of the soil were significantly lower in comparison to the original soil. The decrease of δ^{13}C value suggested the enrichment of maize plant into organic carbon. The percentage amount of maize derived carbon into soil aggregates were presented in the Table VII-4 and shows that ~7% of organic carbon in larger aggregates was derived from maize independent on aggregate layer, while in 8-5mm aggregate size-class the percentage of maize derived carbon was about 12% in the exterior region and was significantly higher (p=0.05) in interior regions.

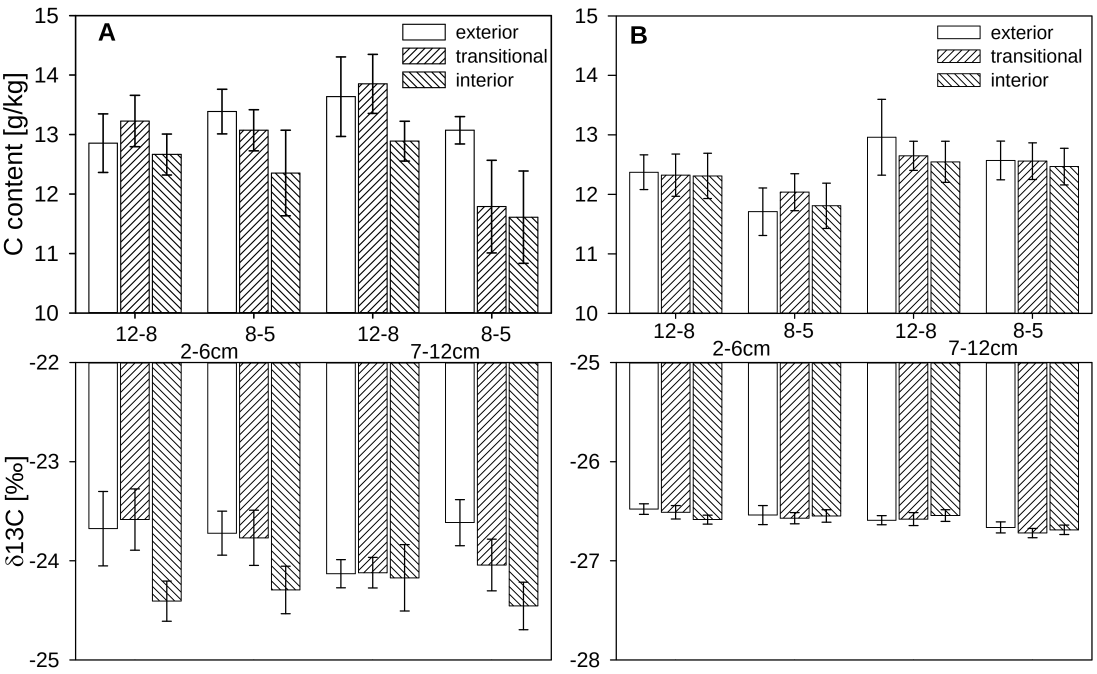

Figure VII-4 *C_{org} content and δ^{13}C identification for A) maize soil with wheat plants grown; B) wheat soil with maize plants grown*

Table VII—4 *Maize derived carbon after six weeks grow on wheat soil in different aggregate layers of two size classes and depth in the cylinder (p=0.05)*

depth [cm]	2-6					7-12				
size class [mm]	12-8		8-5			12-8		8-5		
	mean	+/-	mean		+/-	mean	+/-	mean		+/-
exterior	0,07	0,003	0,12	a	0,005	0,06	0,003	0,11	a	0,003
transitional	0,07	0,004	0,14	b	0,003	0,06	0,004	0,13	b	0,003
interior	0,07	0,002	0,15	b	0,004	0,07	0,003	0,14	c	0,003

5 Discussion

The distribution of the organic carbon in structured soils has been known as very heterogenic and the published data have proofed different patterns of carbon distribution and association with different soil particles as well as aggregates of different sizes. The distribution of organic carbon in aggregated soils has been very often explained with aggregate hierarchy where larger aggregates contain more organic carbon than smaller ones due to their role as a binding agent (Elliott, 1986; Oades and Waters, 1991; Jastrow and Miller, 1998; Six *et al.*, 2000). In addition organic matter (OM) associated with macroaggregates has been reported as more labile than OM in microaggregates (Elliott, 1986; Jastrow *et al.*, 1996), enriched in microbial biomass (Gupta and Germida, 1988) and in particulate organic matter

(Cambardella and Elliott, 1992). Here presented results showed opposite trends; the larger aggregates contained less organic carbon that the smaller ones which was however in agreement with the results of Puget *et al.* (1995) who found such trend in aggregates separated by dry sieving in contrast to wet sieved aggregates. Such results suggested that organic matter which in wet soils was the binding agent for soil particles have lost under dry conditions their stabilising properties and was not only the weakest point.

The higher contents of organic carbon in the <2 mm aggregate fraction suggested that during dry sieving the organic carbon attached to the aggregates in secondary coarse pores was separated from the aggregates and located in the smallest fraction as free organic matter. Also the less negative δ^{13}C values of the smallest aggregate fraction could be a hint to the accumulation of fresh plants debris as not mineral associated organic matter.

The distribution of organic carbon in soil has been reported as affected by soil tillage (Angers and Chenu, 1997; Bossuyt *et al.*, 2002; Deen and Kataki, 2003; Denef *et al.*, 2004). It has been suggested by Elliott (1986) that the organic matter that binds microaggregates into macroaggregates was the primary source of organic matter lost upon cultivation, since the macroaggregates were the most affected during tillage (Tisdall and Oades, 1982). In Rotthalmünster soil from conventional and conservative tillage the main changes in organic carbon distribution were in Ap soil horizons where the soil was cultivated and aggregates were destroyed. In conventional tilled soil due to turnover of soil material the δ^{13}C values were less negative than in the other horizons while most of plants debris stayed in the upper horizons and did not affect the deeper soil. The result corresponds with the findings of Balesdent *et al.* (1987) who also found higher differences in δ^{13}C in upper soil after maize growth than in the subsoil. The changes in δ^{13}C values of smaller aggregates in deeper horizon suggest that the fresh organic matter was transported and associated with smaller aggregates than the larger ones. This idea could be also supported by the results from δ^{13}C values in soil aggregates after six weeks growth of maize plants on wheat soil under greenhouse conditions. Fresh organic carbon with lower isotopic signal was better associated with the smaller aggregate size class than with the larger one.

