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Fertilization induced changes in soil stability at the microscale revealed by rheometry

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Start by doing what's necessary;
then do what's possible;
and suddenly you are doing the impossible.

Francis of Assisi

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LIST OF ABBREVIATIONS

A	Area (m^2)
a	Ion activity (-)
AC	Air capacity (% v/v)
Al	Aluminium
AP	Annual precipitation (mm)
Ba	Barium
C	Carbon; clay (% w/w)
C_2, C_3	Pore continuity indices (μm^2)
c	Cohesion (Pa); concentration ($mol \cdot L^{-1}$)
c_c	Cohesion due to cemented bonds (Pa)
c_c'	Effective cohesion due to cemented bonds (Pa)
c_n	Coefficient of cyclic compressibility (-)
Ca	Calcium
CEC	Cation exchange capacity ($mmol_c \cdot kg^{-1}$)
Cl	Chlorine
Cr	Chromium
Cs	Caesium
Cu	Copper
e	Void ratio ($cm^3 \cdot cm^{-3}$)
e_u^1	Interpolated void ratio after 1st loading cyclic loading event ($cm^3 \cdot cm^{-3}$)
$EC_{2.5}$	Electrical conductivity of 1:2.5 soil-water ratio ($\mu S \cdot cm^{-1}$)
F	Force (N)
f	Frequency (Hz)
f_c	Factor to implement weakness of cemented bonds (-)
Fe	Iron
Fe/Al	Ratio of dithionite soluble Fe to Al (-)
$Fe_{o/d}$	Ratio of oxalate to dithionite soluble iron (-)
FYM	Farmyard manure
G	Shear modulus (Pa)
G*	Complex shear modulus (Pa)
G’	Storage modulus (Pa)
G“	Loss modulus (Pa)
g	Gravitational acceleration ($m \cdot s^{-2}$)

H	Hydrogen
h	Distance (m); altitude (m)
I	Ionic strength of a solution (mol · dm^{-3})
K	Potassium
$K_{A/B}$	Selectivity constant for cation exchange (-)
K_{CAL}	CAL soluble potassium (mg · kg^{-1})
K_{diff}	Difference between actual K content and recommended K content (mg · 10^{-2} · g^{-1})
K_{input}	Fertilizer K (kg · ha^{-1})
K_{sat}	Ratio of exchangeable K to total cation exchange capacity (-)
k_a	Air permeability (μm^2)
k_l	Air conductivity (m · s^{-1})
k_s	Saturated hydraulic conductivity (cm · d^{-1})
LVE	Linear viscoelastic
Li	Lithium
LL	Liquid limit (% w/w)
M	Torque (Nm)
M_d	Dithionite soluble metal oxide (g · kg^{-1})
M_i	Molarity of an ion (mol · dm^{-3})
M_o	Oxalate soluble metal oxide (g · kg^{-1})
M_{ex}	Exchangeable cation ($mmmol_c$ · kg^{-1})
MAT	Mean annual temperature (° C)
mFYM	Mineral fertilization equivalent to farmyard manure
Mg	Magnesium
Mn	Mangenese
N	Nitrogen; number of load cycles in cyclic loading (-)
n	Number of data (-)
Na	Sodium
NH_4^+	Ammonium
NO_3^-	Nitrate
O	Oxygen
P	Phosphorous
P_c	Precompression stress (kPa)
P_{CAL}	CAL soluble phosphorous (mg · kg^{-1})
PL	Plastic limit (% w/w)
PAW	Plant available water (% v/v)
r	Radius (m); coefficient of correlation (-)

R^2	Coefficient of determination (-)
Rb	Rubidium
S	Sand (% w/w)
s	Deflection distance (m)
Si	Silicon
SIC	Soil inorganic carbon (% w/w)
SOC	Soil organic carbon (% w/w)
SOM	Soil organic matter (% w/w)
t	Time (s)
TC	Total carbon (% w/w)
Th	Thorium
TP	Total porosity (% v/v)
U	Silt (% w/w)
u_a	Pore air pressure (Pa)
u_w	Pore water pressure (Pa)
v	Velocity ($m \cdot s^{-1}$)
YP	Yield point
Z_i	Charge of an ion (-)
Zn	Zinc
2xFYM	Farmyard manure plus mineral fertilization equivalent to farmyard manure

LIST OF SYMBOLS

γ	Deformation (%)
$\dot{\gamma}$	Shear rate (s^{-1})
δ	Angle of internal friction (°); phase shift angle/loss angle (°)
δ'	Effective angle of internal friction (°)
ε_A	Air-filled porosity (% v/v)
η	Viscosity ($Pa \cdot s$)
η_a	Viscosity of air ($Pa \cdot s$)
θ_{grav}	Gravimetric water content (% w/w)
π	Pi
ρ_l	Density of air ($kg \cdot m^{-3}$)
σ	Normal stress (Pa)

σ'	Effective stress (Pa)
τ	Shear stress (Pa)
τ_{max}	Maximum shear stress (Pa)
τ_B	Bingham yield stress (Pa)
χ	Chi factor (degree of saturation) (-)
Ψ_M	Matric potential (kPa)

1 INTRODUCTORY ASPECTS

1.1 Introduction

Soil physical properties are generally studied at the macro- or mesoscale when investigating e. g. pore characteristics like size and functionality as well as structural stability via precompression stress test, compressibility measurements, determination of aggregate stability and so on (Fredlund and Rahardjo, 1993; Mitchell, 1993; Marshall et al., 1996; Hillel, 1998, Lal and Shukla, 2004; Hartge and Horn, 2009). However, many times the performance of a soil at the meso- or macroscale originates in the particle-particle interactions at the microscale. Hence, new methods for describing those processes in-between single grains are needed and are provided by rheometry. The corresponding science, rheology, in general is since long a part of soil science, as the fundamental works by Kravtchenko (1966), Suklje (1969), Keedwell (1984), Vyalov (1986) and Cristescue and Ene (1988) show. However, the soil scientific approach focussed mainly on the flow and deformation behaviour at a large scale, like exhibited e. g. by a landslide (Geertsema, 2006). One of the main achievements was the characterization of soil as a material exhibiting not only plastic but also elastic behaviour (Keedwell, 1984; Vyalov, 1986). Nonetheless, rheometry experienced further development mostly in other areas of research, especially with regard to quality assurance of food, cosmetics as well as industrial materials like oils, paints, coatings and concrete (Platt, 1986; Prentice, 1992; Kahovec, 2000; Brummer, 2006). Consequently, rheological tests and models for the interpretation of the results were designed for almost every purpose, ranging from the determination of flow and deformation behaviour during different shearing processes, in dependence on temperature and shear rate, to resilience (thixotropy) or the flow behaviour as a function of time (Kulicke, 1986; Barnes et al., 1989; Collyer, 1993; Collyer and Clegg, 1998; Phan-Thien, 2002; Gehm, 1998; Mezger, 2006). With respect to soil science, the main aspect has been the investigation of clay suspensions, used e. g. as drilling fluids and how their performance is influenced by amendments or suspension-tool interactions, as described in Schulz (1998), Neaman and Singer (2000), Sakairi et al. (2005), Citeau et al. (2006), and Kovzung et al. (2007) to mention but a few. Occasionally, results gained in those investigations on suspensions with high solid content may be transferred to the behaviour of clay rich soil samples. Nonetheless, research is needed with regard to naturally structured soils consisting of a large variety of grain sizes and grain shapes as well as several additional substances, and thus accumulated to a large heterogeneity of single particles in a sample. First attempts of investigating field-like soil compounds were made by Ghezzehei and Or (2000, 2001, 2003) and Or and Ghezzehei (2002), and recent works proved the suitability of rheometry for the determination of particle-particle interactions (Markgraf et al., 2006; Markgraf and Horn, 2006; Markgraf and Horn, 2007; Karmakar and Kushwaha, 2007; Barré and Hallett, 2009; Czibulya et al., 2010). They dealt with the impact of different textures, matric potential as well as various substances known for their ability to link particles (e. g. organic matter, Fe oxides, root exudates) on the flow and deformation behaviour at the microscale. But still we lack detailed information about the interactions of several soil stability influencing parameters, for instance the impact of different salts dissolved in the soil solution but also at exchange sites in dependence on texture and matric potential. As the knowledge about interactions between single particles receives more attention nowadays especially with regard to modelling soil physical processes at the meso- and macroscale, the present work is designed to contribute to the disclosure of processes at the microscale of soil samples. Special attention was paid to the cation potassium (K) as several studies revealed a positive effect on water use efficiency (Amberger, 1955; Amberger et al., 1974; Bradbury and Malcolm, 1977; Eakes at el., 1991; Egilla et al., 2001; Huang, 2001). This was generally attributed to changes in the plant response to K fertilization, e. g. via reduced transpiration rate (Brag, 1972; Bradbury and Malcolm, 1977; Lindhauer, 1985; Egilla et al., 2001) but also to a change in soil structure (Amberger, 1974). As the work by Arienzo et al. (2009) proved, the information about the impact of K on soil structure is limited. Hence, the present work focuses generally on the impact of fertilization, also with regard to organic versus mineral fertilization, but mainly on the impact of K on the shear resistance of soil at the microscale.

1.2 State of the art

1.2.1 Basic building blocks of soil structure

To distinguish between different mechanisms and processes of particle-particle interactions, first an overview of the soil components and their characteristics is necessary. Of the three phases gaseous, liquid and solid mass, the solid mass is the basic element. According to their size, the mineral particles are classified as sand, silt and clay. Of those three mainly the clay fraction is responsible for bonds between particles either by linking larger particles or being the linked particles themselves. However, the clay fraction does not only consist of clay minerals but also of oxides and hydroxides of aluminium, silicon, and iron that may also act as cementing substances or coat particles (Mitchell, 1993). Furthermore, the different clay minerals themselves are not equally distributed in the clay fraction as kaolinites are > 0.2 µm, while montmorillonite are < 0.2 µm (Schwertmann and Niederbudde, 1993).

Typically for clay mineral particles is their plate- or needlelike shape (Hillel, 1998) and their general composition of two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminium- or magnesium-oxygen-hydroxyl octahedra (Van Olphen, 1977; Velde, 1992; Jasmund and Lagaly, 1993; Bohn et al., 2001; Velde and Barré, 2010). The resulting silica and alumina sheets build two-layer minerals, consisting of one silica and one alumina sheet, as well as three-layer minerals, consisting of one alumina or magnesia sheet between two silica sheets. While kaolinites belong to the first group, smectites, vermiculites and illites represent the second group. With the help of X-ray diffraction patterns the distinguishment of clay minerals is possible due to the different distances between layers, namely 7.1-7.2 Å for two-layer clays and at least 9.2 Å for three-layer clays.

As a consequence of isomorphous substitution, the tetravalent Si in tetrahedral sheets is partly replaced by trivalent Al, which in turn can be replaced by Fe, Cr, Zn, Li and others in the octahedral sheet, which leads to a deficiency of positive charge and hence a negatively charged surface (Velde, 1992; Mitchell, 1993; Bohn et al., 2001). Attempting compensation, clay minerals adsorb cations, but only with such weak bonds that they can be exchanged easily, creating hereby a cation exchange capacity (CEC). The surface area of clays, already comparatively large due to their shape, is increased further, as the interlayer are also able to attract exchangeable cations, though they are partly sunk in the cavities of the tetrahedal sheet (Van Olphen, 1977). In dependency of the clay mineral type, the CEC is variable, hence expandable clays like smectites offer a larger CEC than non-expandable clays (Velde and Barré, 2010). The reason is the specific surface that is much larger in 2:1 clay minerals than in kaolinites which possess exchange sites only on their outer surface (Jasmund and Lagaly, 1993). But also illites tend to display exchange sites only at the outer surface as K cations are strongly adsorbed on the interlayer thus allowing only for the edge cations to be exchanged.

Despite the generally negative surface charge, clay minerals exhibit a different behaviour at the edges that developed due to disrupture of the octohedral sheet. Here, the surface resembles that of alumina particles, resulting in a positive double layer in acid solution and a negative double layer in alkaline solution (Chang et al., 1993). While the positive layer is caused by Al ions, the negative layer exists in the wake of adsorbed hydroxyl ions. Furthermore, pH-dependent charge is provided by functional OH groups (Si-OH, Al-OH, Fe-OH) (Schwertmann and Niederbudde, 1993; Bohn et al., 2001).

1.2.2 Fundamental mechanisms of interparticle interaction

1.2.2.1 Attractive and repulsive forces - chemical bonds

According to Bohn et al. (2001), ionic or electrostatic bonding occurs only between oppositely charged ions like Na^+ and Cl^-, being very strong and resulting in hard solids. While this bonding is undirected, covalent bonding due to shared electron pairs between identical or similar atoms is also strong, but directional. Weak bondings appear where hydrogen links ions, mostly to layer silicates, in hydrogen bonding, though the lack of strength can be compensated for by a larger amount of bonds. Another group of bonds is represented by the van der Waals forces acting between each pair of atoms in two particles (Van Olphen, 1977). Hence, they depend mainly on size and shape of the particles. If several different bonds exist in a crystal, the weakest one is decisive (Bohn et al., 2001).

Between particles also repulsive forces are present. At the contact points the very high Born repulsion occurs which results from an overlap between electron clouds and prevents the interpenetration of matter (Mitchell, 1993). At larger distances beyond physical interference, another repulsive force exists due to the diffuse double layer (Lagaly, 1993): As described in the previous paragraph, clay minerals attract cations to their negatively charged surface. The electrostatic attraction between negatively charged surface and positive cations pulls the latter to immediate proximity of the particle surface in a dry state. Upon wetting, single cations leave this so-called Stern layer due to Brownian motion and enter the solution albeit staying near the surface. Consequently, the cation concentration diminshes with distance to the particle surface, thus creating a diffuse electrostatic double layer. This layer is compressed in its thickness with increasing valency of ions and concentration in the solution (Van Olphen, 1977; Hillel, 1998). Repulsion is a result of overlapping diffuse double layers of two particles that increases the smaller the distance between the particles. However, the more compressed the layer, the less repulsion prevails. This leads to net attractive forces if the electrolyte concentration in the surrounding solution is high, and hence to flocculation of clay particles.

Depending on their own inherent charge and pH and enhancement by ions, clay minerals can be linked to eachother in different constellations of edge to face, edge to edge or face to face associations (cf. Lagaly, 1993). The edge-edge associations are of less importance as they do not pronouncedly change the behaviour of clay suspensions. More important are face-face connections that are mostly unaffected by pH and lead to ribbon-like clusters of higher stability the larger the area of overlap. The extreme version of this alliance is a pile of minerals as often exhibited by kaolinite. Ribbon-like connections appear throughout with all cations, but to a lesser extent with Na (only at high solution concentration). The association creating the largest increase in volume is edge to face, favoured by a acid pH, leading to a scaffold-like structure. At higher pH and electrolyte concentration the dominating association is, however, face to face due to electrostatic attraction (Lagaly, 1993).

1.2.2.2 Sorption on soil surfaces

Soils have the outstanding ability to adsorb ions and molecules from the soil solution and to desorb them again. The origin of this ability is found on mineral and organic surfaces (McBride, 2000) with their different surface functional groups that occur wherever a valence-unsatisfied OH^- or H_2O ligand is bound to a metal ion, like it is the case for non-crystalline aluminosilicates, oxides and hydroxides of Fe, Al and Mn but also at the edges of clay minerals. Even larger adsorption can be found in organic matter with its large variety of functional groups: hydroxyl (-OH), carboxyl (-COOH), phenolic ($-C_6H_4OH$) and amine ($-NH_2$) (Bohn et al., 2001). This kind of sorption is often highly specific, only slowly reversible and also pH-dependent due to the presence of H^+ as low pH increases anion adsorption. At the edges of clay minerals positive charges exist at low pH that are neutralized by anions while in the wake of increasing pH protons are dissociated and the charge is more negative. Thus, the anion capacity of clay minerals is the higher the lower the pH, while the cation exchange capacity is the higher the higher the pH. As kaolinites tend to stack without swelling, their edge area is increased above average, enhancing pH-dependent charge (Bohn et al., 2001).

Despite this pH-dependent charge, permanent charge is exhibited by the negatively charged surface area of clay minerals as described in chapter 1.2.1. The amount of exchange sites is determined by the specific surface of the exchanging solid; in clay minerals this is related to the expandability (Lagaly, 1993). However, the cation exchange capacity is supplemented by the cation exchange sites on organic matter (SOM) (Velde and Barré, 2010). The amount of exchange sites varies with SOM quality as e. g. Haynes and Naidu (1998) found organic matter to have a higher CEC when derived from mineral fertilization than when derived from farmyard manure. As reviewed by Von Lützow et al. (2007) some authors found SOM to increase cation exchange capacity (CEC) while others observed a larger CEC after elimination of SOM in montmorillonitic clay.

The ratio of different cations at the surface cannot be determined only by the composition of the soil solution but also has to consider the chemical activity of the specific ion. Generally, the higher the concentration of a single cation in the soil solution, the higher the probability to adsorb to clay surfaces, but the adsorption depends also on valency, the cation itself, as well as other factors like pH and temperature (Bolt et al., 1976; Lagaly, 1993; Scheffer and Schachtschabel, 2010). In the wake of coulombic preferences, some colloids adsorb specific cations predominantly, e. g. Mg by vermiculite (Bohn et al., 2001).

For two monovalent cations the following equation describes the state of equilibrium (Eq. 1.1) where A^+ and B^+ are cations either adsorbed (a) to an exchange site or dissolved in the solution (s):

$$\Xi]A^+_a + B^+_s \leftrightarrows \Xi]B^+_a + A^+_s \qquad (1.1)$$

The ratio of dissolved to adsorbed cations for each cation, displayed as ion activity a (-), can be related by a coefficient K, enabling to conclude which cation is favoured over the other (Eq. 1.2).

$$(a_A/a_B)_a = K_{A/B} \cdot (a_A/a_B)_s \qquad (1.2)$$

If $K_{A/B}$ is > 1 the favoured cation is A, while it is B if $K_{A/B}$ is < 1. However, K depends e. g. on the degree of exchange: The more B cations were already exchanged the less B cations can be exchanged beyond this. To determine the exchange of cations of different valency the Gapon equation can be used which takes into account the valency (Eq. 1.3 and 1.4) (Lagaly, 1993; Bohn et al., 2001). It is:

$$\Xi]\ A^+_a + 0.5 \cdot C^{2+}_s \leftrightarrows 0.5 \cdot \Xi]C^{2+}_a + A^+_s \qquad (1.3)$$

$$(a_A/a_C)_a = K_{A/c} \cdot (a_A/a_C^{0.5})_s \qquad (1.4)$$

Besides the dependency of K on the ratio of adsorbed to dissolved cations, it is also strongly affected by the ion radius as exhibited in this replacability series (Mitchell, 1993; Lagaly, 1993; Bohn et al., 2001) beginning with the least competitive i. e. smallest cation Li^+:

$$Li^+ < Na^+ < NH_4^+ = K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Cu^{2+} < Al^{3+} < Fe^{3+} < Th^{4+}$$

The binary exchange data as described previously are not always directly transferable to ternary exchange data (Sposito and LeVesque, 1985). As described by Evangelou and Lumbanraja (2002) for NH_4^+, K^+ and Ca^{2+}, the presence of K changed the selectivity of a clay mineral of NH_4^+ towards Ca, while Poonia et al. (1986a, 1986b) found farmyard manure to increase K^+ preference over Ca and Mg.

1.2.2.3 Binding and dispersing agents

1.2.2.3.1 Cations

Despite the dispersing or flocculationg impact of single ions, the total ionic strength of soil solution influences interparticle forces as described in chapter 1.2.2.1: A small amount of any salt added to a clay suspension leads to flocculation (Velde, 1992) while a low electrolyte concentrations can result in lower aggregate stability in water due to clay dispersion (Abu-Sharar et al., 1987; Levy et al., 2003).

To determine the general ionic strength I ($mol \cdot dm^{-3}$) of a soil solution, both concentration and ion charge have to be taken into account (Eq. 1.5), where M_i = molarity ($mol \cdot dm^{-3}$) and Z_i = charge of each ion (Bohn et al., 2001).

$$I = 0.5 \cdot \sum M_i \cdot Z_i^2 \qquad (1.5)$$

Despite soluble cations, the main impact of cations results from exchangable cations. Hence, the cation exchange capacity of a soil is generally closely linked to aggregate stability due to cationic bridging by polyvalent ions (Tisdall, 1996; Dimoyiannis et al., 1998). However, as insight in those processes was gained many times in laboratory experiments, Schwertmann and Niederbudde (1993) advise against the direct transfer of those results to a soil as there is seldom enough water for a comprehensive hydration of cations. Furthermore, soil structure development can decrease accessibility of exchangeable cations (Hartmann et al., 1998; Jasinska et al., 2006).

Sodium (Na)

Generally, monovalent ions are said to be of a dispersive character, especially Na as it is not tightly adsorbed by the surface and thus increases the diffuse double layer (Emerson, 1994). In this regard, Lagaly (1993) recommended the replacement of all exchangable cations by Na to receive total clay dispersion (supplemented by slightly alkaline pH to avoid edge-face associations). As reported by Köster and Schwertmann (1993) and Lagaly (1993) some smectites even tend to delaminate in water or solutions of low electrolyte concentration if Na is the dominant interlayer cation and thus disintegrate into small plates or thin piles of only few silica layers. In so-called quick-clays (sediments with formerly high NaCl concentration) the eluviation of salts causes the Na-saturated clay minerals to dissociate, which in turn enables landslides of several hundred thousand cubicmetre volume (Torrance, 1999). At a smaller scale, leaching of Na-saturated soils causes the sealing of surface and thus e. g. poor seedling emergence due to the dense packing (Rycroft et al., 2002; Kyei-Baffour et al., 2004). Rengasamy and Olsson (1991) and Greene et al. (2002) reported about hard-setting of soils due to Na saturation and found illite/smectite interstratified materials to be more prone to dispersion than kaolinites ore illites as a result of the higher surface area of interstratified clays (Barzegar et al., 1995). The dispersive impact of monovalent cations also caused lower Atterberg limits but higher tensile strength (Dexter and Chan, 1991). Assumedly, the most dispersion in water coincides with the largest strength in dried state due to a denser particle arrangement.

Substitution of NaCl by KCl is a useful method to stabilize those quick clays, especially as most plant roots repel NaCl to a great extent (Bohn et al., 2001). However, generally, the application of gypsum is recommended to improve the soil structure of sodic soils (Armstrong and Tanton, 1992).

Calcium and magnesium (Ca, Mg)

Ca and Mg can act on soil structure as exchangeable cations but also after precipitation as secondary carbonate coatings (Bronick and Lal, 2005). However, the latter happens rather under arid and semi-arid conditions. Hence, the main impact of Ca and Mg is their ability to link particles due to polyvalency, which is more pronounced for Ca (Zhang and Norton, 2002), and to enhance microaggregation when acting as bridges between organic colloids and clays (Oades, 1984). Some studies even found a negative impact of Mg on soil structure (Keren, 1989; Zhang and Norton, 2002), assumedly as a result of the higher swelling of Mg saturated clays, causing rupture of existing aggregates (Bronick and Lal, 2005). Emerson and Smith (1970) found Mg-washed soils to disperse at lower water contents compared to Ca-washed soils. Ca is in general responsible for strong linkages between clay particles but also between clay particles and sand grains: The platelets cover the grain thus creating large areas of contact, connected by polyvalent ions, the more intensely the thinner and more flexible the clay mineral (Lagaly, 1993).

Potassium (K)

Potassium is a specific cation as the adsorbation on highly active clay mineral interlayers (e. g. mica, illites, some vermiculites) leads to contraction of the interlayer, presumably due to the ability of K ions to fit excactly into the cavities in the silica sheets. Furthermore, dehydration of K ions requires less energy than of cations with similar size, e. g. Ba^{2+}. This process, called K fixation, is responsible for a lack of fit between K fertilization and K availability in the soil as most of the K is fixed directly (Bohn et al., 2001; Velde and

Barré, 2010). Assimakopoulos et al. (1994) observed an increase in K fixation upon drying if excessive amounts of exchangable K were present (< 1.5 % of CEC, cf. 3 % found by Ahmad and Davis, 1970) but a release of interlattice K at lower K saturation. Another study revealed a higher K fixation capacity in soils with more illites and vermiculites whereas smectite-dominated soils had lower K fixation (Goli-Kalanpa et al., 2008). K ions such adsorbed to vermiculites, however, are easier released than K ions in illites that were developed by diagenetic and metamorphic procesesse (Schwertmann and Niederbudde, 1993).

Due to either fixation or release of K, clay minerals can be transformed from vermiculites and smectites to illites and vice versa, respectively (Niederbudde and Fischer, 1980; Tributh, 1981; Tributh et al., 1987; Garz et al., 1993; Srinivasa Rao and Khera, 1994). According to Barré et al (2007) this transformation is a short-term process allowing 2:1 clay minerals to contribute to the available K pool in soil with more than 3 t ha^{-1}. Nonetheless, some authors could not observe such mineralogical changes despite K depletion, which was e. g. ascribed either to competetive ions in the soil solution (Brümmer and Schroeder, 1976; Tye et al., 2009) or atmospheric depositions of K (Dreibrodt et al., 2002). Besides those impacts directly related to the presence of K, a transformation in clay mineralogy induced by K can indirectly change soil properties as different clay minerals are found to influence soil stability differently, e. g. tensile strength of aggregates decreased with predominant clay mineral: smectitic > illitic > kaolinitc soils (Barzegar et al., 1995; Ruiz-Vera and Wu, 2006).

With regard to the application of slurry manure, Auerswald et al. (1996) found K to be dispersive in a laboratory experiment and hence increase erodibility but the field experiment revealed no increased erodibility due to manure treatment. Also Arienzo et al. (2009) report about the ambiguous impact of K in literature as some authors found K to resemble Na (= dispersive) (Quirck and Schofield, 1955; Rengasamy, 2002; Pernes-Debuyser and Tessier, 2004) or Ca (= stabilizing), while others assigned K an intermediate influence (Reeve et al., 1954). Investigations by Chen et al. (1983) revealed an increase of hydraulic conductivity with higher K saturation for two soils but the opposite for another soil which was richer in illites and had a higher affinity to K^+. Furthermore, they observed that K enrichment resulted in a dense network of clay microaggregates that filled up the pore space.

Arienzo et al. (2009) relate those different results to differences in clay mineralogy as a negative impact of K was mostly accompanied by a predominance of kaolinites or illites while hydraulic conductivity was improved on smectite-containing soils as Boek et al.

(1995) observed swelling inhibition by K^+ ions. With regard to distillery effluent, highly enriched with K, Pathak et al. (1999) observed lower bulk density, higher saturated hydraulic conductivity, improved water retention, so did Hati et al., (2007). However, on an Inceptisol, the distillery effluence caused a decrease in infiltration rate (Singh and Bahadur, 1998), similar to the impact of K in irrigation water observed by Peacock (2007, cited in Arienzo et al., 2009). Detrimental effects of manure amendment are also generally ascribed to excessive amounts of Na^+ and K^+ in animal waste material (Haynes and Naidu, 1998; Pernes-Debuyser and Tessier, 2004).

Ammonium (NH_4^+)

Ammonium has only a short lifetime in soil as it is soon nitrified to NO_3^- (Green et al., 1994). As a cation very similar to K, NH_4^+ can be also fixed by clay minerals, hence K and NH_4^+ are competitive in fixation (Dontsova et al., 2005; Velde and Barré, 2010). However, Evangelou and Lumbanraja (2002) found for vermiculite a NH_4^+-Ca exchange isotherm indicating almost no preference, while K addition strongly increased NH_4^+ selectivity, presumably due to collapsing interlayers. With regard to interparticle forces, Haynes and Naidu (1998) report a dispersive impact of NH_4^+, especially in the wake of the application of large animal waste amounts, which leads to the mineralization of organic N. However, as mentioned earlier, NH_4^+ is transformed within several weeks and thus does not impede aggregation severely.

1.2.2.3.2 Oxides

Due to weathering processes of primary silicates, oxides and hydroxides of aluminium, iron, manganese and silicon evolve from dissolved elements and thus enable the indexing of pedogenic processes (Blume and Schwertmann, 1969). Some of the Al ions can adsorb to exchange sites and exert very effective connections in the wake of polyvalency (Bolt et al., 1976), but generally the necessary mobility of the ions is only reached at acid pH where, in turn, the structure enhancement cannot compensate for the decline in the soil’s suitability for plant growth (Scheffer and Schachtschabel, 2010). Hence, the stabilizing impact of Fe and Al cations is most important in acidic soils (e. g. Oxisols) low in clay content and SOC (Oades and Waters, 1991).

First, amorphous oxides occur that develop into crystalline oxides due to aging. Si oxides crystallize only slowly, whereas Al oxides need low Si concentrations and lack of clay minerals to come into being, otherwise, clay minerals adsorb Al ions or they form metal-organic complexes with organic matter (Köster and Schwertmann, 1993). Fe oxides play a decisive role when it comes to the determinination of the degree of weathering of a soil as Fe ions transform into oxides almost immediately where they were released. Due to their color-changing properties they can be easily spotted in a soil profile. Main Fe oxides are goethite (α-FeOOH), hematite (α-Fe_2O_3), lepidocrocite (γ-FeOOH), ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$). While the yellow to auburn coloured goethite is the most common Fe oxide, in older sediments it is replaced by the red coloured hematite. At low Fe^{3+} concentration, the ions form goethite, while at higher concentration due to high pH and fast oxidation of Fe^{2+} the preferred oxide is ferrihydrite, and at low pH (carbonate free clay soils) lepidocrocites ouccur. Fe oxides as well as Mn oxides are generally of only low solubility but can be deoxidized and hence mobilized by plants so they are either plant-available or can be dislocated in the soil.

Oxides are thought to contribute distinctively to microaggregation of clay soils (McBride, 2000), mainly consisting of kaolinites as well as goethite and hematite, thus causing a structure similar to that of a sandy soil (Schwertmann and Niederbudde, 1993). Very high amounts of oxides lead to ferricrete, a solid and massive compound of soil and oxides. Edwards and Bremner (1967) reported that sonic vibration could not destroy microaggregates of clay associated with humified organic matter and polyvalent metals. Microaggregation by Fe oxide-hydroxide is closely related to humic acid (Kuron and Walter, 1964; Mosley et al, 2003, Kögel-Knabner et al., 2008).

1.2.2.3.3 Soil inorganic carbon

Soil structure is strongly influenced by soil inorganic carbon (SIC) but in interaction with soil organic carbon (SOC) because SOC acts as a source of Ca^{2+} and induces microbial CO_2 respiration (Bronick and Lal, 2005). At low SOC concentrations, SIC replaces SOC in stabilizing soil particle linkages (Boix-Fayos et al, 2001) while high SIC contents reduce decomposition of SOC (Clough and Skjemstad, 2000). Impediment of aggregation, increased clay dispersion and reduced aggregate stability in the wake of liming was reported by Castro and Logan (1991), Roth and Pavan (1991) and Dimoyiannis et al. (1998). However, according to Beese et al. (1979) liming can also increase shear resistance and decrease compressibility, but also reduce surface cracking, raise water storage capacity (Hoyt, 1981) and increase aggregate stability (Czeratzki, 1957, 1972). Furthermore, Scott et al. (2003) found liming to increase plant emergence on otherwise hard-setting soils as it preserved soil structure. According to Haynes and Naidu (1998) the ambiguous impact of liming is a result of 1. a short-term effect causing dispersion of soil colloids, 2. flocculating and cementing effect of $CaCO_3$ and 3. indirect impact via enhanced plant growth and thus stimulated soil biological activity, as confirmed also by Stenberg et al. (2000). The dispersive effect is a consequence of increasing pH which destroys bonds created by highly active Al^{3+} and H^+ ions at acid pH.

1.2.2.3.4 Soil organisms

Surprisingly, only 10-20 % of the total amount of bacteria live in the soil solution whereas 80-90 % are bound to the solid soil phase (Hattori, 1973). Especially in clay-rich soils (> 30 %) microorganisms contribute to aggregation (Chesters et al., 1957) as a result of the high specific surface as well as energetic interaction between particle and cell surface albeit the negative charge of bacteria and fungi surface (Anderson, 1991). Depending on the grain-size distribution, microorganismens are found predominantly inside aggregates (sandy soils) or at the surface of aggregates (clayey soils) (Chenu et al., 2001). Microorganisms associate with mineral particles via hydrogen bond or polyvalent cations, and furthermore, exudate polysaccharides which allow adhesion on the one hand and on the other hand act like a protecting film against ingestion and drying. Depending on their origin, polysaccharides are of different quality: Exudated by plants, they are decomposed rather fast whereas bacterial and fungal polysaccharides are more recalcitrant, which is further enhanced by entering micropores (< 0.2 µm) or by polymerisation, the latter creating decomposition-resistant humus. But even agents of the same orgin, e. g. plants, may differ as Armbrust et al. (1982) reported more stable aggregates according to the following sequence of crops: soybean, grain sorghum, winter wheat.

Soil aggregation is also influenced by macrofauna, e. g. by earthworms that either compact or loose soils by bringing them into an intermediate state most suitable for plant growth and structural stability (Barré et al., 2009). Due to ingestion, soil can be destabilized, as the gut passage destroys some bonds (e. g. carbonate derived bonds) or it is stabilized due to the increase in organic matter and (in the wake of drying) hydrophobicity of the earthworm casts (Zhang and Schrader, 1993; Schrader and Zhang, 1997; Winsome and McColl, 1998). Furthermore, they increase the density of the bulk soil adjacent to their burrows (Schrader et al., 2007).

Plant roots affect the soil in a mechanical and chemical way, either by enmeshing especially coarse particles (Oades and Waters, 1991; Oades, 1993) or by the release of exudates (Oades, 1993; Haynes and Beare, 1997; Angers and Caron, 1998; Bronick and Lal, 2005). Another soil-physical aspect of roots is the increase of shear resistance due to their pillar-like shape (Makarova et al., 1998; Wu and Watson, 1998; Bischetti et al., 2009; Zhang et al., 2010) as well as the enhancement of cracking due to wet-dry cycles (Velde and Barré, 2010). Exudated mucilage (e. g. polygalacturonic acid) can link particles and decrease infiltration into aggregates due to hydrophobicity (Czarnes et al., 2000). But also fungi stabilize the soil similar to roots by their hyphae (Oades and Waters, 1991; Tisdall, 1991). Milleret et al. (2009) investigated the interactions of earthworms, arbuscular mycorrhizal (AM) fungi and plant roots and determined synergistic effects of roots and fungi in the absence of earthworms but also an overall self-organization of the soil-plant-microbe complex. In this respect, Bedini et al. (2009) found increased aggregate stability with AM fungi and the hydrophobic proteinaceous substance produced by the fungi while Hallett et al. (2009) stated that in their experiments roots had a stronger impact on soil structure than AM fungi. To some extent, roots and hyphae are encrusted by inorganic soil components thus slowing down decomposition (Oades and Waters, 1991).

1.2.2.3.5 Soil organic matter

According to Bohn et al. (2001) soil organic matter (SOM) consists to 95 % of dead plant material and partially decayed and resynthesized plant and animal residues. Upon decomposition leaves and roots add to this pool of SOM. Humus, on the contrary, is defined only as that component that has been transformed into a stable form by microorganisms that used energy of oxidation of organic carbon. Substances easily decomposed are monomers of sugars, amino acids and fats, followed by starch and proteins, while cellulose is longer-lasting, exceeded only by lignin and hydrocarbons. The process is accelerated by temperature (Bohn et al., 2001). Despite a classification according to decomposability, Golchin et al. (1994) classified organic matter in dependency of spatial distribution as either free particulate, occluded particulate or as colloidal or clay-associated SOM. In clay minerals organic molecules become incorporated into the interlayer sites due to complexing cations (Velde, 1992; Velde and Barré, 2010). The larger the molecules the more easily they can be incorporated directly without a need for cations with the help of van der Waals or hydrogen bonding. Other mechanisms of the incorporation of organic matter into clay minerals are e. g. exchange of inorganic with organic cations or the development of organic substances directly in the interlayer due to redox reactions (Lagaly, 1993). Large molecules orientated almost perpendicular to the sheets can increase the interlayer distance to up to 50 Å which is 2-3 times the size of the silicate itself. However, a strong interaction was observed with pH as low (0-2) and higher (> 5) pH causes desorption of organic matter (Velde, 1992). Large organic molecules can be adsorbed also on non-expandable clays. The thus evolving clay-organic complexes connect especially fine clay platelets by bonds so strong that even intense dispersion cannot separate clay and humic substances (Schwertmann and Niederbudde, 1993). Moreover, the adsorption on mineral surfaces impedes decomposition, due to reduced accessibility in the wake of microaggregation. This holds true especially for easily decomposable polysaccharides. Thus, in soils of higher clay content, SOM content is increased (Bohn et al., 2001). Kahle et al. (2002) also revealed a strong relationship between SOC and the specific surface area of the silicate minerals. As detected by Heil and Sposito (1995), organic matter roughened the surface of illites, thus decreasing the amount of contacts where van der Waals forces can attract particles mutually. This explained former investigations where organic matter decreased flocculation (Heil and Sposito, 1993). Also Schwertmann and Niederbudde (1993) report that humic substances adsorb on the edges of clay minerals and hence impede the development of a cardhouse structure. Investigations by Ekwue (1990) proved the importance of the quality of the organic matter itself: Organic matter from grassland significantly increased aggregate stability and shear strength whereas peat significantly reduced both stability parameters.