Augustin *et al.* (1995) found that in structured soils due to the preferential flow of water and soil solution as well as different microbial activity and root distribution gradients could be present in soil aggregates. The higher contents of organic carbon in the exterior region of aggregates was reported (Ellerbrock and Gerke, 2004; Park and Smucker, 2005b) together with higher microbial activity (Hattori, 1988; Horn *et al.*, 1994b). However the analyzed soil aggregates showed only a slight tendency of higher content of organic carbon in the exterior regions in comparison to the aggregate interiors. Additionally there were no significant differences in the isotopic signal of aggregate exteriors and interiors due to relative high standard deviations. Any pattern could be found either because of the high heterogeneity or due to the mixing of the material from the exterior and other aggregate regions during peeling.

The results have also shown that even after such a short period of time of six weeks growing maize plants on soil where before only C_3 vegetation was grown can be identified using $\delta^{13}C$ analyses, which supports the suggestion of Horn and Smucker (2005) that plant root carbon accumulations on surfaces of soil aggregates extracted from rhizosphere soils can be identified under controlled greenhouse conditions in container studies and about 20 months in rotational field studies.

6 Conclusions

The distribution of soil organic carbon and $\delta^{13}C$ analyses in different aggregates size classes have shown that larger aggregates contained less organic carbon than the smaller ones. In addition larger aggregates contained mostly older organic material and in the smaller aggregates higher contents of fresh organic carbon were present. The analyses of organic carbon and $\delta^{13}C$ in aggregate concentric layers did not show any significant differences, but only a slight tendency of higher organic carbon content in some aggregate exterior regions. In addition the experiment of growing maize plants on soil aggregates where previously only C_3 vegetation was planted have proven that even after a short period of six weeks under greenhouse conditions was sufficient to distinguish the fresh organic carbon accumulated in soil aggregates.

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General conclusions

The amount of organic matter in soils depends on the balance between the rate of deposition of plant residuals in or on soil and the rate of mineralization of the residue carbon by soil biota (Baldock and Nelson, 2000). However, not only the amount but also the distribution of organic carbon in particular soil is important for its functionality.

The distribution of organic carbon under different management systems, and its effect on water repellency and the mechanical stability were determined on silty loam Anthrosol and Luvisol soil from Rotthalmünster field experimental site. In addition soil samples were collected from the forest site in Bucken (stagnic Luvisol) and field experimental site in Ritzerau (Cambisol).

Organic carbon allocation depends not only on the type and input of the vegetation but also on the soil use practices. The distribution of the soil organic carbon is related to the structure of the soil and the association to different size of soil aggregates. In the soils from Rotthalmünster higher contents of organic carbon were found in the Ah horizons under pasture, and in agricultural soils in Ap horizons where its content was reduced in the subsoil. The organic carbon distribution also varied between aggregates of different sizes from each horizon. Separation of soil aggregates into different size classes in dry conditions resulted in an increase of organic carbon with decreasing size of the aggregates, reaching the highest content in aggregate size class <2 mm. Not only the content of organic carbon was in this size class the highest, but it contained mostly fresh organic carbon probably not associated with the mineral fraction.

Structured soils due to the preferential flow of soil solution and root distribution in soil aggregates may develop gradients of elements content. The determination of organic carbon distribution and $\delta^{13}C$ signal within soil aggregates have shown only slight tendency of higher C_{org} accumulation in the exterior aggregate region in comparison to the interior regions. Neither the depletion of C_{org} after percolation nor the enrichment of fresh C_{org} in aggregates after greenhouse experiment have shown any significant differences in distribution of carbon within soil aggregates.

In contrast to the soil material from Rotthalmünster the analyses of organic carbon distribution in Sw-Al horizon of stagnic Luvisol have shown reduced contents of C_{org} in the aggregate exteriors in comparison to the interior regions.

In all Rotthalmünster soils soil aggregates the higher amounts of hydrophilic groups were found in the exterior regions of aggregates than in the interior. Small differences between aggregate interior and exterior were also found in chemical elements content distribution; K, Fe and Al have shown reduced contents in exterior regions in comparison to the interior regions, in contrast to the Na content which have shown higher content at the aggregate surface. The concentration of microorganisms was also higher on the aggregate surface and depleted in aggregate center. In addition the water repellency measurements on the outer surface of the aggregates have shown in Anthrosol (maize) and in Ap horizon of Luvisol (wheat) higher repellency indices than in aggregate interior which has probably from the microbiological activity.

Water repellency investigation of Rotthalmünster soil has shown only slight reduction of infiltration rate under field moisture and air dry conditions. Higher levels of repellency were detected in topsoil horizons in comparison to subsoil. In addition it has been detected that the spatial variation of water repellency depends on size of investigated aggregates. Smaller aggregates showed higher levels of repellency than larger ones, and the difference was especially pronounced in cultivated soils.

In Rotthalmünster soils there was no correlation found between the organic carbon content or the amount of hydrophobic groups and water repellency.

Mechanical properties like strength of soil aggregates and bulk density is mainly influenced by the type of soil management. Aggregates from cultivated horizons had lower strengths of soil aggregates in comparison to aggregates from deeper horizons not affected by tillage. In addition smaller aggregates were mostly stronger and had higher bulk density than larger ones.

No correlation found between the content of organic carbon, hydrophobic groups content and aggregate strength suggest that in dry soils organic carbon has lost its stabilizing properties and even contributes to formation of failure zones in those places were organic matter is accumulated.

Peeling of soil aggregates with help of soil aggregate erosion (SAE) chamber is not only a good method of separation of the material from the exterior, transitional and interior regions, but it can also provide information of the strength of the aggregate at different concentric layer.

The positive relationship between the tensile strength and erosive strength of the aggregates suggest that the tensile strength of the aggregate is controlled by the sum of the strengths of each concentric layer.