Polysaccharides are mostly produced by microorganisms and roots but also due to the decomposition of particulate organic matter (Jastrow, 1996). According to the theory of Monnier (1965, described in Abiven et al., 2009) polysaccharides exert a strong bonding force on particles but only for a short time period. Besides the direct linkage they can cluster in a gel-like substance and act like a glue (Haynes and Beare, 1997). Other glueing substances are humates, water-insoluble salts of humic acid bond to polyvalent cations (Bohn et al, 2001), phenols (Bronick and Lal, 2005) and lipids (Dinel et al., 1997).

Several authors found the effectiveness of organic substances in bonding particles to be a function of decomposability, thus revealing a strong but transient effect of easily decomposable substances and a less strong but long-lasting effect of recalcitrant substances (Tisdall and Oades, 1982; Kay, 1998; Martens, 2000; Abiven et al., 2009). This phenomenon is further enhanced by the isolation of normally labile organic matter in intra-aggregate pore space (Bronick and Lal, 2005). According to Von Lützow (2007), the transient mono- and polysaccharides act intensely after 2-3 weeks for 4-6 months, while maximum of the less effective cellulose is reached only after 6-9 months.

Organic matter is also of importance due to its water storage capacity (Asmus, 1990; Ekwue, 1990; Haynes and Naidu, 1998) which can attain 80 to 90 % water by weight (Bohn et al., 2001). Although this does not directly link particles, the persistence of water availability also at lower matric potentials ensures the lasting influence of menisici (Zhang, 1991; Bachmann and Zhang, 1991). In this regard of physical influence of organic matter, particulate organic matter has to be considered, consisting of large particles (250-2000 µm), either free or linked to soil partices (Bronick and Lal, 2005). Despite its ability to act as a nucleus for macroaggregate formation, it can refine the soil texture and thus grant the soil properties of soils richer in clay with respect to mechanical (size, expandability) and chemical aspects (cation exchange capacity). Generally, the presence of organic matter decreases bulk density (Ekwue, 1990; Pagliai and Antisari, 1993; Haynes and Naidu, 1998; Kay, 1998). Despite less contact points between mineral particles, that is generally considered as the main criteria for compressibility and stability (Hartge, 2000), increasing shear strength due to organic matter was reported (Ekwue, 1990; Horn, 1993) as well as higher tensile strength (Kavdir et al., 2004).

Another interaction with water reflects the generally negative impact of water on soil structure as it causes slaking of aggregates (Dexter, 1988; Le Bissonnais, 1996). Thus, a decrease of wetting rate helps prevent slaking which can be observed due to hydrophobicity by organic matter (Hallett and Young, 1999; Bronick and Lal, 2005; Hallett, 2008) and thus led to increase in water-stable aggregates (Rose, 1990; Ekwue, 1990). Mostly, hydrophobicity only develops after drying (Dekker et al, 1998; Hallett, 2008). This phenomenon, indeed inducing a good soil microstructure, can cause decreasing water capacity at the meso- and macroscale (Haynes and Naidu, 1998; Hallett, 2008).

1.2.2.4 Interactions with water: swelling and shrinkage

The liquid phase can have influences on particle-particle interaction, especially together with other, non-mineral particles. In this respect, water can hydrate dissolving ions like e. g. Na, thus changing the structure of water distinctively (Hillel, 1998), as can be seen in the increase of surface tension of water due to salts (Hartge and Horn, 1999) or the increase of viscosity of water due to e. g. model root and fungal exudates (Barré and Hallett, 2009). But hydration takes also place when expandable clays swell. According to Norrish (1954) two stages of swelling can be distinguished, the first being stepwise expansion of the layers due to the addition of monolayers of water (crystalline swelling), the second a continous expansion (osmotic swelling). The latter is a consequence of the tendency to diminish a concentration gradient between the bulk soil solution with a comparatively high concentration and the interlayer poor in ions. According to Low (1992, cited in Zhang et al., 1995), the two stages correspond to short-range swelling and long-range swelling as well as short-term forces and long-term forces, respectively. Exchangeable ions cause long-range repulsion forces between parcticles, resulting in lower compressibility of the clays (Bolt, 1956). Dontsova et al. (2004) found increasing water sorption on clay minerals with increasing ionic potential of the exchanged cation in the following order: $K^+ < Na^+ < Ca^{2+} <$ 50:50 $Mg^{2+}/Ca^{2+} < Mg^{2+}$. Monovalent cations caused less water sorption than divalent cations, and more hydrated cations (Na^+ and Mg^{2+}) more than larger cations (K^+ and Ca^{2+}). In agreement with this, Di Maio et al. (2004) detected decreasing compressibility due to increased soil solution concentration, enhanced by higher smectite amount. The authors assumed increase resistance to interparticle sliding as the reason which was confirmed by direct shear tests for some soils (Di Maio, 1996). In previous investigations the shear strength of kaolin was unaffacted by the solutions (Di Maio and Fenelli, 1994).

Swelling is the more pronounced the more expandable the clay mineral is, e. g. smectites. Schwertmann and Niederbudde (1993) even report the development of rills at the shear plane of smectite-rich soils, so-called slickensides. Usually, shrinkage is the first process of soil structure development as it causes cracks and hence macropores (Horn and Smucker, 2005). The capillary forces pull the mineral partices together, thus increasing the number of contact points. Shrinkage is the more pronounced the easier particles can be rearranged. However, if soil particles are already connected by a network of roots or cementing substances, shrinkage can disrupt this network (Barzegar et al., 1996). In accordance to this, Ghezzehei and Or (2000) found aggregates to coalesce and thus reduce interaggregate porosity in the wake of repeated wetting and drying cycles. However, in general a more negative matric potential increases the effective stress as the developing menisci strengthen the linkages between particles at the area of contact (Mitchell, 1993). Hence, the soil stability, determined e. g. as shear strength, increases (Bönsch and Lempp, 2007), also as a result of higher solid-solid friction (Karmakar and Kushwaha, 2007). But even at constant bulk density and water content (of sufficient height), soils can be strengthened due to age-hardening either by thixotropic particle rearrangement or cementation mechanisms Dexter et al. (1988).

1.2.2.5 Interactions with pH

Several studies investigated the effect of pH on rheology of clay suspensions and found increasing viscosity of the suspension (equivalent to higher level of flocculation) with very high and very low pH (Chang et al., 1993; Durán et al., 2000; Tarchitzky and Chen, 2002a; Tarchitzky and Chen, 2002b; Ramos-Tejada et al., 2003). At very low pH a scaffolding structure is formed by edge-to-face assocations while a high pH and ionic strength reduces the thickness of the electrical diffuse double layer and thus the repulsive forces. Chang et al. (1993) confirmed the later explanation by increasing ionic strength similarly with the help of NaCl. Furthermore, Durán et al. (2000) found a more elastic than viscous behaviour of suspensions at acid pH, hence indicating a re-creation of bonds destroyed in the oscillation movement. This pH-dependent behaviour is more pronounced for 1:1 clay minerals: Kaolinites e. g. exhibit a yield stress τ_B at low pH, where a complex cardhouse structure exists, whereas at alkaline pH the yield stress is incapable of measurement (Lagaly, 1993). Bentonites on the contrary display high yield stresses at low and high pH levels whereas at intermediate pH even newtonian flow can be observed. While the loss of structure at acid pH happens due to the same processes as observed for kaolinites, the increase at alkaline pH values is a consequence of delamination processes (the sheets are separated and hence cause a rough and irregular structure). Saturation with polyvalent cations, e. g. Ca^{2+}, shifts this turning point to lower pH values. The slope of the increase of τ_B with increasing pH is also increased due to the cementation of ribbon-like clay association by Ca cations.

1.2.3 Impact of interparticle interaction at the mesoscale: Atterberg limits

Both Atterberg limits and parameters derived in oscillating shear tests like those presented in this work can be called rheological parameters as they are determined by similar mechanisms, namely the ability of particles to slide past each other, either due to enough free water or due to a distance between particles large enough to reduce inter-particle attraction (Warkentin, 1961). Hence, several investigations on liquid and plastic limit (LL, PL) give hint on the impact of salts and other non-mineral substances in soils on shear resistance during an oscillating shear test. Warkentin (1961) found NaCl to decrease inter-particle repulsion enabling flow at lower water contents (i. e. a lower LL). Another important influencing factor is pH. While non-expandable clays exhibited edge-face associations at low pH and hence high LL, neutral clays were still flocculated but exhibited lower attractive forces. At high pH the main force is repulsion keeping particles in parallel arrangement, which in turn results in a higher LL again. The addition of salt causes face-to-face association that, however, have a lower LL than the parallel arranged clay minerals “fixed” by repulsion (Warkentin, 1961).

Furthermore, the LL decreases with increasing valency of the exchangeable ion LL if the clay is a high-swelling one but increases if the the clay is less expandable (Warkentin, 1961). The reason is a more intense flocculation of the low-swelling clays that rely more on the particle arrangement than on the repulsive or attractive surface forces. With respect to this, Dolinar and Trauner (2004) stated that for nonexpanding clay minerals LL depends on size and quantity of clay grains (i. e. the intergrain water) while for expanding minerals LL depends on the quantity of interlayer *and* intergrain water. Furthermore, Dolinar et al. (2007) concluded when investigating artificial soil samples of monomineralic clays and quartz that for non-expandable minerals PL and LL are a function of surface area and clay content whereas for expandable clays they are a function of both surface area, clay content and interlayer water content. A model developed with the input data of mineral composition and surface area had very good estimates where the remaining lack of fit was ascribed to organic matter. Hence, several authors found found soil organic carbon (SOC) to increase Atterberg limits (Blanco-Canqui et al., 2006; De Jong et al., 1990), while others stated that SOC was a good predictor of Atterberg limits only on less expansive soils (Mbagwu and Abeh, 1998; Joosse and McBride, 2003). In other studies, plasticity index was decreased (Zhang, 1994) or unaffected by SOC (Ball et al., 2000).

1.2.4 Impact of interparticle interaction at the microscale

As described in chapter 1.1 the common implementation of rheometry in soil science is the investigation of clay mineral suspensions. The common determination of rheological properties of clay suspensions measures the relationship between a shear force and the resulting shear rate when enclosed between two areas. With the help of the schematic drawing in Fig. 1-1 the concept can be explained.

The upper plate with area A is moving at a certain velocity v ($cm \cdot s^{-2}$) while the velocity of the lower plate equals 0. Hence, a gradient of v develops despite a constant ratio of shear velocity v and distance h (cm) ($\Delta v \cdot \Delta h^{-1}$). Provided that the flow is laminary instead of turbulent, the shear stress necessary for the movement τ (force F per area A, Pa) is proportional to the shear rate ($\Delta v \cdot h^{-1}$), expressed by the proportionality factor of η (Pa · s), the viscosity (Eq. 1.6).

$$\tau = \eta \cdot \dot{\gamma} \qquad (1.6)$$

If the viscosity is independent of shear rate, the flow behaviour is called newtonian, like that of water, where η barely depends on temperature. However, only few materials are real newtonian fluids, most exhibit different behaviour. Some other possibilities are displayed in Fig. 1-2. Clay mineral suspensions exhibit mainly a yield stress τ_B, that must be exceeded before flow starts; if the subsequent viscosity is constant the Bingham model can be applied while the Casson model must be considered if the viscosity decreases with increasing shear rate (Lagaly, 1993; Heller and Keren, 2002).

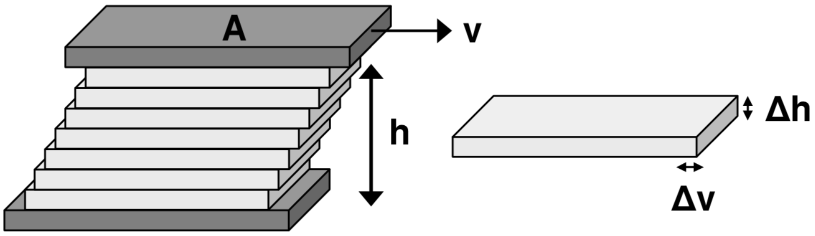

Figure 1-1: Schematic representation for the determination of flow and deformation behaviour

The existence of a yield stress τ_B derives from a shear resistant inner structure of the material that must be overcome (e. g. by destruction and/or parallel orientation of particles) although a yield stress is precluded by the theory of flow behaviour of clay minerals postulated by Battacharya and Letcher (1980): A smectite is said to behave like a liquid due to parallel alignment and like a solid due to transverse alignment, and in parallel alignment the particles should be able to slide past one another freely. Where the destruction of the network is not irreversible, thixotropie shows up as a consequence of bond recovery. To implement shear-thinning and shear-thickening (dilatancy) behaviour, the Bingham model can be supplemented by the Herschel Bulkley index (Mezger, 2006), which enabled Laribi et al. (2005) to detect shear thickening (dilatancy) with increasing clay content. According to Ghezzehei and Or (2000), the Bingham model can also be used to describe the flow and deformation behaviour of soil. However, recently Jeong et al. (2009) fitted data of 12 soils with different mineralogies and grain-size distributions with power law and found higher coefficients of determination than with the Bingham model.

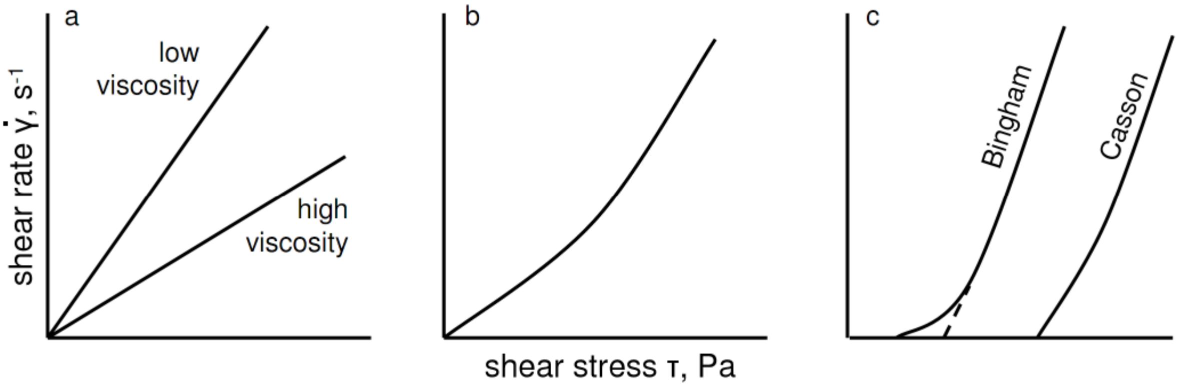

Figure 1-2: Selected flow curves of different materials: a) newtonian flow with low or high viscosity (due to high and low temperature of the same material or due to different materials at the same temperature), b) pseudoplastic flow, c) plastic flow with yield stress according to Bingham or Casson model (redrawn after Lagaly, 1993)

Shear forces acting directly on a pile of irregularly interstratified minerals cause a stepwise strain in this pile thus creating a stair-like morphology (Köster and Schwertmann, 1993). Generally, the plate-like structure of clays poses a challenge in predicting the deformation and flow behaviour. Neaman and Singer (2000) found higher viscosity and yield stress (indicating shear resistance of the suspension) the larger the length-width ratio of model particles was. Due to chemical interactions, clay particles can form a complex and stable structure, but once associations are disrupted, they tend to align with their long axis parallel to the shear stress acting on the shear plane (Mitchell, 1993; Cetin, 2004). In solutions, where the movement is less restricted, chemical bonds can be re-activated (due to attractive forces) so the suspension exhibits thixotrophic behaviour (De Kretser and Boger, 2001; Galindo-Rosales and Rubio-Hernández, 2006). However, several studies revealed higher viscosity with increasing solid concentration in the suspension in the wake of increased particle interference, eventually dilatancy (Chen et al., 1990; Neaman and Singer, 2000; Laribi et al., 2005). With regard to clay mineral Laribi et al. (2005) found pure smectites to have a higher Herschel-Bulkley yield stress than interstratified smectites, presumably due to a brittle structure in the presence of illites that collapses more easily upon stress.

1.3 Research objectives

The present work is part of a project of four groups in total. While the other groups of scientists investigated the effect of different potassium fertilization levels in interaction with water and salt stress on plant growth and yield as well as the long-term effect of differentiated fertilizer treatment on clay mineralogy and water retention, the objective was to determine the impact of fertilization on the interparticle forces displayed by shear resistance against oscillating shear forces. Bearing in mind the processes described previously, K might influence particle interaction either as an exchangeable cation or as an ion in the soil solution. Hence, soil samples from a common pool of long-fertilization trials with different levels of K fertilization as well as organic fertilization management, but also disturbed samples from glacial till were investigated to test the following hypotheses:

I. **How does K influence the forces between particles if it is present in the soil solution?** This research objective deals mainly with a short-term effect of K when it is present in the soil solution and how it changes the shearing resistance of a soil sample.

II. **What is the effect of K on microstructural properties in a long-term range?** This hypothesis is tested with the help of several long-term fertilization trials that consist of plots with different levels of K fertilization up to K depletion. The shear resistance of the soils is determined at several drainage levels and afterwards related to the physico-chemical properties of the soil to determine interactions between K fertilization and both soil properties resulting from fertilization as those site-specific properties.

III. **In what kind is the shear resistance at the particle-particle level influenced by organic matter? Which part of this influence can be related to the chemical change itself and what is the share of soil structuring processes? How do organic and K fertilization management interfere with each other with respect to the soil structure and shear resistance?** To test this hypotheses, a long-term fertilization trial is investigated that was set up to reveal the impact of organic versus mineral fertilization as well as the depletion of K on yield. The comparison of results from rheological measurements with results of common soil physical measurements like precompression stress is a first approach to scale rheological properties at the microscale up to the mesoscale. With the help of undisturbed and remoulded samples, an attempt is made to distinguish between the impact of fertilization itself or its indirect effect on soil aggregation e. g. via increased plant growth.

2 IMPACT OF POTASSIUM CONCENTRATION AND MATRIC POTENTIAL ON SOIL STABILITY DERIVED FROM RHEOLOGICAL PARAMETERS

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2.1 Abstract

The soil solution influences the soil stability in different ways: via water content as due to drainage menisci contract particles, and via the chemical composition including different ions in different amounts. While the first aspect was at least examined on the mesoscale, the second aspect remains widely unexplored when it comes to the influence of single ions on the microscale of soils. Previously published papers indicate a higher soil stability under the influence of potassium that cannot be explained only by its positive effect on plant growth and the enhanced shrinkage and swelling processes caused thereby. Parameters derived from rheological measurements can be used to examine the influence of soil solution in different compositions and matric potentials on soil microstructure. The rheological parameters were obtained by means of an amplitude sweep test where soil samples are subjected to oscillating forces with increasing deflection. From the sample's resistance towards this deformation storage modulus G' and loss modulus G" are derived, representing elastic and plastic deformation, respectively. Characteristic stability values of the moduli curves are the end of the linear viscoelastic (LVE) range indicating irreversible deformation and the yield point indicating flow. Additionally, the maximum shear stress during the test was used to characterize the maximum resistance of the sample against deformation.

In our investigations we found higher soil stability on the microscale with higher ion concentration and more negative matric potentials. With potassium chloride the LVE range extended and the yield point shifted to higher deformation and stress values. Consequently, the influence of potassium chloride resulted in a higher stability of the microstructure based on the storage and loss modulus as well as the shear stress. With increasing ion concentrations in the soil solution a further increase in microstructural strength was detected.

Regarding the influence of matric potential both the shear stress at the end of the LVE range and the maximum shear stress increased with more negative matric potentials, because a higher drainage intensity resulted in higher effective stresses caused by stabilising menisci, cemented bonds due to precipitation of salts and increased number of

contact areas between particles. Additionally, the yield point attained higher values for storage and loss modulus, respectively.

2.2 Introduction

For the determination of soil stability, soil is considered as a three-phase system consisting of solid, liquid and gaseous material. The interaction between the three phases strongly influences the ability of the soil to withstand mechanical and hydraulic stresses. Especially the liquid phase, the soil solution, can alter the soil stability in different ways. On the one hand there is the water content as due to drainage menisci contract particles. On the other hand the liquid phase owns a special chemical composition including different ions in different amounts. The first aspect was examined several times and is described in detail, e. g. in Fredlund and Rahardjo (1993), Mitchell (1993) and Iwata et al. (1995). However, the aspect of chemical composition lacks investigation especially regarding the influence of single ions at the particle to particle level. Markgraf and Horn (2006) found a higher soil stability due to potassium in the soil solution that cannot be attributed to the stabilising influence of improved plant growth due to higher potassium rates. Markgraf and Horn used homogenised soil mostly unaffected by plant growth, and, therefore, the increase in stability was only partly the result of shrinkage and swelling processes in the wake of water removal by roots and water supply by rain. Hence, potassium itself seems to account for the microstructural stability of soil. It can help to sustain the network between soil particles and to install new linkages between them. This in turn enables clay and silt particles to accumulate to pores of small diameter (0.2 – 50 µm) which are able to store water in a plant available way. Consequently, potassium can contribute to the preservation and improvement of soil structure and its resistance to shearing and loading forces as well as to the storage capacity of the soil for plant available water.

Until now, the influence of the soil solution chemistry is rarely taken into account when investigating soil stability. Yet Rosenqvist (1984) already stated that shear strength τ (Pa) does not only depend on normal stress σ (Pa), cohesion c (Pa), and angle of internal friction δ (°) as described in the Mohr-Coulomb failure criterion (Eq. 2.1) but is also influenced by the soil solution itself.

$$\tau = c + \sigma \cdot \tan\delta \qquad (2.1)$$

Terzaghi's concept of effective stress was developed for consolidating soils but can be combined with the Mohr-Coulomb equation to define the shear strength of a saturated soil (Eq. 2.2, according to Fredlund and Rahardjo, 1993):

$$\tau = c + (\sigma - u_w) \cdot \tan\delta \qquad (2.2)$$

The effective stress term consists of total normal stress σ on the failure plane at failure minus pore water pressure at failure u_w (Pa). For unsaturated soil also the pore air pressure u_a (Pa) has to be considered as shown in Eq. 2.3, although its magnitude is small:

$$\tau = c + (\sigma - u_w) \cdot \tan\delta + (u_a - u_w) \cdot \tan\delta' \qquad (2.3)$$

Here δ′ denotes an angle representing the rate of increase in shear strength relative to the matric suction ($u_a - u_w$).

Coulomb's failure equation does only indirectly include the cementing effect of precipitated mineral substances at the areas of contact between particles via the parameter c but an explicit consideration and quantification of the effect are missing. This is surprising, because already Rosenqvist (1984) explained that in all natural geological deposits secondary cementation exists which originated from inorganic components like calcium carbonate but also from organic matter. Depending on its quality, the latter can generate stable bonds with and between mineral components that stabilise the soil through increased hydrophobicity against slaking during wetting (Zhang and Hartge, 1992; Goebel et al., 2005). Attractive and repulsive forces that act between charged particles are also neglected. The cementing bonds might be defined as non-reversible, and therefore, they are part of the cohesion term. The second group of reversible bonds as well as attractive and repulsive forces, however, can be characterized as a kind of internal stress. The internal and external stresses result together in the effective stress.

In previous studies, rheometry was found to be an appropriate method to investigate soil particle interactions at the microscale. Many of the studies used suspensions. The influence of pH (Chen et al., 1990; Chang et al., 1993; Abend and Lagaly, 2000; Duràn et al, 2000; Neaman and Singer, 2000a, 2000b; Tarchitzky and Chen, 2002), ionic strength, temperature (Chang et al., 1993), as well as salt concentration and solid content (Abend and Lagaly, 2000) of clay mineral suspensions on rheological behaviour were investigated. The impact of ionic strength alone was also determined many times (Keren, 1988; Chen et al., 1990; Ramos-Tejada et al., 2001; Sakairi et al., 2005). Abend and Lagaly (2000) discovered that very low and very high salt concentrations caused high yield stresses, which means that the state of yielding, i. e. flow as a result of the internal breakdown of the stabilising structure due to mechanical stresses (via shear rate), is reached only at higher stresses. Additionally, the plastic viscosity as the slope of shear stress vs. shear rate curves was increased, too. While the type of salt had only little influence on rheological parameters, the counter-ion seemed to be more important. The impact of salinity was also investigated by Torrance (1999). Sodium decreased yield stress distinctively whereas calcium caused far higher yield stress values at quite low absolute salinities. Torrance concluded that the impact of different inorganic cations is as follows: monovalent < divalent < trivalent but bearing in mind differences in the efficiency of ions of the same valence. In this regard Rosenqvist (1955), e. g. found K to be more effective than Na. The dispersing effect of sodium on suspensions of clay saturated by Ca or Mg was also proved by Keren (1989) and is utilised for the separation of particles for the grain size distribution analysis (Hartge and Horn, 2009).

Results gained for clay suspensions of high solid content can be taken as an indication for the behaviour of clay rich soil samples. But we still lack information about naturally structured soils instead of suspensions with high water content and solids consisting only of a certain grain size or clay mineral. Rheological investigations of soils in its natural saturation state instead of using suspensions were done by Ghezzehei and Or (2000, 2001). They described their results with the help of the Bingham model that Vyalov (1986) stated to be applicable to soil deformation behaviour. A rheometer for determining rheological parameters of soil samples was used by Ghezzehei and Or (2001), Markgraf et al. (2006) and Markgraf and Horn (2006, 2007). Those investigations dealt with the impact of water content and clay type (Ghezzehei and Or, 2001) but also with the impact of salinity on natural compounds of soil. For example, Markgraf et al. (2006) and Markgraf and Horn (2006) have shown that NaCl increases the microstructural stability of soils.

The paramount aim of this investigation was to study the impact of pore water chemistry and pore water pressure on soil stability. The first research objective was to study the effect of increasing ionic strength on rheological parameters of soil samples with a rheological test. The second objective was to evaluate the influence of matric potential on the deformation behaviour in unsaturated samples.

2.3 Theoretical background on rheometry

Rheological behaviour ranges from perfectly elastic to perfectly viscous behaviour. The former was described first by Hooke's law which expresses a linear relation between shear stress τ acting upon a body and the resulting deformation γ (%), as can be seen by the example of a spring. Here, any deformation is reversible. Perfectly viscous substances, however, can be described with the help of Newton's law. Here, the shear stress acting upon a liquid is proportional to the shear rate, the proportionality factor being the viscosity, constant for a given temperature. In contrast to perfectly elastic substances, the deformation of perfectly viscous substances is irreversible, i. e. it is plastic. This behaviour is typical for a dashpot.

Soil is neither a perfectly elastic nor plastic substance. Instead it can be classified as viscoelastic material which exhibits both elastic and plastic behaviour (Markgraf and Horn, 2006; Markgraf et al., 2006).

The rheological measurements conducted for this work can be explained with a two-plate-model (see Fig. 2-1). Here, a soil sample is enclosed between two plates, where the lower one is fixed and the upper one is moving in an oscillating manner. The deflection distance s (m) of the upper plate follows a sigmoidal course whereas at the lower plate s = 0. The corresponding shear stress τ results from the force F (N) needed to generate the shear deformation along the shear surface A (m^2) (Eq. 2.4). The deformation γ is calculated from the distance s and the gap between the plates h (m) (Eq. 2.5).

$$\tau = F/A \tag{2.4}$$

$$\gamma = s/h \tag{2.5}$$

During the so-called amplitude sweep test the oscillation amplitude increases as the deformation is raised, e.g. from 0.0001 % to 100 % where s = h.

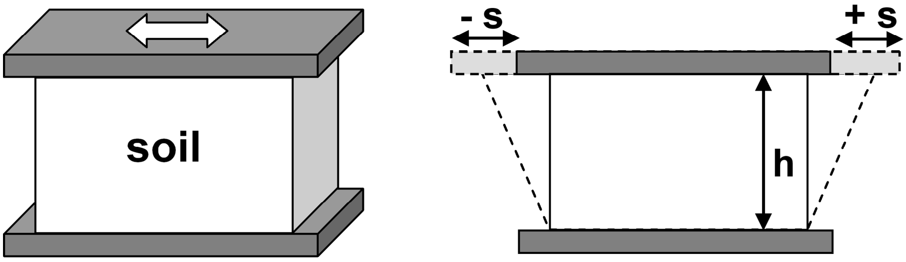

Figure 2-1: Two-plate-model of oscillation (s = deflection distance, h = gap between plates) (adapted from Mezger, 2006)

Because of the oscillating movement the resulting graphs also show a sigmoid course (see Fig. 2-2). The relationship between the given deformation and the resulting shear stress is characteristic for a material. Perfectly elastic substances, e. g. react directly on the deformation, and, therefore, the preset and the resulting curve are in phase. Maximum deflection of the upper plate equals maximum shear stress. Perfectly viscous samples exhibit the opposite behaviour. They show a shift of exactly 90°, i. e. at maximum deflection τ = 0. Hence, this phase shift angle δ can be used to classify the flow and deformation behaviour of a sample (Tab. 2-1). For soil as a viscoelastic material δ ranges between 0° and 90°.

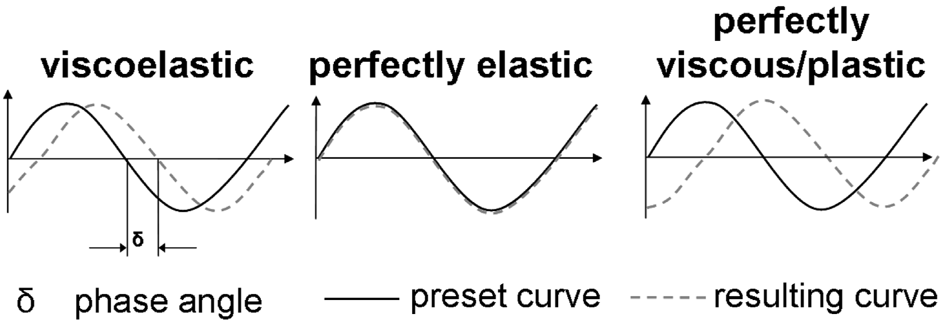

Figure 2-2: Phase shift angle δ between sigmoid preset and resulting curves representing different materials, ranging from perfectly elastic to perfectly viscous)

Table 2-1: Classification of flow and deformation behaviour based on loss factor tan δ, phase shift angle δ and storage and loss modulus G' and G''

Perfectly elastic	Mainly elastic	Yield point	Mainly viscous	Perfectly viscous
tan δ = 0	0 < tan δ < 1	tan δ = 1	tan δ > 1	tan δ = ∞
δ = 0	0 < δ < 45°	δ = 45°	45° < δ < 90°	δ = 90°
G' >> G"	G' > G"	G' = G"	G' < G"	G' << G"

The resistance of the sample against the deformation is recorded as torque M (Nm). From this and the radius r (m) of the plate the shear stress can be calculated with Eq. 2.6:

$$\tau(t, M) = (2\cdot M)/(\pi\cdot r^3) \qquad (2.6)$$

Besides the general course of the shear stress during the amplitude test, the maximum shear stress can be used to characterize the maximum resistance of a sample against the oscillating movement. Furthermore, it enables us to compare the results with those derived from the more common shear tests, e. g. the frame shear test, where the maximum shear strength as a function of normal stress is recorded.

The shear stress is derived from the deformation γ and the shear modulus G (Pa) as shown in Hooke's law (see Eq. 2.7), G being constant for a given perfectly elastic substance.

$$\tau = G \cdot \gamma \qquad (2.7)$$

In an oscillation test this shear modulus turns into a complex shear modulus G* since it consists of elastic and viscous parts. As can be seen in Eq. 2.8 the shear stress is then described by means of storage and loss modulus G’ and G”, each representing the elastic and viscous behaviour of the sample, respectively.

$$\tau(t) = G^* \cdot \gamma(t) \text{ with } |G^*| = [(G')^2 + (G'')^2]^{1/2} \quad (2.8)$$

Both moduli again depend directly on deformation, shear stress and phase shift angle (Eq. 2.9):

$$G' = \tau/\gamma \cdot \cos\delta \text{ and } G'' = \tau/\gamma \cdot \sin\delta \quad (2.9)$$

To classify a sample’s flow and deformation behaviour the loss factor tan δ is used which describes the ratio of elastic to viscous behaviour, G”/G’ (Fig. 2-3 and Tab. 2-1). Fig. 2-3 illustrates a typical result of an amplitude sweep test showing the parameters storage and loss modulus G’ and G” as well as the loss factor tan δ as a function of deformation. The arrows mark the characteristic values used for the interpretation of the test.

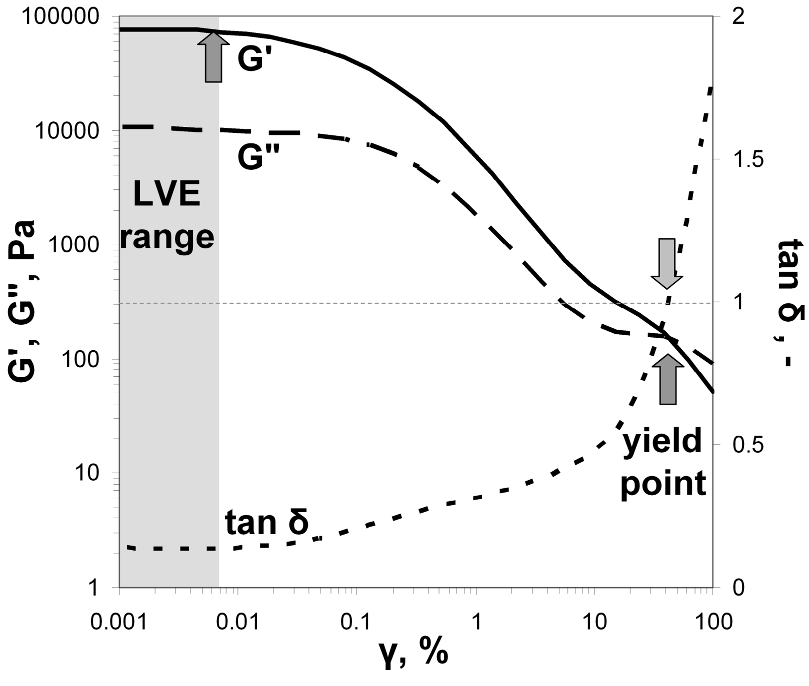

Figure 2-3: Typical result of an amplitude sweep test (—G’,— — — G”, - - - tan δ)

At the beginning of the test G’ is higher than G”, i. e. the sample exhibits mainly elastic behaviour (tan δ < 1). As long as the linear viscoelastic (LVE) range is not exceeded deformation is fully reversible. Increasing deformation (increasing deflection values) beyond the LVE range causes cumulative irreversible distortion of the sample indicated by a decrease of both G′ and G″. Note that the decrease of G″ is smaller than of G′ corresponding to an increase of tan δ which reflects a more viscous deformation behaviour. The yield point is reached when tan δ = 1 meaning that G′ equals G“. Hence similar shares of elastic and viscous behaviour occur and the sample is considered to start flowing. A further increase of deformation causes a state where G″ exceeds G′ and tan δ increases steeply above 1 indicating that a threshold of microstructural resistance of the sample is reached.

More detailed information about rheological fundamentals is given in the introductory works by Keedwell (1984), Vyalov (1986), Gehm (1998) and Mezger (2006).

2.4 Material and methods

2.4.1 Soil samples and preparation

For the measurements specimen were prepared from two kinds of material, namely glacial till from Schleswig-Holstein, to examine the impact of different salt concentrations and silty loess from the experimental field Dikopshof in Bonn, Germany, to determine the effect of decreasing matric potential on the mentioned rheological parameters.

The glacial till is characterized by a sand content of 42 % and a silt content of 38 % together with a high calcium carbonate content of 17 %.