The use of soil and type of cultivation influence the physical properties of the soil. In this research the highest differences were detected between grassland soils and cultivation soil, and less pronounced between conventional and conservation tillage systems. In cultivated soils especially in topsoil horizons the higher heterogeneity of properties was found than in not disturbed horizons or grassland soils. Due to different vegetation grown on the conventional and conservation sites in some cases it was not possible to recognize if higher influence on some properties had the vegetation type or the tillage system. In addition conservation tillage system was introduced for relatively short time and it may not be enough to recognize the changes in soil properties. The most pronounced changes were detected during percolation experiment where in conventional tilled soils the hydraulic conductivity was much higher in comparison to conservation tillage, and as an effect of reduced hydraulic conductivity less organic carbon was leached out than in other soil.

Outlook

- Distribution of organic carbon in aggregates from different size classes after separation by dry sieving result in higher accumulation of fresh organic matter in smaller aggregates, which is the easiest accessible for leaching and mineralization.
- The gradients within soil aggregates in chemical and physical properties are not necessary detectable in all soil aggregates. In Rotthalmünster soil the differences in organic carbon content were not significant, but the differences were found in microorganisms' distribution, hydrophilic groups content and water repellency. In addition the aggregate exterior was enriched in chemical elements like K, Fe and Al and the interior had higher content of Na in some aggregates.
- Subcritical levels of water repellency were found in soils from Rotthalmünster, with small variation between aggregates under different water tension. Soil management, vegetation type and the horizontal position influences the intensity of hydrophobicity and the special variation is especially pronounced in aggregates of different size classes.
- There was no correlation found between organic carbon content, the amount of hydrophobic or hydrophilic groups' content in aggregate and the level of hydrophobicity.
- Strength of soil aggregates is related to the soil management practices, soil horizon and size of the aggregate. Organic carbon content and the hydrophobic groups' content may negatively influence the strength of dry aggregates.
- Erosive strength of the aggregates can be determined during peeling of aggregates in soil aggregate erosion chambers and the erosive strength of each concentric layer contributes to the total aggregate strength

Appendix

***Appendix-Table I** Water sorptivity (S_w), ethanol sorptivity (S_e) and water repellency of soil aggregates determined on aggregate surface and aggregate interior*

maize
conventional tillage

horizon	aggregate layer	S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]			R		
		mean	st. err	sign.	mean	st. err	sign.	mean	st. err	sign.
Ap1	exterior	0,168	0,007	a	0,217	0,010	a	2,555	0,126	c
	interior	0,339	0,023	c	0,250	0,008	ab	1,539	0,091	ab
Ap2	exterior	0,244	0,011	ab	0,266	0,011	ab	2,213	0,137	bc
	interior	0,347	0,033	c	0,279	0,022	b	1,657	0,128	ab
Sw-M	exterior	0,242	0,021	ab	0,222	0,018	ab	2,165	0,367	abc
	interior	0,307	0,022	bc	0,223	0,016	ab	1,453	0,081	a

wheat
conservation tillage

horizon	aggregate layer	S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]			R		
		mean	st. err	sign.	mean	st. err	sign.	mean	st. err	sign.
Ap	exterior	0,185	0,008	a	0,210	0,007	a	2,32	0,138	c
	interior	0,289	0,015	b	0,195	0,006	a	1,41	0,089	ab
rAp	exterior	0,355	0,018	cd	0,223	0,015	a	1,30	0,114	ab
	interior	0,391	0,020	de	0,323	0,024	b	1,72	0,175	b
Bt	exterior	0,432	0,014	e	0,233	0,013	a	1,08	0,083	a
	interior	0,298	0,015	bc	0,332	0,013	b	2,26	0,125	c

***Appendix-Table II** Organic carbon content and CH, C=O absorption bands in exterior, transitional and interior region of soil aggregates from different management and horizons.*

MAIZE	**Ap1**						**Ap2**						**Sw-M**					
	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-
exterior	1.34	0.06	1.14	0.08	4.72	0.18	1.42	0.02	1.49	0.04	6.21	0.19	0.62	0.05	0.48	0.33	4.08	0.21
transitional 1	1.28	0.05	1.05	0.05	4.46	0.13	1.41	0.03	1.41	0.07	6.33	0.27	0.59	0.05	0.38	0.30	3.65	0.35
transitional 2	1.37	0.07	0.90	0.07	3.05	0.11	1.38	0.02	1.41	0.08	5.87	0.47	0.58	0.06	0.38	0.32	3.16	0.31
interior	1.36	0.07	0.97	0.10	3.50	0.14	1.37	0.06	1.38	0.08	5.16	0.30	0.51	0.07	0.19	0.35	4.20	0.28

WHEAT	**Ap**						**rAp**						**Bt**					
	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-
exterior	1.24	0.06	0.98	0.04	4.05	0.20	1.08	0.02	1.29	0.06	5.66	0.14	0.34	0.03	n.d.	-	n.a.	-
transitional 1	1.29	0.10	1.06	0.12	3.81	0.19	1.06	0.03	1.10	0.09	5.80	0.11	0.32	0.03	n.d.	-	n.a.	-
transitional 2	1.24	0.06	0.86	0.03	4.54	0.18	1.05	0.03	0.98	0.10	5.20	0.15	0.31	0.04	n.d.	-	n.a.	-
interior	1.17	0.03	0.71	0.06	4.12	0.21	0.99	0.03	0.93	0.04	4.83	0.23	0.26	0.08	n.d.	-	n.a.	-

GRASSLAND A	**Ah**						**rAp**						**Sw-M**					
	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-
exterior	1.14	0.08	1.54	0.10	4.58	0.15	0.87	0.14	0.45	0.05	5.03	0.32	0.62	0.07	0.16	0.15	n.d	-
transitional 1	1.06	0.06	1.71	0.09	n.a.	-	0.85	0.14	0.34	0.06	n.a.	-	0.60	0.08	0.08	0.16	n.d	-
transitional 2	1.03	0.05	1.64	0.07	n.a.	-	0.81	0.16	0.18	0.10	n.a.	-	0.62	0.09	0.16	0.17	n.d	-
interior	1.01	0.03	1.56	0.12	3.74	0.20	0.79	0.15	0.17	0.08	4.93	0.20	0.63	0.08	0.13	0.19	n.d	-