The soil was air-dried at 20° C and sieved to <0.63 mm diameter. Afterwards, five specimens per treatment with a height of 4.5 mm and 36 mm in diameter were prepared with a defined bulk density of 1.5 g cm^{-3}. Subsets of samples were saturated with deionised water and solutions of defined KCl concentration (0.25, 0.5, 0.75 and 1.0 mol L^{-1}) for 3, 7 and 14 days and measured thereafter.

The concentrations of the salt solutions correspond to those under in situ conditions of salt affected soils (Rengasamy and Olsson, 1991). However, they are partly higher than normal concentrations of agriculturally used soils in humid climates. To estimate the potential ionic strength of a field soil solution we calculated the molarity of a soil solution (0.3 m depth, 1.5 g cm^{-3}) after an application of 200 kg K ha^{-1}. Assuming that the soil is completely saturated the soil solution has a concentration of approximately 0.004 mol L^{-1}. This is much lower than the concentration levels in our investigations. However, if the soil is only partly saturated the concentration increases in the remaining solution to 0.02 mol L^{-1} (20 % volumetric water content). Nonetheless, we chose relatively high concentrations for our investigations to find out if the method is sensitive enough to detect effects of nutrients on rheological parameters. Also, little research has been done on the influence of different salts on rheological properties of soil samples, and, thus, we lack information about the boundary conditions. This experimental setup covers a wide range of salt concentrations, also to detect ranges that need a more detailed consideration in future investigations, e. g. concentrations between 0 and 0.25 mol L^{-1}.

Secondly, we tested samples from the A horizon of a Luvisol from an experimental field with potassium depletion (Dikopshof in Bonn, about 15 km south of Cologne) that were air-dried and sieved to <0.2 mm diameter. Specimen as described before with five replicates per treatment were prepared and saturated by capillary rise to an equilibrium and measured partly in this state of saturation; others were pre-dried to different water potentials ranging from -0.5 to -3 kPa before rheological measurements were conducted. For the purpose of distinct differentiation the samples of glacial till and from the experimental field Bonn will be referred to as glacial till and Bonn loess in the following. Some physical and chemical properties of the two investigated soil substrates are given in Tab. 2-2.

Table 2-2: Some physical and chemical properties of the investigated soil material

Soil material	**Glacial till**				**Bonn loess**			
Texture (%)	Sand	41.8	Coarse	3.6	Sand	5.9	Coarse	0.1
			Medium	11.6			Medium	1.8
			Fine	26.8			Fine	4.0
	Silt	38.5	Coarse	12.8	Silt	67.1	Coarse	41.7
			Medium	14.1			Medium	19.4
			Fine	11.6			Fine	6.0
	Clay	19.7			Clay	26.9		
pH ($CaCl_2$)	7.3				6.1[a]			
$CaCO_3$ (%)	16.9				0.0´[b]			
C_{org} (%)	0.3				0.8[b]			

[a] Reeb, unpublished.

[b] Jahn, unpublished.

2.4.2 Rheological measurements

The stability parameters were measured with a rheometer MCR 300 (Anton Paar, Stuttgart, Germany) with a parallel-plate measuring system 25 mm in diameter. The gap between the profiled plates was set to 4 mm following Mezger (2006) who recommended that the distance between the plates should at least be 5-10 times the diameter of the largest particle in the sample. The conducted amplitude sweep test is described in detail in section 2.3. The pre-settings for the conducted amplitude sweep test were derived by Markgraf et al. (2006) and are shown in Tab. 2-3.

Table 2-3: Pre-settings of the conducted amplitude sweep test according to Markgraf et al. (2006)

Parameter	Range/Value
Deformation	$\gamma = 0.0001 – 100$ %
Frequency	$f = 0.5$ Hz
Measuring points	30

2.5 Results

2.5.1 General observations

The general course of the storage modulus with increasing deformation shows distinct differences between samples saturated with deionised water compared to those saturated with potassium chloride (Fig. 2-4). Starting at a high level of 100,000 and 450,000-600,000 Pa for samples saturated with deionised water and 1 mol L^{-1} concentration of potassium, respectively, the storage modulus G’ soon decreased at deformation values of 0.01-0.1 %.

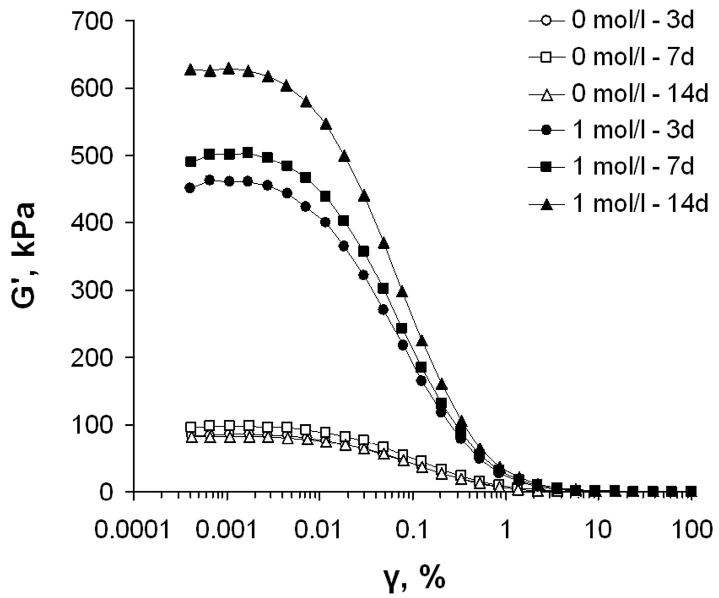

Figure 2-4: Storage modulus G′ of glacial till samples as a function of the deformation γ and of different solution concentrations after different aging times (3, 7 and 14 days)

The effect of equilibration time on the storage modulus can be clearly seen for samples saturated with salt solution. Increasing equilibration times increased the storage modulus (Fig. 2-4). Furthermore, the storage moduli of the samples saturated with 1 mol L^{-1} KCl solution were much higher than those for samples saturated with deionised water (Fig. 2-4). In the LVE range the storage modulus G′ for 1 mol L^{-1} KCl was almost sixfold higher as for deionised water. However, differences in G′ became smaller as the deformation increased. For example, we measured 80 Pa at 100 % deformation. The same trend is also true for the samples with lower concentrations.

The ratio of G″ and G′, i.e. the loss factor tan δ, is obviously not influenced by aging time (Fig. 2-5). It shows nearly the same trend after 3, 7 and 14 days for samples with the same treatment. But tan δ is influenced by salt concentration. Samples saturated with salt solution showed generally higher values, i. e. the viscous portion of the flow behaviour is higher, and, therefore, the structure is less stable. Furthermore, the curves represent sections with different and characteristic behaviours. At low deformation values until approximately 0.01 % the ratio remains constant. The samples with deionised water then showed a steady increase in the ratio whereas the samples with salt solution reached a second plateau around 0.5 % deformation. At about 2 % deformation they also increased steeply. As a consequence, the salt-free samples attained the yield point (tan δ = 1) first indicating a transition to mainly viscous/plastic behaviour at an earlier stage of the test as for the salt samples. At deformations beyond the yield point the differences between samples with and without salt solution are not significant anymore.

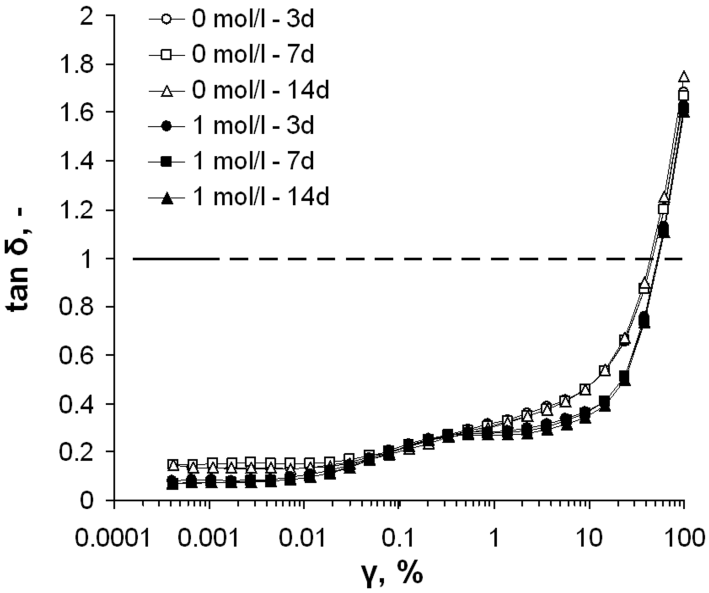

Figure 2-5: Loss factor tan δ of glacial till samples as a function of the deformation γ and of different solution concentrations. The dashed line represents the transition from mainly elastic to mainly plastic behaviour

Also, the shear stress itself is influenced by different aging times (Fig. 2-6). The effect is more pronounced for the samples saturated with KCl solution than for those saturated with deionised water. The highest shear stresses are found after saturation with 1 mol L^{-1} KCl solution for 14 days. For deionised water extended aging time did not significantly increase shear stress.

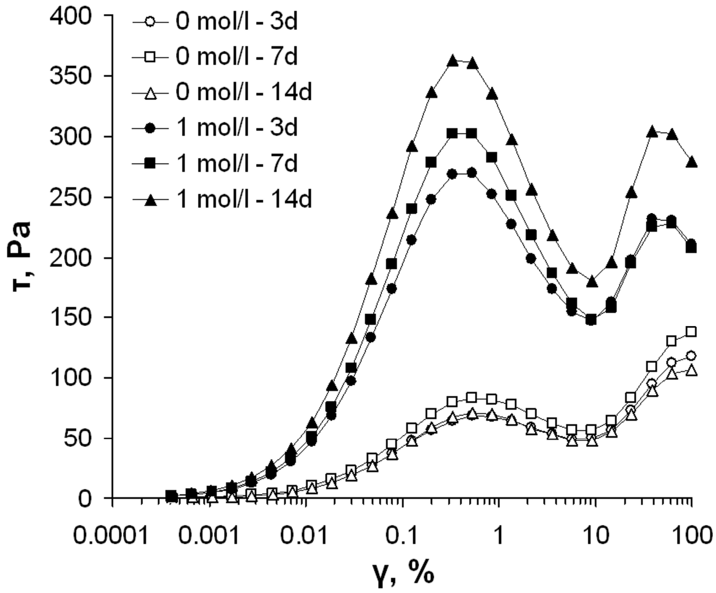

Figure 2-6: Shear stress τ as a function of the deformation γ and of different KCl solution concentrations and aging times

In the following graphs only the values for 3 days equilibration time will be shown. Increasing salt concentration of the saturating solution caused an increase in the storage modulus (Fig. 2-7). Already the lowest salt concentration, i. e. 0.25 mol L^{-1} KCl solution in our experiments, caused a distinct increase in storage modulus compared to the sample with deionised water, whereas the highest values were obtained for the samples saturated with 1 mol L^{-1}. However, with higher deformation the differences between the values tend to diminish.

The effect of increasing potassium chloride concentration on the loss modulus G" can clearly be seen (Fig. 2-8). With increasing salt concentration higher values were recorded. Furthermore, considering the samples saturated with deionised water, the loss modulus decreased slowly until 0.05 %, fell steeply afterwards and approached a value of zero at deformations beyond 1 %. The higher the salt concentration the higher was the loss modulus and the more pronounced was a peak at a deformation of about 0.05 %. The most distinct peak appeared at the samples saturated with 1 mol L^{-1} KCl solution.

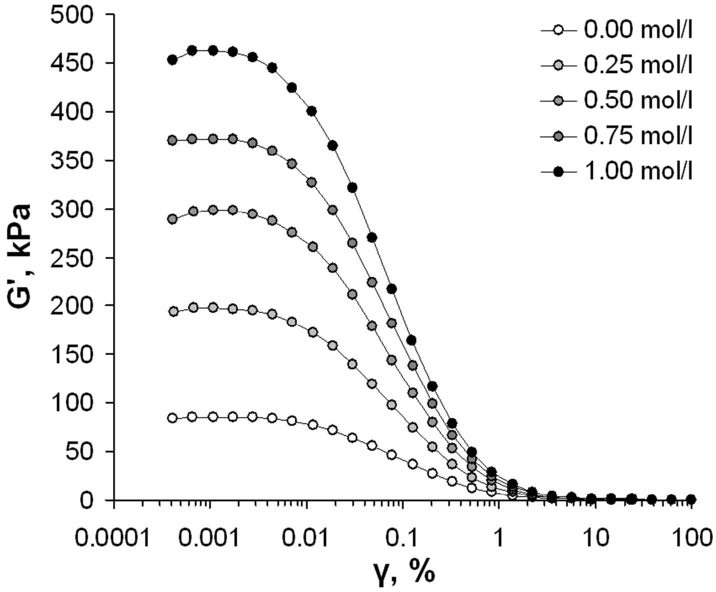

Figure 2-7: Storage modulus G′ of glacial till samples as a function of the deformation γ and of different KCl solution concentrations after 3 days of equilibration time

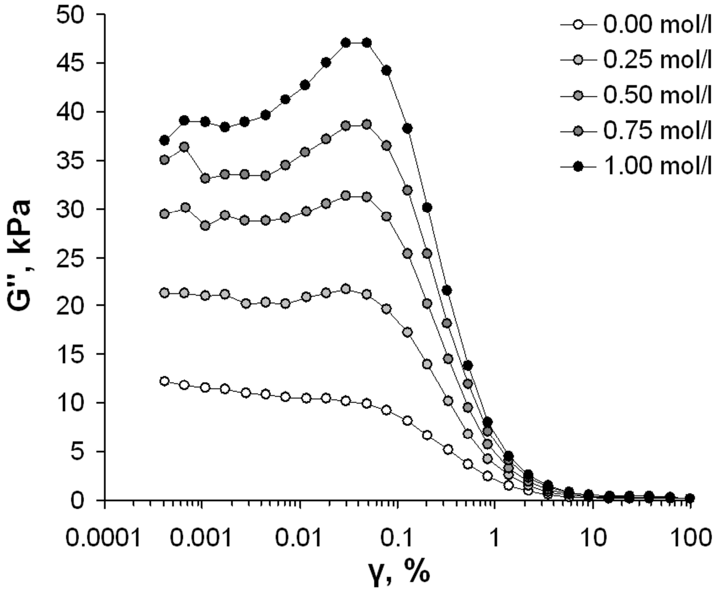

Figure 2-8: Loss modulus G″ of glacial till samples as a function of the deformation γ and of different KCl solution concentrations

2.5.2 Rheological parameters in the linear viscoelastic (LVE) range

To compare statistically the stability of differently treated samples characteristic rheological parameters were derived. Shear stress at the end of the LVE range increased linearly and highly significant with increasing KCl concentration (Fig. 2-9) which indicates a stabilisation of bonds between soil particles. The deformation and therefore the lateral displacement acting upon the samples is comparatively low, hence the absolute shear stress values range from 6.9 to 32.3 Pa.

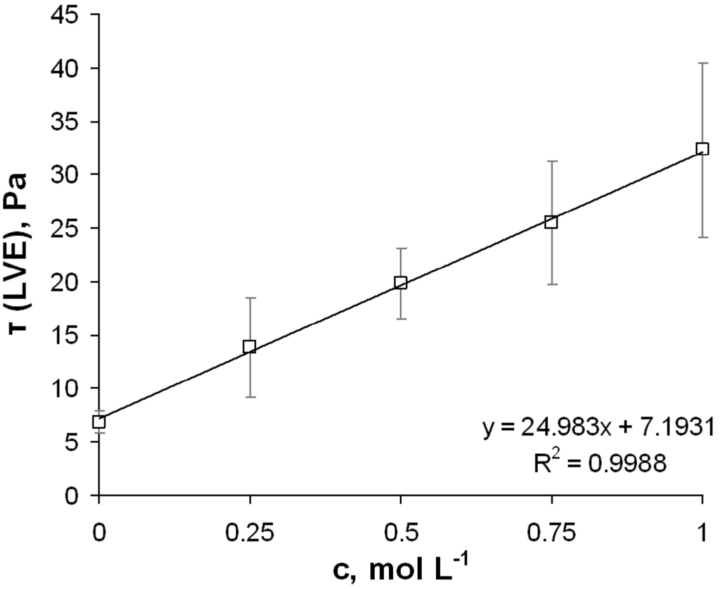

Figure 2-9: Shear stress τ at the end of the LVE range of glacial till samples as a function of the KCl concentration. Error bars show one standard deviation

2.5.2.1 Maximum shear stress

As already shown in Fig. 2-6 the shear stress indicates a higher stability with higher concentration of soil solution for the complete deformation range. Especially the maximum shear stress during the amplitude sweep test is positively related with the increasing KCl concentration in the saturating solution (Fig. 2-10). The soil sample, therefore, can provide a higher resistance against deformation if there are more cations in the soil solution. Compared to the shear stresses at the end of the LVE range the maximum shear stresses reach higher values and range from 70 to 272 Pa for 0 and 1 mol L^{-1} KCl, respectively.

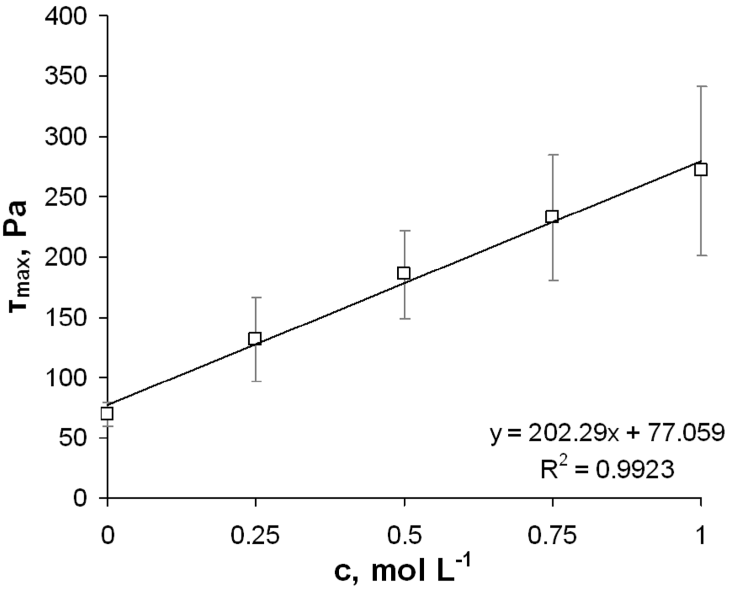

Figure 2-10: Maximum shear stress τ of glacial till samples as a function of the KCl concentration. Error bars show one standard deviation

The maximum shear stress during an amplitude sweep test can be compared to the shear stress resulting from regular shear tests on the mesoscale (e. g. frame shear test). At the maximum shear stress a normal force of 0.03 N and 0.5 N for solution concentrations of 0.0 and 1.0 mol L^{-1}, respectively, were recorded. With a plate diameter of 2.5 cm the area equals 4.91 10^{-4} m^2. Hence, the corresponding stress values are 61.1 and 1018 Pa for 0 and 1 mol L^{-1} KCl concentration, respectively.