GRASSLAND B	**Ah**						**rAp**						**Sw-M**					
	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-	Corg %	+/-	CH group	+/-	C=O group	+/-
exterior	1.36	0.08	1.77	0.12	6.10	0.19	0.96	0.05	1.02	0.06	5.59	0.28	0.72	0.11	0.15	0.21	n.d	-
transitional 1	1.36	0.04	1.78	0.06	n.d.	-	0.95	0.09	0.91	0.10	n.d	-	0.69	0.10	0.05	0.23	n.d	-
transitional 2	1.38	0.03	1.63	0.06	n.d.	-	0.87	0.06	0.99	0.19	n.d	-	0.64	0.09	0.03	0.22	n.d	-
interior	1.42	0.05	1.84	0.08	5.54	0.25	0.85	0.07	0.79	0.14	4.48	0.23	0.59	0.08	0.05	0.22	n.d	-

n.a. - not available data n.d. - not detectable

Appendix-Table III *Water repellency (R), sorptivity of water (S_w) and sorptivity of ethanol (S_e) of soil aggregates of three size classes, different soil horizon and management*
Capital letters (ABC) identify significant differences between aggregate size classes (p=0.05); and small letters between soil horizons

Maize

soil depth (cm)	agg size (mm)	R [-]			S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]		
		mean	st.err	stat.	mean	st.err	stat.	mean	st.err	stat.
Ap1	15-12	2.39	0.15	A ab	0.41	0.04	B d	0.47	0.02	AB cde
	12-8	6.08	0.45	B c	0.17	0.05	A a	0.52	0.03	B b
	8-5	5.54	0.49	B c	0.16	0.01	A a	0.42	0.02	A ab
Ap2	15-12	2.26	0.11	A a	0.42	0.03	C d	0.47	0.02	A bcde
	12-8	3.18	0.26	B b	0.28	0.02	B bc	0.42	0.02	A a
	8-5	5.01	0.29	C bc	0.16	0.01	A a	0.41	0.02	A ab
Sw-M	15-12	2.57	0.23	A ab	0.34	0.03	B cd	0.41	0.02	A abcd
	12-8	2.84	0.18	A ab	0.29	0.02	B bc	0.40	0.02	B a
	8-5	4.17	0.26	B abc	0.17	0.01	A a	0.34	0.01	B abcd

Wheat

soil depth (cm)	agg size (mm)	R [-]			S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]		
		mean	st.err	stat.	mean	st.err	stat.	mean	st.err	stat.
Ap	15-12	3.02	0.19	A ab	0.29	0.03	B abc	0.42	0.02	A abcd
	12-8	2.78	0.23	A ab	0.32	0.03	B c	0.42	0.01	A a
	8-5	4.41	0.25	B abc	0.17	0.01	A a	0.38	0.02	A ab
rAp	15-12	2.73	0.23	B ab	0.32	0.03	B bcd	0.41	0.02	A abcd
	12-8	1.90	0.23	A a	0.26	0.02	B bc	0.38	0.02	A a
	8-5	4.28	0.21	C abc	0.17	0.01	A a	0.37	0.01	A ab
Bt	15-12	3.74	0.23	A bc	0.19	0.01	A a	0.35	0.01	A a
	12-8	3.24	0.29	A b	0.23	0.02	A ab	0.35	0.02	A a
	8-5	3.86	0.24	A ab	0.18	0.01	A abc	0.34	0.01	A a

Grassland A

soil depth (cm)	agg size (mm)	R [-]			S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]		
		mean	st.err	stat.	mean	st.err	stat.	mean	st.err	stat.
Ah	15-12	4.66	0.65	A c	0.26	0.02	B abc	0.56	0.04	B e
	8-5	4.55	0.46	A abc	0.20	0.01	A ab	0.43	0.02	A ab
rAp	15-12	2.79	0.30	A ab	0.34	0.02	B cd	0.45	0.03	A abcde
	8-5	3.95	0.45	A ab	0.21	0.02	A abc	0.44	0.03	A ab
Sw-M	15-12	2.41	0.22	A ab	0.34	0.03	B cd	0.39	0.02	A abcd
	8-5	4.36	0.21	B abc	0.20	0.02	A abc	0.43	0.02	A ab

Grassland B

soil depth (cm)	agg size (mm)	R [-]			S_w [mm $s^{-1/2}$]			S_e [mm $s^{-1/2}$]		
		mean	st.err	stat.	mean	st.err	stat.	mean	st.err	stat.
Ah	15-12	3.22	0.34	A ab	0.34	0.04	A cd	0.49	0.03	A de
	8-5	3.36	0.36	A a	0.28	0.02	A c	0.46	0.05	A b
rAp	15-12	3.18	0.19	A ab	0.24	0.01	A abc	0.37	0.01	A abc
	8-5	3.34	0.03	A a	0.23	0.02	A abc	0.39	0.02	A ab
Sw-M	15-12	3.64	0.35	A abc	0.22	0.02	A ab	0.36	0.02	A ab
	8-5	3.10	0.27	A a	0.26	0.04	A bc	0.36	0.02	A ab

***Appendix-Table IV** C_{org} content (%) in different size-class aggregates*
Capital letters (ABC) identify significant differences between aggregate size classes (p=0.05); and small letters between soil horizons

		C content [%]								
	size class	mean	st. err	sign.	mean	st. err	sign.	mean	st. err	sign.
		Ap1			Ap2			Sw-M		
MAIZE	15-12	1,26	0,015	BC gh	1,27	0,005	B h	0,88	0,003	B d
	12-8	1,09	0,007	A f	1,19	0,011	A g	0,81	0,004	A d
	8-5	1,24	0,004	B f	1,19	0,014	A f	0,88	0,012	B d
	5-2	1,29	0,012	C f	1,19	0,009	A ef	0,98	0,003	C cd
	2-1.25	1,47	0,008	D i	1,40	0,005	C h	0,98	0,007	C d
	1.25-0.63	1,51	0,010	D g	1,47	0,004	D g	1,02	0,005	D d
	0.63-0.125	1,82	0,005	E g	2,00	0,005	E h	1,11	0,005	E d
		Ap1			rAp			Bt		
WHEAT	15-12	1,19	0,005	AB g	1,01	0,005	A ef	0,29	0,012	A a
	12-8	1,16	0,014	A g	1,01	0,007	A ef	0,43	0,007	B a
	8-5	1,16	0,011	A f	1,01	0,009	A e	0,47	0,012	BC a
	5-2	1,18	0,006	AB e	1,04	0,004	B d	0,43	0,007	B a
	2-1.25	1,21	0,006	B g	1,08	0,011	C f	0,45	0,011	BC a
	1.25-0.63	1,21	0,007	B f	1,14	0,006	D ef	0,46	0,006	BC a
	0.63-0.125	1,36	0,003	C e	1,21	0,004	E	0,48	0,003	C a
		Ah			rAp			Sw-M		
GRASSLAND A	15-12	1,53	0,033	A i	1,05	0,008	BC f	0,48	0,003	A b
	12-8	1,14	0,019	A i	0,95	0,017	AB e	0,56	0,003	B b
	8-5	1,57	0,004	AB h	0,96	0,032	AB de	0,60	0,003	B b
	5-2	1,61	0,006	B h	0,93	0,016	A c	0,59	0,002	B b
	2-1.25	1,69	0,006	C j	1,04	0,006	ABC e	0,61	0,006	BC b
	1.25-0.63	1,80	0,010	D i	1,08	0,012	C e	0,66	0,006	C b
	0.63-0.125	1,80	0,012	E i	1,12	0,043	C d	0,74	0,029	D b
		Ah			rAp			Sw-M		
GRASSLAND B	15-12	1,04	0,008	A f	0,96	0,002	DE e	0,65	0,004	AB c
	12-8	1,34	0,006	BC h	0,85	0,002	B d	0,64	0,006	AB c
	8-5	1,32	0,008	B g	0,81	0,007	A c	0,65	0,006	AB b
	5-2	1,33	0,033	B g	0,88	0,002	C c	0,62	0,034	A b
	2-1.25	1,41	0,006	C h	1,00	0,009	F d	0,74	0,009	C c
	1.25-0.63	1,61	0,020	D h	0,92	0,014	D c	0,71	0,012	BC b
	0.63-0.125	1,66	0,014	D f	0,99	0,006	EF c	0,75	0,012	C b

***Appendix-Table V** Tensile strength (kPa) of aggregates from different vegetation, soil horizon and aggregate size in kPa.*

The small letters (abc) show statistical significance among aggregate size classes (p=0.05), the capital letters (ABC) show the statistical significance among soil horizons (p=0.05)

vegetation	horizon	tensile strength [kPa]								
		15-12 mm			12-8 mm			8-5 mm		
		mean	st.err		mean	st.err		mean	st.err	
Maize	Ap1	140	11	aA	162	17	aA	141	17	aA
	Ap2	250	16	aB	314	25	aB	250	29	aB
	Sw-M	339	19	aC	427	26	bC	348	21	cC
Wheat	Ap	139	10	aA	153	14	aA	181	22	aA
	rAp	361	29	aB	368	32	aB	348	32	aB
	Bt	292	39	aB	344	23	aB	309	24	aB
Grassland B	Ah	143	24	aA	189	20	aA	210	28	aA
	rAp	267	22	aB	307	15	abB	334	19	bB
	Sw-M	284	23	aB	257	24	aB	392	22	bB
Grassland A	Ah	238	20	aA	217	17	aA	238	30	aA
	rAp	277	19	aA	284	16	aB	293	27	aA
	Sw-M	267	21	aA	271	22	aAB	307	29	aA

Appendix-Table VI *Percolation of soil samples with water and Na-pyrophosphate solution, volume of eluat, C concentration, and total carbon loss (TOC) from the samples and the calculated hydraulic conductivity (k)*

maize	sample	eluat volume	total eluat volume	C concentration	TOC	k
I R11	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	5.1	21		52.43	1.101	0.01400
	5.2	23		53.03	2.321	0.00387
	5.3	20	64	54.06	3.402	0.00354
pyrophosphate	5.1	24		67.77	5.028	0.00300
	5.2	20		76.93	6.567	0.00373
	5.3	25		81.37	8.601	0.00233
	5.4	21		91.60	10.525	0.00367
	5.5	20		98.10	12.487	0.00299
	5.6	20	194	96.20	14.411	0.00270
water	5.1	19	213	100	16.311	0.00218

maize	sample	eluat volume	total eluat volume	C concentration	TOC	k
II R34	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	3.1	50		21.55	1.078	0.083
	3.2	46		17.58	1.886	0.169
	3.3	50		14.63	2.618	0.106
	3.4	37		13.82	3.129	0.153
	3.5	45		11.77	3.659	0.096
	3.6	45		10.85	4.147	0.212
	3.7	58		9.79	4.715	0.085
	3.8	52		11.37	5.306	0.080
	3.9	40		10.58	5.729	0.066
	3.10	25	448	14.20	6.084	0.033
pyrophosphate	3.1	21		17.65	6.455	0.030
	3.2	16		16.24	6.715	0.039
	3.3	21		17.89	7.090	0.027
	3.4	18		20.83	7.465	0.046
	3.5	15		23.23	7.814	0.015
	3.6	18		24.24	8.250	0.023
	3.7	14		25.35	8.605	0.014
	3.8	19		28.54	9.147	0.007
	3.9	22		30.02	9.808	0.000
	3.10	18		34.26	10.424	0.003
	3.11	19		41.44	11.212	0.004
	3.12	23		42.09	12.180	0.003
	3.13	20		42.66	13.033	0.004
	3.14	20		46.83	13.970	0.003
	3.15	20		54.51	15.060	0.003
	3.16	20		84.03	16.740	0.001
	3.17	20		105.60	18.852	0.003
	3.18	20		96.17	20.776	0.004
	3.19	20		97.50	22.726	0.005
	3.20	20		89.53	24.516	0.003
	3.21	19	851	82.30	26.080	0.004
water	3.1	22	873	123.80	28.804	0.003