2.5.2.2 Yield point

The yield point indicates the transition from mainly elastic to mainly viscous behaviour. At that point the inner structure of a sample will be irreversibly destroyed and the sample begins to flow. For the characterization of the micromechanical behaviour of a soil sample the deformation and the storage modulus at the yield point are of interest as shown in Fig. 2-11 and 2-12, respectively. Fig. 2-11 indicates that the transition to mainly plastic behaviour is shifted to higher deformation values with increasing KCl concentration. With higher potassium concentration in the soil solution a higher resistance must be exceeded to reach a viscous state (Fig. 2-12). The effect of increasing KCl concentration is more pronounced for the parameter storage modulus compared to the parameter deformation at the yield point. A soil solution of 1 mol L^{-1} KCl doubled the storage and loss modulus, respectively, whereas it increased the deformation only by ~ 15 %.

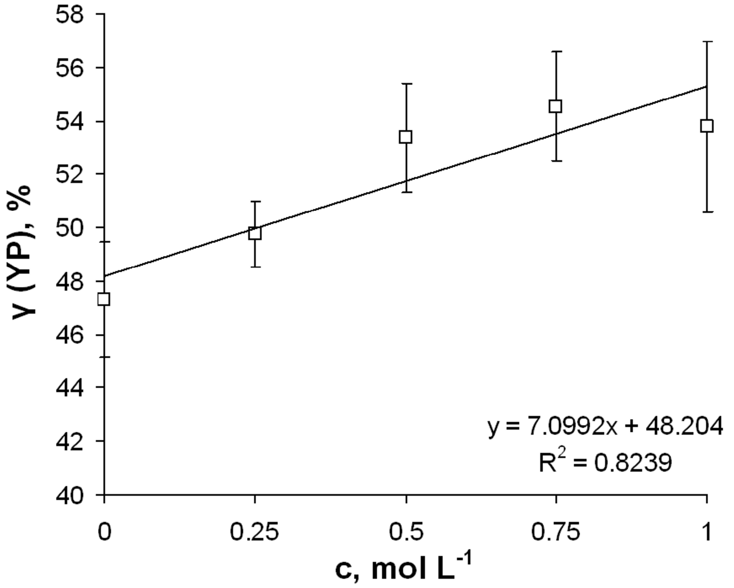

Figure 2-11: Deformation γ at the yield point of glacial till samples as a function of the KCl concentration. Error bars show one standard deviation

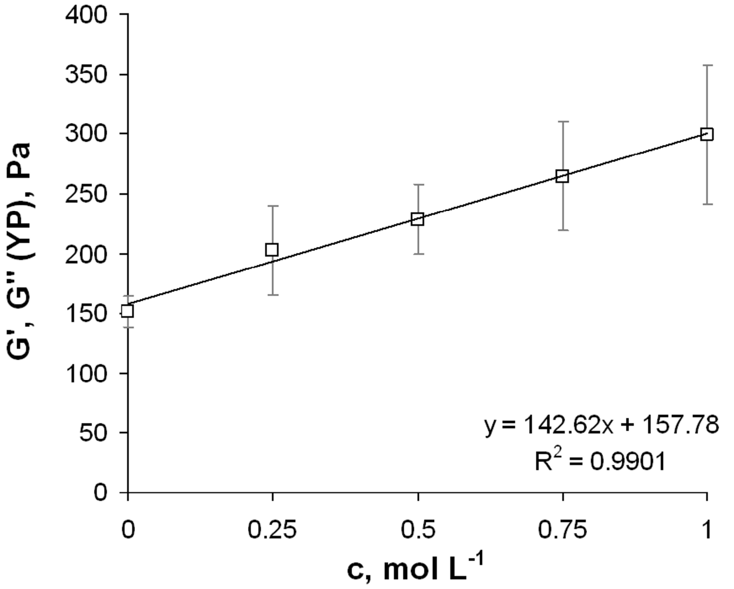

Figure 2-12: Storage modulus G’ and loss modulus G” of glacial till samples at the yield point as a function of the KCl concentration. Error bars show one standard deviation

2.5.2.3 Influence of matric potential

The following graphs show the results of the amplitude sweep tests with homogenised soil samples from the long time fertilization trial with K depletion in Bonn. All samples were measured after equilibrating them to different matric potentials in order to investigate the effect of water menisci forces on inter-particle strength.

The shear stress at the end of the LVE range increases with decreasing matric potential (Fig. 2-13). The more negative the matric potential, the higher the stress that must be exceeded to cause irreversible deformation.

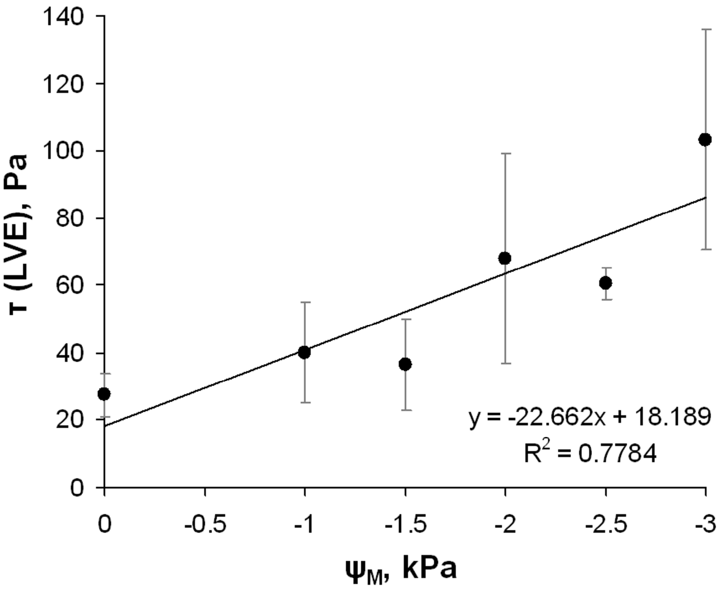

Figure 2-13: Shear stress τ at the end of the LVE range of Bonn loess samples as a function of the matric potential. Error bars show one standard deviation

The parameter τ_{max} is influenced in the same manner (Fig. 2-14). A more negative pore water pressure causes higher shear resistance and therefore a higher stability. The same is true for the yield point (given in Fig. 2-15) which is shifted to higher storage and loss modulus values.

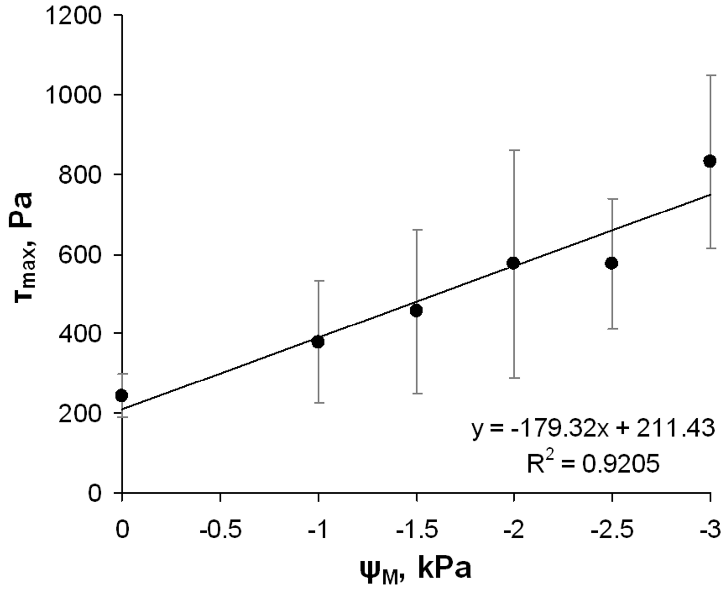

Figure 2-14: Maximum shear stress τ of Bonn loess samples as a function of the matric potential. Error bars show one standard deviation

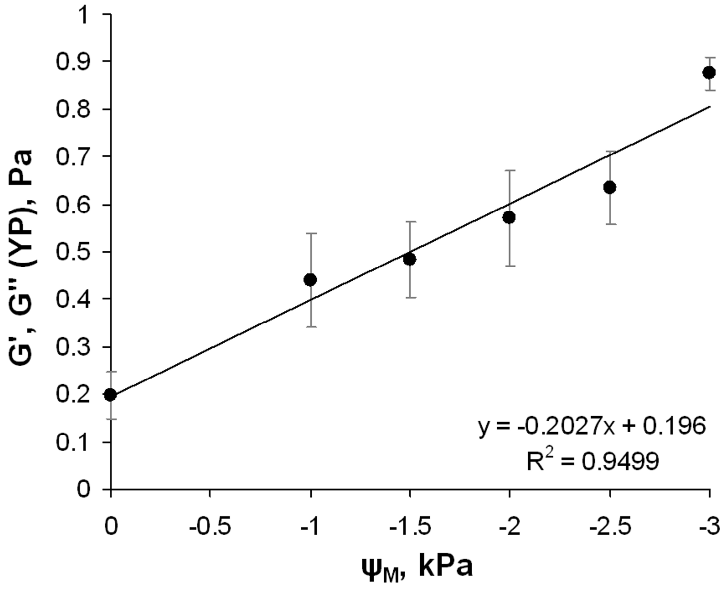

Figure 2-15: Storage and loss modulus G' and G" at yield point of Bonn loess samples as a function of the matric potential. Error bars show one standard deviation

Compared to the influence of increasing salt concentration the influence of increasing drainage is less clear and does not always obey a linear relationship. A direct comparison of the absolute values given in Tab. 2-4 shows that the Bonn loess samples at 0 kPa matric potential are more stable than the glacial till samples saturated with deionised water (27.5 and 6.9 Pa, respectively). A matric potential of -3 kPa caused a shear stress at the end of the LVE range threefold as high as under saturated conditions. To obtain an equivalent increase of τ_{max} with KCl solution a concentration of 0.5 mol L^{-1} is necessary.

Table 2-4: Comparison of the stabilizing effects of matric potential Ψ_M and salt concentration in the soil solution on the maximum shear stress τ_{max} of glacial till and Bonn loess, respectively

	KCl concentrations and matric potential, respectively					
c (KCl), mol L^{-1}	**0**	**0.25**	**0.5**	**0.75**	**1.0**	
τ_{max}, Pa (glacial till)	6.9	13.8	19.9	25.5	32.3	
Ψ_M, kPa	**0**	**-1**	**-1.5**	**-2**	**-2.5**	**-3**
τ_{max}, Pa (Bonn)	27.5	40.0	36.5	67.9	60.5	103.3

2.6 Discussion

2.6.1 Influence of soil solution chemistry

2.6.1.1 Influence of salts on attractive and repulsive forces

The results presented in this study are consistent with the electrical double layer theory for particle-solution interactions in colloidal systems as explained by Van Olphen (1977). According to this theory, repulsion and attraction between particles depend on the distance between them. It is well known that an increase of the concentration in the soil solution reduces the thickness of the electrical double layer around the particles and therefore reduces the repulsive forces between them. As, in contrast, the attractive van der Waals forces remain constant independently of electrolyte concentration, the summation of repulsive and attractive forces results in different net potential curves. Hence, a low electrolyte concentration causes predominantly repulsion whereas at a high electrolyte concentration no repulsion at all exists. Consequently, our results confirm this theory as we proved the stabilising effect of increased KCl concentration. The more K^+ ions are in the solution the smaller are the repulsive forces. Thus, particles are attracted by each other and form clusters of particles that in turn cause a higher shear resistance.

According to the Van Olphen theory (1977), a short-range repulsion causing decreasing attraction between particles with increasing concentration can also be detected. This repulsion consists of two possible forces. The first is the Born repulsion caused by the resistance to interpenetration of crystal lattices. The second results from a water layer absorbed by the particle surface. The work required to desorb the water causes a short-range repulsion. Both short-range repulsive forces determine a very steep rise of the net potential curves at very low particle distances. As a result the net attracting force at short-range distances decreases with increasing electrolyte concentration and increases again after reaching a minimum (Chen et al., 1990). The corresponding Bingham yield values derived with montmorillonite suspensions showed the same development, so did plastic viscosity (Chen et al., 1990; Abend and Lagaly, 2000; Ramos-Tejada et al., 2001). Our results did not show those characteristics as the ionic strength was raised directly to 0.25 mol L^{-1}, while this phenomenon was observed by Abend and Lagaly (2000) and Chen et al. (1990) at 0-0.005 mol L^{-1} NaCl, and it took a concentration of 0.05 mol L^{-1} to exceed yield stress and plastic viscosity derived with pure water. Therefore, at 0.25 mol L^{-1} the curves of the rheological parameters are already on their ascending part.

2.6.1.2 Influence of salts as cementing substances

In clay suspensions undergoing shear deformation, interparticle bonds are permanently broken and rebuild (Chen et al., 1990). Goodwin (1975) explained the decrease of viscosity at high shear stress by a lack of a rebuilding ability. A breakdown of clay platelet associations is caused by both shear stress and Brownian motion (if the movement is mostly unrestricted as, e. g. in a suspension). However, the build-up of new bonds originates only from Brownian motion. Higher shear stress, therefore, reduces the number of bonds and the breaking force of the remaining bonds increases. Keren (1988) stated that Bingham yield stress of a suspension is a function of the number of particle-particle linkages as well as of the energy necessary to break those linkages. According to Torrance (1999) soil materials consisting of non-swelling minerals are characterized by particles that do not attract each other. Their shear resistance will consequently be low. However, if mutual attraction exists and the particles are connected to each other in a network throughout the whole volume shear resistance as well as yield stress increase. Furthermore, factors influencing the connection between particles also have an impact on shear resistance and yield stress, e. g. soil solution chemistry in terms of precipitated mineral substances at the areas of contact. Besides, Torrance (1999) mentioned that even if particles act as individual units they can interfere physically because of the restricted mobility which may be the case especially at low water contents. In a suspension particles can orientate themselves parallel or in every other direction, depending on pH, salt concentration and kind of ion in the suspending solution. In soil samples, even made of homogenised material, particles are restricted to their predetermined positions resulting from the process of sample preparation. Saturation results in swelling which corresponds to a change of volume but widely preserves the internal arrangement of the particle network. Only during shear displacement a rearrangement of the network will take place with particles being shifted into new positions. During the amplitude sweep test the increasing deformation can rearrange the randomly organized clay platelets by changing the structure from scaffolding to parallel orientated particles. Evidence for this process is given by the development of the shear stress during the test. First, the stress increases until a maximum is reached. The scaffolding structures which are the more pronounced the higher the salt concentration is, are destroyed as the bonds are broken. The shear stress is reduced suggesting that the clay platelets form parallel associations. However, larger particles in the sample, namely silt, as well as medium and fine sand is assumed to result in a second maximum of shear stresses. Higher deformation corresponds with a higher deflection at the outmost brim of the upper plate. Note that at 10 % deformation, the distance s at this point equals 0.4 mm or 400 µm which corresponds to the diameter within the sand fraction. Therefore, one explanation for the change of shear stress with deformation is the breakdown of chemically caused bonds between clay platelets at lower deformation (first maximum) followed by a local minimum where the small scale structure is assumed to weaken. Finally, the resistance of larger particles becomes effective at larger deformation resulting in additional friction as such particles get into contact during their movement. At that point shear stresses increase to a second peak and subsequently decline towards the end of the test with yet larger deformation. As the present results show, the second maximum is more pronounced for the samples saturated with deionised water although the material and, therefore, the particle size distribution is the same. Further investigations with other materials, especially with clay-like material that lacks the diffuse ionic layer (e. g. microsil) or non-swelling clays with low cation exchange capacity like kaolinite are needed to determine if and how far the observed phenomena are caused by different textural classes and swelling behaviour.

With increasing deformation the differences between the salt concentrations decreased for the storage modulus G’. As described above during the test the increasing deflection causes the breaking of rigid bonds between the particles. Although a higher salt concentration denotes a higher number of such bonds with increasing deformation those bonds are degraded so that the samples with different treatments show similar shear stresses at higher deformation values. The bonds resulting from the salt have a more rigid than elastic character. This can be seen at the peak that developed in the loss modulus G” with increasing salt concentration. The peak denotes an increase in “plastic stability” as the bonds are not elastic and are not rebuilt immediately but are rather rigid. Once they are destroyed they can not account for the microstructural stability. The peak results from the increasing force necessary to rearrange the particles in the soil sample. This rearrangement is restricted by particle linkages due to attractive forces between the particles as well as due to cementation with precipitated salts. At low deformation values, the weakest bonds are broken whereas more pronounced deformation also affects more stable linkages. Furthermore, the increasing deformation at the yield point also suggests that the bonds between particles become stronger and are more effective against greater spatial displacements caused by higher deflection angles.

The calculated stress values are rather low when compared to a regular shear test at the mesoscale. Frame shear tests generally do not consider such small stresses, mostly they are extrapolated. Lebert and Horn (1991) found for a silty material a shear strength of approximately 20-30 kPa at a stress of approximately 1 kPa. However, the material they used was predesiccated to -6 kPa. This is distinctively higher than the maximum shear stress we found for our material measured rheologically in an undrained state (70-272 Pa). The same is true for values derived by Horn and Fleige (2003). In their study with silty soils at a matric potential of -6 kPa the cohesion ranged from 2 to 12 kPa and the angle of internal friction from 29° to 35°. If we apply the Mohr-Coulomb failure equation a shear stress of 0.06 kPa and 1 kPa corresponds to a shear strength of 10.0-12.0 kPa and 10.5-12.5 kPa, respectively. Besides differences in the chemical composition, this is mainly due to the stabilising influence of the matric potential (Hartge and Horn, 2009). This is also in agreement with the findings of Mohamedzein and Aboud (2006) who detected decreasing shear parameters (cohesion and angle of internal friction) with increasing water content. Hence, mainly the higher water content of the glacial till samples in this work reduced the shear strength value compared to those described in the literature above.

2.6.1.3 Soil components responsible for increasing stability due to higher salt concentration and special regards to potassium

The influence of increasing salt concentration on strength is mainly based on the clay fraction. This was shown by Mishra et al. (2005) who found the more pronounced effects of increasing salt concentration on strength the higher the bentonite percentage in basalt soil-bentonite mixtures. But also within the clay fraction differences can appear due to different clay mineral types. It is possible that during the equilibration time transformation of clay minerals took place as clay minerals of K depleted soils tend to fix K (Tributh et al., 1987). Generally, weathering causes transformation of clay minerals from illites to vermiculites or smectites (Schroeder, 1976; in Tributh et al., 1987). This is usually accompanied by a release of potassium to the soil solution and its continuous removal by plants or seepage. However, if smectites or vermiculites are present, then they can adsorb potassium ions and are transformed to illites as a consequence of cation exchange (Garz et al, 1993; Wild, 1988). Potassium is generally favoured over sodium but not over divalent cations like calcium. Only if potassium is present in excessive amounts it is adsorbed preferentially by clay minerals (Niederbudde, 2002). But even at low K concentration some clays tend to prefer K over Ca and Mg (K selectivity). Compared to other ions K ions are large in diameter, their hydration shell is thinner, and they can be more easily dehydrated. Once a K ion is dehydrated it is adsorbed very firmly. Consequently, a high number of K ions adsorbed in the interlayer reduces the distance between the layers to 1 nm and thereby creates an illite clay mineral (K fixation) (Scheffer and Schachtschabel, 2002).

As the the soil used in this paper lacks fertilization smectites and vermiculites exist presumably, and the processes described above can take place if the potassium concentration of the soil solution is increased. If a transformation of clay minerals from smectites to illites took place the latter behave in a different way than the smectites with their high capacity for swelling. Comparative investigations of pure and interstratified smectite clays were done by Laribi et al. (2005). They discovered a quantitative difference in yield stress which was higher for pure smectite. On the contrary, Laribi et al. (2005) found illites to cause a more brittle structure and therefore K fixation would not explain the increase in the rheological parameters storage modulus and shear stress at the end of the LVE range and at the yield point, respectively. Furthermore, in some publications K caused less aggregation than divalent cations like Ca. Walter (1965b) found Na and K to be anticipating microaggregation whereas Ca and Mg produced larger aggregates. The largest aggregates emerged from silt and clay saturated with H. Similar results were gained by Wolkewitz (1960) who stated that Na acts as dispersing agent, whereas K and Mg block aggregation and Ca and H enhance it. But Laribi et al. (2005) used suspensions where the particles are not restricted in movement and are more easily reorientated parallel to the shear zone while in our measurement compacted soil samples were saturated and therefore lack a freedom of movement.

The process of saturation with deionised water can also cause leaching of ions from the soil and result in destabilisation. Under those conditions addition of salts to the saturating solution could help to restore the original state of the structure or to decrease the deterioration of existing bonds, e. g. due to the divalent cation calcium, respectively. Keren and Ben-Hur (2003) found such an influence when initially percolating soil columns with salt solutions followed by pure water. A gradual decline in the salt concentration of the percolating fluid had no impact whereas after an abrupt decrease (from 50 mmol L^{-1} to deionised water) dispersed clay was found in the percolate. The sudden change resulted in a concentration gradient between mineral surface and solution that had to be compensated by ion movement. With regard to our results this could also help to explain the differences between the two soils as the more stable Bonn loess contains bonds due to organic matter that are not destroyed with saturation, instead organic matter reduces wettability (Goebel et al., 2005; Zhang and Hartge, 1992).

2.6.1.4 Influence of different equilibrium times

The effect of aging is somehow surprising as Arnold (1970, cited in Wild, 1988) stated that in a 2:1 clay with potassium depletion that is exposed to a highly concentrated K solution the cations will be converted into a non-exchangeable form within minutes. These findings are not in agreement with our results which always showed a much longer equilibration period. This might be explained by the exchange process itself which obeys a logarithmic function and therefore shows a steep increase in transformation rate within the first minutes and later on approaches a parallel to the axis of abscissae. Therefore, even after one week a transformation from soluble potassium to non-exchangeable potassium could take place and therefore K fixation. This longer time span is also in agreement with the findings of Walter (1965a). He examined the effect of aging of Fe oxydhydrate on aggregate stability and found even after 12 months an increase of aggregate stability and additional aggregation during that time.

Sparks and Carski (1985) described the kinetics of potassium exchange as depending on the kind of clay mineral present in the soil. They found higher adsorption for smectite than for vermiculite and kaolinite. Additionally, the adsorption was a non-linear function of time; it followed an exponential course. Existing smectites in the glacial till, therefore, on the one hand imply a high adsorption, and on the other hand a persistent residual adsorption that does not reach equilibrium after 3 days.

2.6.2 Influence of reduced water content and matric potential on Bonn loess samples

Although the investigations by Torrance (1999) were done with suspensions they showed decreasing yield stress values with increasing water content. Neaman and Singer (2000b), Ramos-Tejada et al. (2003) and Laribi et al. (2005) experienced similar effects of the suspension concentration on shear stress in dependence of shear rate. Saturation in our case meant a gravimetric water content of about 34 %; drainage reduced this value to

28 % (at -3 kPa). Torrance (1999) tested yield stress over a range of about 50-70 % water content and the most distinct changes appeared at the low water contents. Therefore, the relatively small decline of 5 % water content due to equilibrating the samples from -0 to -3kPa was sufficient to cause pronounced differences in the rheological parameters τ at the end of the LVE range, τ_{max} and the shear moduli G' and G". Torrance also pointed out that at low water content a shear-thickening behaviour occurs which derives rather from physical interference between particles than from attractive electrostatic interactions. The effect of restricted movement of soil particles within not oversaturated soils, as they are considered in this study, compared to a suspension becomes even more obvious in drained (unsaturated) samples where additionally menisci forces determine interparticle friction. Karmakar and Kushwaha (2007) focused on the rheology of unsaturated soil samples at different moisture content and compaction levels. Their measurements with a vane rheometer revealed a stabilising effect of soil compaction as the particles are compressed and therefore loose their ability to slide. Furthermore, higher moisture content decreased the viscosity at the same compaction level. Change of moisture content also altered the yield stress which showed similar developments. The higher the moisture content the lower was the yield stress as a consequence of reduced solid-solid friction. Ghezzehei and Or (2000, 2001) also proved the stabilising effect of matric potential. Ghezzehei and Or (2001) explained the stabilising effect of reduced water content also by a decrease in the amount of water molecular films that cover clay domains and quasi-crystals. If we also consider the fact that the intergranular spacing is reduced we have to expect soil samples more resistant to deformation. This corresponds to our findings as a more negative matric potential and lower moisture content resulted in higher shear resistance. It is however to be expected that this relation strongly depends on the χ factor (effective stress equation by Bishop, 1959) which denotes the level of saturation. As a consequence of decreasing water content the menisci exhibit stronger contracting forces but the amount of menisci is strongly decreased. On the one hand this leads to weaker particle linkages due to a reduction in the contact area of water menisci. On the other hand the loss of the water molecular film results in a higher shear resistance between particles as a consequence of higher friction.

2.6.3 Comparison of different silty soil materials influenced by soil solution chemistry and matric potential

The differences in soil stability between the two soil samples may derive from the difference in particle size distribution that was not reduced significantly by sieving the glacial till samples to 630 µm so they lack the fraction of coarse sand. The more stable Bonn loess contains a higher percentage of clay and silt but less sand. This is in agreement with the findings of Torrance (1985) who examined the effect of different particle size distributions on the rheology of Leda clay and found decreasing yield stress with decreasing clay content. Mishra et al. (2005) and Conlon (1983, cited in Torrance, 1985), discussed the effect of different clay contents. Conlon (1983), e. g. pointed out that increasing clay content caused increased shear strength and therefore a higher stability although higher clay contents corresponded to higher water contents. Hence, we found higher strength values for the Bonn loess with more clay than the less stable glacial till. Additionally, it is to be assumed that organic matter is responsible for part of the stabilisation of the Bonn samples, especially as they were derived from the topsoil of agriculturally used fields and have a organic carbon content twice as high as the glacial till samples. Blanco-Canqui et al. (2006) described the stabilising effect of organic matter based on the Atterberg limits. Increasing soil organic matter content appeared along with increasing water content and higher liquid limit, plastic limit and plasticity index, respectively. This did only account for the topsoil, while with depth the degree of correlation decreased. Blanco-Canqui et al. concluded that in the subsoil the Atterberg limits were influenced predominantly by clay content and to a lesser extent by organic matter content. In our case, both the clay content and the organic matter stabilise the soil and increase the rheological parameters storage modulus and shear stress at the end of the LVE range and at the yield point, respectively.

We compared the influence of solution chemistry with that of the matric potential. We found that for the stabilising effect on saturated samples that is caused by -3 kPa can also be generated by a potassium chloride concentration of 0.5 mol L^{-1}. As such high concentrations are rather untypical for agriculturally used soils in Northern Europe the stabilising influence of negative matric potential will be predominant under typical climatic and chemical conditions. In soils with generally higher salt concentrations the stabilising effect of salt can excel that of decreased matric potential. According to Jurinak (1990, cited in Rengasamy and Olsson, 1991) there is an approximate relationship between the salt concentration c and the electrical conductivity EC: 0.1 dS m^{-1} = 1 mmol L^{-1}. Therefore, 0.5 mol L^{-1} corresponds to an EC of 25 dS m^{-1}. In most salt affected to saline (EC > 4 dS m^{-1}) soils the EC is much lower, as, e. g. reported by Ilyas et al. (1997) and Kahlown and Azam (2003) for soils in Pakistan. But Amezketa and de Lersundi (2008) found soils adjacent to a river in Spain whose EC reached 64 dS m^{-1} due to repeated flood events. Also in Shiraz, Iran, rather high EC values were detected by Mahjoory (1979, cited in Qadir et al., 2008), ranging from 25 to 39 dS m^{-1} within a soil profile of 1.65 m depth in a poorly drained area.

Crosbie et al. (2009) observed an increase of EC in surface water of Australian wetlands from 13 dS m^{-1} up to 95 dS m^{-1} due to a change in management. So besides the salinity of the soil itself, irrigation water can contribute to salinisation, especially with a EC of 5.9-22.7 dS m^{-1} (Moreno et al., 2001). Needless to say that different kinds of salt have different impacts on the soil and its properties but it becomes obvious that salt concentrations as high as in our measurements are quite common even in agriculturally used soils.

2.7 Conclusions

The main aspects of the investigations in this paper were to define the impact of two major factors on rheological behaviour of soil samples that were prepared from glacial till and loess material from an experimental field in Bonn, Germany. With increasing concentrations of dissolved potassium chloride the rheological stability parameters shear stress τ at the end of the linear viscoelastic (LVE) range, the maximum shear stress τ_{max}, and the storage modulus G' and loss modulus G" at the yield point were enhanced. Hence, we could clearly prove and quantify the stabilising effect of salt on soil strength on the microscale level for saturation conditions much lower than usually used for rheometry, i.e. suspensions.

Additionally, we considered in our study the impact of negative matric potentials at unsaturated conditions on the rheological parameters. We found that instead of electrical attraction the stabilising forces mainly depend on the water menisci emerging between particles. Although the absolute water content was reduced marginally stability of the soil observed increased with decreasing matric potential.

Our measurements confirmed the assumption that potassium influences the soil stability not only via improved plant growth and support of microorganisms. Instead, the presence of the cation itself increased soil stability measured with rheometry. Yet the mechanisms causing the increase in stability need further investigations, especially regarding the change in clay minerals and their contribution to soil stability.

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3 FLOW AND DEFORMATION BEHAVIOUR AT THE MICROSCALE OF SOILS FROM SEVERAL LONG-TERM POTASSIUM FERTILIZATION TRIALS IN GERMANY

3.1 Abstract

The present work investigated the effect of different potassium fertilization on soil stability. Therefore, we used soil material from different long-term fertilization trials in Germany and examined the rheological properties by means of an amplitude sweep test. In this test, soil is subjected to oscillating shearing with increasing deflection and the rheological parameters: storage modulus G' and loss modulus G" are derived from the shear strength of the soil. The deformation behaviour of the soil was determined by the values of G' and G" at the end of the linearviscoelastic (LVE) range (indicating irreversible deformation) and at the yield point (indicating flow) as well as the maximum shear stress during the test.

The results showed an ambiguous influence of potassium which depends strongly on the soil properties. On the one hand, an increased ion concentration in the soil solution leads to increasing attractive forces and therefore higher shear resistance of the soil as defined by the DLVO theory. With increasing desiccation, potassium like other salts can precipitate at the contact areas between particles and lead to cementation. On the other hand, potassium as a monovalent ion does not enhance covalent and ionic bonding between clay minerals when accommodated on the negatively charged surface. This holds true for most of the examined soil types while only sandy soils showed an increase in soil strength due to potassium fertilization. Potassium depletion further resulted in increased interaction of fertilization with other impacts. Thus, the destabilizing effect of K was more pronounced under liming as without liming and interacted with predesiccation. Subsequent modelling with selected soil parameters confirmed the high influence of matric potential as the coefficient of determination could be improved by separating the data sets depending on the actual matric potential. The modelling also revealed the interactions with other soil parameters, e. g. pH, oxides, texture, exchangeable cations as well as lack or surplus of K in relation to recommended K content. In conclusion, structural stability of soil at the microscale can only be fully understood when taking into account as many possible influencing parameters as possible.

3.2 Introduction

Potassium (K) is the second most important mineral to nitrogen with respect to the absolute amount assimilated by plants (Follett et al., 1981; Tisdale et al., 1985). Nonetheless, the natural resources in soils by far exceed the uptake by plants as soils contain a lot of total potassium. But the pool of easily available K is restricted to only 2-10 % of the total K amount in soil, 90-98 % being relatively unavailable (Follett et al., 1981). While the first pool is either dissolved in the solution or held by electrostatic attraction at the negatively charged surface of clay particles and organic matter, the latter consists of K stored partly in potassic feldspars and micas but mostly in micaceous clay minerals (illites or interstratified clay minerals) (Tisdale et al., 1985; Scheffer and Schachtschabel, 2010). However, several studies were able to account for potassium release from the interlayer of illites when the soil solution falls below a certain level of K concentration (among others Finck, 1957; Srinivaso Rao and Khera, 1994; Barré et al, 2007). The extent of this release and also of its counterpart, the fixation of K in interlayers, strongly depends on the amount and type of clay minerals present. While intensely weathered clay minerals as smectites and vermiculites contribute to the pool of exchangeable K, illites keep K fixed in their interlayers. K deficiency in the soil solution causes rather rapid exchange of K against other cations on the smectite and vermiculite surfaces and K release of moderate rate from the expanded margins of illites to reinstall the equilibrium. Despites its reputation of being non-exchangeable, in some cases, this pool accounts for 80-100 % of the plant K uptake (Srinivasa Rao and Khera, 1994; Hinsinger, 2002).

K in plants is translocated to the younger, meristematic tissues due to its high mobility if present in short supply. Symptoms of deficiency therefore first show up in older parts of the plant, as there are chlorosis of interveinal areas and margins of the lower leaves, accompanied by general stunting with little or no reduction in tillering (Prabhu et al., 2007). The functions of K are allocated to six areas according to Tisdale et al. (1985): 1. Enzyme activation. 2. Water relations. 3. Energy relations. 4. Translocation of assimilates. 5. Nitrogen uptake and protein synthesis. 6. starch synthesis. The range of multiple tasks of K in plants stresses its importance. Mostly, K is also the limiting element (cf. Evans and Sorger, 1966) and the soil needs fertilization for a satisfactory crop yield.

In the past several long-term trials on K fertilization were installed in different climatic and soil regions of Germany to detect optimal fertilization rates but also to observe the consequences of potassium depletion and over-fertilization. The present work deals with the impacts of K concentrations on soil physical properties. In disregard of structural changes at the macroscale in the bulk soil, the focus of our investigations is put on the deformation and flow behaviour at the microscale, the level of particle-particle interactions. With the help of rheometry small samples are examined under the influence of a sigmoidal shear stress after different levels of pre-desiccation.

The effect of K on soil structural stability is ambiguous given that several studies revealed destabilizing as well as stabilizing effects due to the presence of K. A first approach of rheological investigations of soil stability at the microscale done by Markgraf and Horn (2006) revealed an increase in soil stability due to higher potassium rates. One explanation is the decrease of electrostatical repulsion in the wake of increased electrolyte concentration in the soil solution according to the electrical double layer theory for particle-solution interactions in colloidal systems (Van Olphen, 1977). Hence, particles can approach more easily and connect to a complex three-dimensional structure. Recent rheological investigations of short-term influence of K on soil stability distinctively showed a stabilizing effect ascribable to K concentration (Holthusen et al., 2010) and proved former results of Chen et al. (1990), Abend and Lagaly (2000), Ramos-Tejada et al. (2001) gained by investigating suspensions. On the contrary, K is said to have a dispersive character and tends to hamper aggregation (Wolkewitz, 1960; Walter, 1965).

However, K can fortify bonds between particles with the help of cementation. Due to drying, water menisci evolve between particles at the areas of contact. In the remaining soil solution a further desiccation or evaporation, respectively, increases the solution's concentration and eventually exceeds the maximum solubility of the salts – they crystallize and thereby cementate bonds between particles (Soulié et al., 2007).

In addition, K might influence soil stability indirectly, e. g. by increasing plant growth and thereby enhancing shrinkage. Plant growth in turn leads to increase organic matter content that can either stabilize (Zhang and Hartge, 1992) or destabilize soil structure (Blanco-Canqui et al., 2005). Another factor is the pH which depends on nutrient uptake by plants (equal to release of protons), the kind of K fertilizer (KCl e. g.), the actual soil type etc. As described before, also the kind of clay mineral is supposed to depend on K rate in soil (Niederbudde and Fischer, 1980; Tributh et al., 1987; Srinivasa Rao and Khera, 1994). Furthermore, Laribi et al. (2005) state that different clay minerals come along with a different structure and therefore soil stability. Thus, investigating the influence of K on soil stability also means to detect the mechanisms through which K causes either an increase or a decrease in soil strength.

3.3 Material and methods

3.3.1 Investigated sites of long-term fertilization experiments

Disturbed material was collected from the topsoil (0-20 cm depth) of different long-term fertilization trials situated in Germany. An overview of the investigated sites, their climate data as well as grain size distribution of the soils are given in Tab. 3-1 for the experimental trials with increasing K fertilization and with K depletion, respectively.

The experimental setup of the trials differs distinctively, which required a selection according to the K fertilization. Nonetheless, the absolute amounts of fertilizer do not correspond perfectly to the K present in the soil. Therefore, for the interpretation of the results reference will be made to the K content of the soil in mg kg^{-1} soil.