maize	sample	eluat volume	total eluat volume	C concentration	TOC	k
III R8	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	2.1	40		22.05	0.882	0.066
	2.2	20		24.62	1.374	0.073
	2.3	28		23.72	2.039	0.060
	2.4	28		22.96	2.681	0.039
	2.5	32		23.18	3.423	0.036
	2.6	28		18.20	3.933	0.043
	2.7	22		17.54	4.319	0.036
	2.8	22	220	17.81	4.711	0.029
pyrophosphate	2.1	22		20.32	5.158	0.032
	2.2	12		20.46	5.403	0.029
	2.3	20		21.11	5.825	0.026
	2.4	17		21.32	6.188	0.023
	2.5	15		21.81	6.515	0.026
	2.6	25		17.69	6.957	0.046
	2.7	20		14.13	7.240	0.031
	2.8	18		17.72	7.559	0.025
	2.9	16		21.79	7.907	0.016
	2.10	15		23.97	8.267	0.018
	2.11	24		24.82	8.863	0.016
	2.12	16		26.49	9.286	0.010
	2.13	19		29.03	9.838	0.010
	2.14	19		32.41	10.454	0.009
	2.15	20		35.43	11.162	0.009
	2.16	20		36.95	11.901	0.007
	2.17	18		39.46	12.612	0.008
	2.18	22		39.91	13.490	0.008
	2.19	30		45.24	14.847	0.006
	2.20	24		48.69	16.015	0.005
	2.21	20		44.69	16.909	0.009
	2.22	25		46.74	18.078	0.009
	2.23	22		42.94	19.022	0.007
	2.24	20		47.75	19.977	0.009
	2.25	15		45.77	20.664	0.008
	2.26	23		43.06	21.654	0.007
	2.27	20		45.03	22.555	0.007
	2.28	20		47.99	23.515	0.007
	2.29	22		52.27	24.665	0.009
	2.30	20		58.47	25.834	0.008
	2.31	32		85.93	28.584	0.006
	2.32	20		76.97	30.123	0.007
	2.33	20		72.13	31.566	0.008
	2.34	20		77.13	33.108	0.006
	2.35	21		74.63	34.676	0.006
	2.36	20		76.30	36.202	0.005
	2.37	21	973	73.47	37.745	0.006
water	2.38	32		70.00	39.985	0.008
	2.1	22		70.00	41.525	0.010
	2.2	22	1049	75.10	43.177	0.010

maize	sample	eluat volume	total eluat volume	C concentration	TOC	k
IV R6	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	1.1	45		22.95	1.03	0.074
	1.2	22		21.51	1.51	0.081
	1.3	35		19.17	2.18	0.075
	1.4	23		18.91	2.61	0.032
	1.5	53		18.53	3.59	0.059
	1.6	45		13.35	4.19	0.069
	1.7	40		12.18	4.68	0.066
	1.8	20		13.85	4.96	0.047
	1.9	20	303	13.01	5.22	0.060
pyrophosphate	1.1	25		15.63	5.61	0.036
	1.2	20		15.43	5.92	0.049
	1.3	15		14.92	6.14	0.047
	1.4	17		14.72	6.39	0.037
	1.5	21		15.8	6.72	0.046
	1.6	28		15.92	7.17	0.071
	1.7	30		14.76	7.61	0.041
	1.8	25		15.91	8.01	0.039
	1.9	15		14.19	8.22	0.043
	1.10	19		14.75	8.50	0.042
	1.11	24		15.51	8.88	0.037
	1.12	25		16.85	9.30	0.036
	1.13	50		20.58	10.33	0.035
	1.14	20		17.40	10.67	0.025
	1.15	20		17.77	11.03	0.028
	1.16	20		19.86	11.43	0.028
	1.17	19		17.78	11.76	0.026
	1.18	17		23.07	12.16	0.023
	1.19	30		21.02	12.79	0.042
	1.20	24		20.09	13.27	0.018
	1.21	19		21.76	13.68	0.019
	1.22	19		23.07	14.12	0.016
	1.23	22		25.52	14.68	0.013
	1.24	19		28.16	15.22	0.007
	1.25	38		26.31	16.22	0.013
	1.26	20		24.3	16.70	0.014
	1.27	19		26.01	17.20	0.025
	1.28	24		26.79	17.84	0.011
	1.29	24		28.55	18.53	0.016
	1.30	27		31.93	19.39	0.008
	1.31	22		33.83	20.13	0.010
	1.32	30		34.02	21.15	0.010
	1.33	22		35.13	21.93	0.010
	1.34	22		35.84	22.71	0.008
	1.35	20		35.71	23.43	0.009
	1.36	16		35.06	23.99	0.009
	1.37	19		33.92	24.63	0.009
	1.38	20		33.77	25.31	0.009
	1.39	23		49.40	26.45	0.006
	1.40	25		45.30	27.58	0.014
	1.41	20		50.27	28.58	0.008
	1.42	20		59.93	29.78	0.004
	1.43	25		76.07	31.68	0.009
	1.44	25		66.97	33.36	0.008
	1.45	30		61.37	35.20	0.007
	1.46	17		72.77	36.44	0.008
	1.47	20		73.20	37.90	0.007
	1.48	23		67.73	39.46	0.004
	1.49	20	1417	77.07	41.00	0.005
water	1.1	23		70.00	42.61	0.006
	1.2	20	1460	73.03	44.07	0.009

maize V R36	sample nr	eluat volume ml	total eluat volume ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
water	4.1	45		15.50	0.70	0.074
	4.2	50		17.02	1.55	0.183
	4.3	55		13.27	2.28	0.117
	4.4	30		12.71	2.66	0.124
	4.5	45		13.41	3.26	0.096
	4.6	60		10.15	3.87	0.067
	4.7	60		8.38	4.37	0.092
	4.8	45		8.92	4.78	0.074
	4.9	32		13.09	5.20	0.075
	4.10	34	456	11.98	5.60	0.102
pyrophosphate	4.1	50		11.44	6.17	0.072
	4.2	25		9.58	6.41	0.127
	4.3	47		6.23	6.71	0.222
	4.4	50		5.53	6.98	0.157
	4.5	23		6.37	7.13	0.190
	4.6	23		7.25	7.30	0.190
	4.7	32		7.89	7.55	0.151
	4.8	50		5.75	7.84	0.183
	4.9	20		4.65	7.93	0.220
	4.10	20		5.00	8.03	0.220
	4.11	20		5.71	8.14	0.220
	4.12	10		5.72	8.20	0.055
	4.13	22		12.67	8.48	0.056
	4.14	10		13.06	8.61	0.055
	4.15	35		11.65	9.02	0.064
	4.16	21		11.82	9.27	0.073
	4.17	25		13.45	9.60	0.072
	4.18	24		12.66	9.91	0.069
	4.19	25		13.74	10.25	0.066
	4.20	17		14.39	10.49	0.062
	4.21	20		15.82	10.81	0.044
	4.22	14		15.58	11.03	0.049
	4.23	19		16.59	11.34	0.046
	4.24	20		16.07	11.67	0.028
	4.25	20		19.12	12.05	0.024
	4.26	39		15.75	12.66	0.056
	4.27	25		17.00	13.09	0.041
	4.28	30		14.94	13.54	0.040
	4.29	35		15.13	14.07	0.040
	4.30	21		15.43	14.39	0.036
	4.31	27		16.54	14.84	0.036
	4.32	50		18.14	15.74	0.058
	4.33	19		14.64	16.02	0.031
	4.34	23		13.98	16.34	0.033
	4.35	25		14.88	16.71	0.034
	4.36	25		15.72	17.11	0.034
	4.37	24		17.03	17.52	0.015
	4.38	20		17.35	17.86	0.016
	4.39	20		18.75	18.24	0.028
	4.40	20		16.22	18.56	0.026
	4.41	21		15.95	18.90	0.027
	4.42	19		15.61	19.19	0.025
	4.43	47		15.54	19.92	0.022
	4.44	20		14.96	20.22	0.027
	4.45	19		13.87	20.49	0.027
	4.46	20		14.26	20.77	0.026
	4.47	18		14.69	21.04	0.025
	4.48	48		13.38	21.68	0.022
	4.49	34		12.79	22.11	0.039
	4.50	55		14.51	22.91	0.013
	4.51	25		12.75	23.23	0.026
	4.52	30		13.14	23.62	0.024
	4.53	22		14.26	23.94	0.025

maize V R36	nr	eluat volume ml	V summe ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
pyrophosphate	4.54	50		13.83	24.63	0.025
	4.55	20		13.09	24.89	0.027
	4.56	20		14.32	25.18	0.027
	4.57	24		14.35	25.52	0.025
	4.58	50		14.80	26.26	0.019
	4.59	20		16.97	26.60	0.026
	4.60	20		16.71	26.94	0.023
	4.61	32		16.52	27.46	0.024
	4.62	30		15.58	27.93	0.022
	4.63	22		15.21	28.27	0.023
	4.64	31		16.73	28.79	0.022
	4.65	30		17.19	29.30	0.020
	4.66	40		30.00	30.50	0.014
	4.67	20		28.37	31.07	0.021
	4.68	24		27.83	31.74	0.047
	4.69	22		29.07	32.38	0.010
	4.7	45		36.13	34.00	0.012
	4.71	27		47.57	35.29	0.013
	4.72	30		62.77	37.17	0.012
	4.73	34		55.77	39.07	0.015
	4.74	22		51.07	40.19	0.014
	4.75	20		50.30	41.19	0.016
	4.76	35		42.60	42.69	0.015
	4.77	22		66.73	44.15	0.015
	4.78	27		63.50	45.87	0.012
	4.79	22		55.80	47.10	0.016
	4.80	22		56.07	48.33	0.010
	4.81	22		55.30	49.55	0.013
	4.82	21		53.33	50.67	0.012
	4.83	26		45.83	51.86	0.014
	4.84	22		49.67	52.95	0.016
	4.85	25		47.50	54.14	0.036
	4.86	30	2786	45.67	55.51	0.010
water	4.1	22		40.22	56.39	0.015
	4.2	23		38.23	57.27	0.016
	4.3	30	2861	34.07	58.29	0.014

wheat	sample	eluat volume	total eluat volume	C concentration	TOC	k
I R51	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	6.1	21		29.81	0.63	0.004
	6.2	18	39	39.74	1.34	0.001
pyrophosphate	6.1	25		25.78	1.99	0.003
	6.2	22		21.65	2.46	0.010
	6.3	27		21.60	3.05	0.010
	6.4	21		29.15	3.66	0.009
	6.5	22		30.00	4.32	0.010
	6.6	32		28.07	5.22	0.009
	6.7	20		30.40	5.82	0.008
	6.8	22		30.00	6.48	0.015
	6.9	25		48.13	7.69	0.014
	6.10	20		45.17	8.59	0.008
	6.11	20		45.17	9.49	0.014
	6.12	26		40.90	10.56	0.009
	6.13	29		31.07	11.46	0.008
	6.14	21	371	30.67	12.10	0.004
water	6.15w	25		30.00	12.85	0.007
	6.16w	20	416	30.00	13.45	0.007

wheat	sample	eluat volume	total eluat volume	C concentration	TOC	k
II R53	nr	ml	ml	mg/l	mg	cm^3/cm^2*h
water	7.1	20		44.87	0.897	0.003
	7.2	25		60.21	2.403	0.006
	7.3	21		54.32	3.543	0.009
	7.4	19	85	46.22	4.422	0.007
pyrophosphate	7.1	21		37.10	5.201	0.002
	7.2	20		33.12	5.863	0.004
	7.3	21		40.93	6.723	0.003
	7.4	20		38.20	7.487	0.006
	7.5	27		42.33	8.630	0.006
	7.6	20		57.83	9.786	0.012
	7.7	16		60.77	10.759	0.006
	7.8	22		60.07	12.080	0.007
	7.9	23		50.73	13.247	0.007
	7.10	24		50.27	14.453	0.007
	7.11	21		31.87	15.123	0.029
	7.12	21	341	47.70	16.124	0.007
water	7.1	20		45.00	17.024	0.005
	7.2	28	389	45.00	18.284	0.006

wheat III R55	sample nr	eluat volume ml	total eluat volume ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
water	10.1	35		10.60	0.371	0.114
	10.2	50		12.57	1.000	0.162
	10.3	21		11.23	1.235	0.067
	10.4	10		11.02	1.346	0.032
	10.5	20		11.87	1.583	0.063
	10.6	17		14.45	1.829	0.053
	10.8	24		50.49	3.040	0.073
	10.9	26		44.07	4.186	0.079
	10.10	30		33.43	5.189	0.098
	10.11	25		31.94	5.988	0.082
	10.12	26		28.09	6.718	0.085
	10.13	18		30.15	7.261	0.059
	10.14	30	332	28.87	8.127	0.098
pyrophosphate	10.1	20		37.32	8.873	0.065
	10.2	25		28.48	9.585	0.081
	10.3	20		27.5	10.135	0.064
	10.4	27		27.09	10.867	0.086
	10.5	20		33.70	11.541	0.063
	10.6	25		22.87	12.112	0.078
	10.7	25		38.73	13.081	0.077
	10.8	22		57.17	14.338	0.067
	10.9	15		51.40	15.109	0.045
	10.10	20		59.57	16.301	0.065
	10.11	25		44.40	17.411	0.082
	10.12	25	601	42.50	18.473	0.082

wheat IV R77	sample nr	eluat volume ml	total eluat volume ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
water	8.1	22		45.36	1.00	0.001
	8.2	22		40.30	1.88	0.010
	8.3	20		42.87	2.74	0.007
	8.4	33		75.29	5.23	0.011
	8.5	22		77.50	6.93	0.006
	8.6	30	149	80.32	9.34	0.007
pyrophosphate	8.1	21		70.00	10.81	0.002
	8.2	20		70.00	12.21	0.003
	8.3	22		56.77	13.46	0.003
	8.4	20		53.07	14.52	0.004
	8.5	22		130.93	17.40	0.001
	8.6	22	276	70.00	18.94	0.006
water	8.1	19	295	70.00	20.27	0.006

wheat V R81	sample nr	eluat volume ml	total eluat volume ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
water	9.1	35		12.27	0.43	0.029
	9.2	30		32.87	0.99	0.004
	9.3	50		33.63	2.67	0.012
	9.4	30		25.07	3.42	0.038
	9.5	35		20.84	4.15	0.061
	9.6	45		18.17	4.97	0.051
	9.7	31		18.29	5.53	0.054
	9.8	40		16.98	6.21	0.054
	9.10	50		42.39	8.33	0.031
	9.11	36		19.06	9.02	0.024
	9.12	35		18.35	9.66	0.055
	9.13	35		17.44	10.27	0.048
	9.14	38		15.43	10.86	0.052
	9.15	30		14.32	11.29	0.033
	9.16	20		13.88	11.56	0.039
	9.17	30		14.05	11.99	0.041
	9.18	30		15.01	12.44	0.040
	9.19	33		14.79	12.92	0.044
	9.20	28		22.88	13.57	0.042
	9.21	52		16.19	14.41	0.024
	9.22	24		17.75	14.83	0.032
	9.23	24		17.34	15.25	0.034
	9.24	24		18.41	15.69	0.030
	9.25	23		18.42	16.11	0.033
	9.26	21		29.23	16.73	0.042
	9.27	20		24.87	17.23	0.025
	9.28	50		23.56	18.40	0.024
	9.29	22	921	19.65	18.84	0.030
pyrophosphate	9.1	25		25.22	19.47	0.026
	9.2	30		22.97	20.16	0.024
	9.3	32		20.02	20.80	0.021
	9.4	30		17.73	21.33	0.046
	9.5	21		16.98	21.69	0.027
	9.6	25		18.32	22.14	0.015
	9.7	24		16.73	22.54	0.035
	9.8	24		19.33	23.01	0.031
	9.9	20		18.01	23.37	0.029
	9.10	24		15.83	23.75	0.027
	9.11	25		16.03	24.15	0.031
	9.12	20		15.31	24.46	0.041
	9.13	50		15.11	25.21	0.023
	9.14	35		13.31	25.68	0.016
	9.15	25		15.40	26.06	0.029
	9.16	20		18.30	26.43	0.027
	9.17	25		21.07	26.95	0.028
	9.18	30		23.30	27.65	0.028
	9.19	25		22.47	28.22	0.033
	9.20	25		16.87	28.64	0.025
	9.21	51		18.67	29.59	0.647
	9.22	20		25.73	30.10	0.426
	9.23	30		23.53	30.81	0.909
	9.24	22		50.25	31.92	0.880
	9.25	30		44.67	33.26	0.938
	9.26	32		33.67	34.33	0.821
	9.27	25		38.63	35.30	0.806
	9.28	20		66.87	36.64	0.824
	9.29	20		80.87	38.25	0.870
	9.30	21		83.30	40.00	0.840
	9.31	19	1746	79.43	41.51	0.792

wheat V R81	sample nr	eluat volume ml	total eluat volume ml	C concentration mg/l	TOC mg	k cm^3/cm^2*h
pyrophosphate	9.32	23		75.07	43.24	0.667
	9.33	30		33.33	44.24	0.822
	9.34	20		36.00	44.96	0.800
	9.35	21		26.63	45.52	0.764
	9.36	50		27.50	46.89	0.699
	9.37	30		23.70	47.60	0.833
	9.38	35		24.57	48.46	0.729
	9.39	20		24.27	48.95	0.833
	9.40	35		28.37	49.94	0.753
	9.41	35		23.23	50.75	0.680
	9.42	30		21.70	51.41	0.638
	9.43	50	379	19.81	52.40	0.694
water	9.1	20		18.73	52.77	0.667
	9.2	25		20.66	53.29	0.595
	9.3	20		21.15	53.71	0.690
	9.4	39	483	19.88	54.49	0.582