To investigate the impact of other influencing parameters besides K content as well as their interference with K content, several other parameters were determined. An overview of these parameters, their units, the symbols used in the following text as well as the methods applied for the measurement is given in Tab. 3-2.

Table 3-1: Overview of experimental sites with increasing K fertilization (no. 1-5) and with K depletion (no. 6-8). Start, K fertilizer, soil type, altitude (h) and climate (annual precipitation AP, mean annual temperature MAT) according to sources cited in the second column

No.	Experimental site	Start	K fertilizer, K content, other elements	Soil type (parent material)	h m s. l.	AP mm	MAT ° C	Sand[1] %	Silt[1] %	Clay %
1.1 1.2 1.3 1.4	**Bernburg** LLFG, 2007a	1993	KCl, NaCl 50 % K	Chernozem (loess)	80	470	8.9	5.1	73.7	21.2
2.1 2.2 2.3 2.4 2.5	**Spröda** LLFG, 2002; LLFG, 2007b; Albert, pers. comm., 2009	1996	KCl, NaCl 50 % K	Albic Luvisol (glacial sand/till)	120	547	8.8	64.9	29.5	5.6
3.1 3.2 3.3 3.4 3.5	**Pommritz** LLFG, 2002; LLFG, 2008a; Albert, pers. comm., 2009	1996	KCl, NaCl 50 % K	Stagnic Cambosol (loess)	230	674	8.9	15.8	69.7	14.5
4.1 4.2 4.3 4.3 4.4	**Forchheim** LLFG, 2002; LLFG, 2008b; Albert, pers. comm., 2009	1996	KCl, NaCl 50 % K	Cambisol (gneiss)	565	883	6.9	51.1	34.8	14.1
5.1 5.2 5.3 5.4	**Halle** Merbach et al. (2000)	1949	KCl, NaCl 33 % K (-1969), 42 % K (1970-)	Haplic Phaeozem (sandy loess on glacial till)	113	494	9.2	54.0	33.1	12.9
6.1 6.2 6.3 6.4	**Bad Lauchstädt** Körschens and Pfefferkorn, 1998; Blake et al., 1999	1902	KCl, NaCl 33 % K (-1969), 42 % K (1970-)	Haplic Chernozem (loess)	110	484	8.7	5.1	72.4	22.6
7.1 7.2	**Thyrow** Schnieder, 1990	1937	KCl, NaCl 33 % K (-1969), KCl, $MgCl_2$, NaCl 33 % K (1970-)	Albic Luvisol (glacial sand)	40	520	8.6	81.8	14.4	3.8
8.1 8.2	**Bonn** Schellberg et al., 1999 Hüging, pers. comm. (2008)	1904	KCl, NaCl 50 % K	Luvisol (loess)	63	630	9.7	13.1	73.5	13.4

[1] unfertilized reference plot without coarse sand fraction

Table 3-2: Additional parameters used for modeling

Determining factors	Symbol	Unit	Method
Al_d/Fe_d ratio	Al/Fe	-	-
Altitude	h	m above sea level	h, MAT and AP according to Tab. 3-1
Annual precipitation	AP	mm	h, MAT and AP according to Tab. 3-1
C/N ratio	C/N	-	-
Cation exchange capacity	CEC	$mmol_c\ kg^{-1}$ soil	VDLUFA (1993)
Difference to recommended K content	K_{diff}	mg K 100 g^{-1} soil	recommended K content according to VDLUFA (1999)
Dithionite soluble oxides: Al, Fe (Mn, Si)	M_d	g kg^{-1} soil	Mehra and Jackson (1960)
Oxalate soluble oxides: Al, Fe, (Mn, Si)	M_d, M_o		Schwertmann (1964)
Electrical conductivity	$EC_{2.5}$	µS cm^{-1}	soil / water ratio: 1 : 2.5
Exchangeable cations: Na, K, Ca, Mg	M_{ex}	$mmol_c\ kg^{-1}$ soil	VDLUFA (1993)
Fe (oxalate soluble)/Fe (dithionite soluble)	$Fe_{o/d}$	-	-
Gravimetric water content at defined matric potential	θ_{grav}	g 100 g^{-1}	Schlichting et al. (1995)
K content (CAL soluble K)	K_{CAL}	mg kg^{-1} soil	Schüller (1969)
K input	K_{input}	kg ha^{-1}	-
Mean annual temperature	MAT	° C	h, MAT and AP according to Tab. 3-1
Total N content, total C content	N, TC	%	Vario MAX, Elementar GmbH, Hanau, Germany
Inorganic C content	SIC	%	C-mat 550 PC, Stroehlein Instruments, Bruker AXS GmbH, Karlsruhe, Germany
Organic C content	SOC	%	SOC = TC - SIC
P content (CAL soluble P)	P_{CAL}	mg kg^{-1} soil	Schüller (1969)
pH in $CaCl_2$	pH	-	Schlichting et al. (1995)
Ratio of K to CEC, K saturation	K_{sat}	%	-
Matric potential	Ψ_M	kPa	according to Czeratzki (1958), described in Schlichting et al. (1995)
Texture, without coarse sand fraction: clay, silt, sand	clay, silt, sand	%	Schlichting et al. (1995)

The influencing factor K_{diff} is derived from the guidelines for the fertilization of soils with respect to soil texture published by the Association of German Agricultural Research Institutions (VDLUFA) and depends on the actual K content in the soil. The medium class C (optimal for sustainable agriculture) ranges from 5-8 mg K 100 mg^{-1} soil (0-5 % clay) to 11-22 mg K 100 mg^{-1} soil (more than 25 % clay), thereby taking into account that soils poor in clay are unable to keep K from leaching (VDLUFA, 1999). The measured data are given in

Tab. 3-3 and 3-4 according to the numbers in Tab. 3-1 for the corresponding sites and treatments.

Table 3-3: Overview of selected chemical properties of experimental sites with increasing K fertilization (no. 1-5) and with K depletion (no. 6-8). For explanation of parameters see Tab. 3-2

No	K_{input}	K_{CAL}	P_{CAL}	K_{diff}	pH	$EC_{2.5}$	CEC	K_{ex}	Na_{ex}	Ca_{ex}	Mg_{ex}	K_{sat}
	kg ha^{-1}	mg kg^{-1}		mg 10^{-2} g^{-1}	-	µS cm^{-1}	|------------------mmol$_c$ kg^{-1} --------------|					-
1.1	0	90	62	-3.5	7.26	105	212	5.12	0.31	185	10.4	2.41
1.2	70	102	48	-2.3	7.39	95	221	6.93	0.21	179	10.7	3.14
1.3	120	172	63	4.7	7.39	99	225	7.42	0.00	173	10.6	3.30
1.4	180	262	72	13.7	7.17	90	216	9.04	0.15	173	11.7	4.19
2.1	0	93	74	2.8	4.21	131	107	1.77	0.00	10	1.1	1.66
2.2	60	144	78	7.9	4.54	135	95	2.95	0.00	14	1.8	3.11
2.3	120	148	84	8.3	4.55	137	91	3.37	0.00	15	1.8	3.69
2.4	180	181	76	11.6	4.67	138	93	4.27	0.00	17	2.2	4.57
2.5	240	163	77	9.8	4.50	141	96	3.84	0.00	15	1.9	3.99
3.1	0	112	100	-1.3	5.40	228	166	3.57	0.00	73	10.2	2.15
3.2	60	124	92	-0.1	5.53	206	160	3.98	0.00	72	11.2	2.49
3.3	120	130	69	0.5	5.44	241	157	4.28	0.00	74	10.9	2.72
3.4	180	168	77	4.3	5.42	289	163	5.56	0.00	74	10.2	3.41
3.5	240	167	64	4.2	5.50	245	157	5.44	0.00	72	9.2	3.46
4.1	0	56	114	-6.9	5.48	422	191	1.50	0.00	82	10.3	0.79
4.2	60	69	106	-5.6	5.70	348	202	1.99	0.00	88	11.5	0.98
4.3	120	118	108	-0.7	5.55	438	200	3.30	0.00	82	10.5	1.65
4.3	180	123	104	-0.2	5.62	394	194	3.39	0.00	81	10.1	1.75
4.4	240	165	101	4.0	5.54	422	201	4.69	0.00	80	10.8	2.34
5.1	0	36	59	-6.4	5.38	196	153	1.53	0.27	89	4.8	1.00
5.2	53	41	61	-5.9	5.44	197	158	1.57	0.17	95	4.6	0.99
5.3	106	65	62	-3.5	5.29	199	156	2.23	0.36	85	4.5	1.43
5.4	211	107	61	-1.8	5.36	193	151	3.45	0.20	84	4.5	2.27
6.1	0 (-Ca)	48	75	-7.7	6.31	118	263	2.85	0.57	191	11.6	1.08
6.2	115 (-Ca)	84	82	-4.1	6.32	81	198	4.08	0.71	169	12.2	2.06
6.3	0 (+Ca)	59	96	-6.6	7.32	113	267	4.15	0.44	227	13.0	1.55
6.4	115 (+Ca)	111	117	-1.4	7.30	120	265	5.82	0.58	222	12.9	2.19
7.1	0 (+Ca)	31	51	-3.4	5.13	97	87	0.49	0.00	16	1.7	0.56
7.2	100 (+Ca)	62	94	-0.3	4.40	91	89	0.87	0.00	7	1.8	0.98
8.1	0 (+Ca)	33	68	-13.2	6.14	49	119	1.09	0.16	91	4.5	0.92
8.2	116 (+Ca)	85	80	-1.5	6.24	59	89	2.80	0.00	79	4.6	3.15

Table 3-4: Continuation of Tab. 3-3: Overview of selected chemical properties of experimental sites with increasing K fertilization (no. 1-5) and with K depletion (no. 6-8). For explanation of parameters see Tab. 3-2

No.	K_{input}	Al_o	Fe_o	Si_o	Mn_o	Al_d	Fe_d	Si_d	Mn_d	Al/Fe	$Fe_{o/d}$	SOC	N	C/N
	kg ha^{-1}	g kg^{-1}								-	-	%	%	-
1.1	0	1.15	1.29	0.42	0.44	0.71	5.8	0.84	0.50	0.12	0.22	1.52	0.125	12.2
1.2	70	1.19	1.36	0.41	0.45	0.71	5.8	0.77	0.54	0.12	0.24	1.52	0.127	12.0
1.3	120	1.12	1.26	0.41	0.44	0.68	5.8	0.75	0.54	0.12	0.21	1.54	0.125	12.4
1.4	180	1.19	1.36	0.44	0.47	0.65	5.6	0.68	0.52	0.12	0.24	1.56	0.130	12.0
2.1	0	0.80	1.29	0.06	0.27	0.87	3.0	0.16	0.30	0.30	0.44	0.76	0.052	15.8
2.2	60	0.79	1.36	0.06	0.26	0.84	2.8	0.16	0.27	0.30	0.48	0.95	0.069	14.9
2.3	120	0.88	1.33	0.06	0.23	0.92	3.1	0.16	0.28	0.30	0.43	0.99	0.078	13.8
2.4	180	0.80	1.36	0.06	0.21	0.89	3.0	0.13	0.25	0.29	0.45	1.03	0.078	14.2
2.5	240	0.88	1.33	0.06	0.24	0.95	3.1	0.15	0.29	0.31	0.43	0.96	0.072	14.8
3.1	0	0.86	3.06	0.14	0.32	0.95	8.6	0.34	0.39	0.11	0.36	1.17	0.118	10.7
3.2	60	0.80	3.39	0.15	0.31	0.89	8.4	0.35	0.41	0.11	0.40	1.07	0.105	11.0
3.3	120	0.77	3.27	0.15	0.28	0.89	8.3	0.34	0.37	0.11	0.39	1.07	0.106	10.9
3.4	180	0.84	3.30	0.16	0.31	0.88	8.4	0.30	0.41	0.10	0.39	1.10	0.110	10.8
3.5	240	0.84	3.49	0.17	0.36	0.86	7.9	0.29	0.42	0.11	0.44	1.03	0.104	10.6
4.1	0	2.67	4.98	0.24	0.53	2.90	14.1	0.38	0.62	0.21	0.35	1.82	0.160	13.4
4.2	60	2.57	4.75	0.23	0.48	2.92	13.5	0.34	0.60	0.22	0.35	2.02	0.177	13.5
4.3	120	2.50	4.61	0.23	0.47	2.82	13.2	0.31	0.57	0.21	0.35	1.89	0.168	13.3
4.3	180	0.57	1.08	0.23	0.25	2.80	12.9	0.29	0.59	0.22	0.08	1.94	0.176	13.0
4.4	240	2.57	4.91	0.23	0.45	2.87	13.4	0.31	0.60	0.21	0.37	2.00	0.183	13.0
5.1	0	0.88	1.67	0.14	0.27	0.76	6.0	0.36	0.33	0.13	0.28	1.21	0.086	14.6
5.2	53	0.81	1.66	0.13	0.26	0.75	6.1	0.34	0.33	0.12	0.27	1.18	0.081	15.2
5.3	106	0.85	1.76	0.19	0.30	0.78	6.3	0.47	0.36	0.12	0.28	1.22	0.083	15.4
5.4	211	0.77	1.62	0.14	0.31	0.77	6.1	0.40	0.34	0.13	0.27	1.18	0.084	14.7
6.1	0 (-Ca)	1.22	1.42	0.32	0.42	0.97	6.4	0.10	0.47	0.15	0.22	1.77	0.129	13.8
6.2	115 (-Ca)	1.20	1.45	0.32	0.44	0.95	6.4	0.12	0.47	0.15	0.23	1.79	0.139	12.9
6.3	0 (+Ca)	1.38	1.51	0.43	0.41	0.67	4.4	0.06	0.41	0.15	0.35	1.93	0.142	13.6
6.4	115 (+Ca)	1.22	1.40	0.36	0.39	0.74	5.5	0.20	0.47	0.13	0.25	1.95	0.143	13.6
7.1	0 (+Ca)	0.45	0.86	0.03	0.28	0.52	1.9	0.00	0.34	0.28	0.46	0.38	0.020	20.4
7.2	100 (+Ca)	0.46	0.96	0.02	0.30	0.56	1.8	0.10	0.26	0.32	0.54	0.37	0.018	21.5
8.1	0 (+Ca)	0.68	2.90	0.18	0.50	0.73	7.3	0.06	0.57	0.10	0.40	0.81	0.070	11.6
8.2	116 (+Ca)	0.65	2.84	0.18	0.51	0.61	6.4	0.00	0.55	0.10	0.44	0.88	0.076	11.7

3.3.2 Preparation of the material for rheometry

The material was air-dried at 20° C and sieved to < 0.63 mm diameter. Afterwards, the soil was moistened again to 3 to 15 % gravimetric water content (for sandy and clayey soils, respectively) and equilibrated for 12 h in a fridge. For each treatment, 15 specimen with a height of 0.9 cm and 3.6 cm in diameter were prepared with a defined bulk density of 1.5 g cm^{-3}. After saturation with deionised water, subsets of five samples each were drained to -3 and -6 kPa until equilibrium was reached. Before the measurements, the samples were trimmed to a height of 4.5 mm and a diameter of 2.5 cm to fit exactly into the gap between the measuring plates and to avoid boundary effects of surrounding soil material.

3.3.3 Rheological measurements

The measurements were conducted with a rheometer MCR 300 (Anton Paar, Stuttgart, Germany) with a parallel-plate measuring system, 25 mm in diameter. According to Mezger (2006), the gap h between the profiled plates was set to 4 mm as Mezger recommended a gap size of five to ten times the diameter of the largest particle. The rheological test was an amplitude sweep test, described in detail in Markgraf et al. (2006) and Markgraf and Horn (2006) with the presettings as shown in Tab. 3-5.

In this test a soil sample is enclosed between two plates, where the lower one is fixed and the upper one is moving in an oscillating manner, following a sigmoidal course with increasing amplitudes. The corresponding shear stress τ (Pa) is recorded as torque M (Nm) and the radius r (m) of the plate (Eq. 3.1). The deformation γ (%) is calculated from the distance s (m) and the gap between the plates h (m) (Eq. 3.2).

$$\tau(t, M) = (2 \cdot M) \cdot (\pi \cdot r^3)^{-1} \qquad (3.1)$$

$$\gamma = s \cdot h^{-1} \qquad (3.2)$$

The flow or deformation behaviour of a soil during a rheological test is not only characterised by the shear resistance but also by the phase or loss angle δ. This parameter denotes the delay between the preset (γ) and resulting (τ) curve: Perfectly elastic materials like a spring show no delay: the highest deflection of the upper plate is attended by the highest shear resistance. Perfectly viscous materials, on the contrary, show the highest delay of 90° as the maximum deflection equals zero shear resistance. An example for a perfectly viscous material e. g. is water.

Therefore, the main rheological parameters derived from this test are summed up subsequently:

Shear modulus G* $G^* = \tau \cdot \gamma^{-1}$ (3.3)

Storage modulus G' $G' = G^* \cdot \cos \delta$ (3.4)

Loss modulus G" $G'' = G^* \cdot \sin \delta$ (3.5)

The complex shear modulus is rarely used to classify rheological behaviour; usually the storage and loss modulus, representing the stored and lost deformation energy of the sample, respectively, are applied. Additionally, the maximum shear stress τ_{max} during the test can be used to characterize maximum shear resistance of the soil. This parameter also enables us to compare results gained in rheological shear test with those derived from e. g. a frame shear test.

Table 3-5: Presettings of the conducted amplitude sweep test according to Markgraf et al. (2006) and Markgraf and Horn (2006)

Parameter	Range/Value
Deformation	γ = 0.0001 – 100 %
Frequency	f = 0.5 Hz
Measuring points	30

More detailed information about rheological fundamentals is given in the introductory works by Keedwell (1984), Vyalov (1986) and Mezger (2006), whereas more details about the conducted amplitude sweep test can be found in Markgraf et al. (2006), Markgraf and Horn (2006 and 2007), as well as in Holthusen et al. (2010).

3.3.4 Statistical analyses

Statistical analyses were performed with the statistical software R (R Development Core Team, 2010). Linear and polynomial relationship between K content and maximum shear stress were tested with the lm command in the stats package, a procedure used for fitting linear models. For modelling the effect of different influencing parameters on rheological characteristics backward stepwise regressions to minimize the Akaike's information criterion (AIC) were conducted with the stepAIC command in the MASS package. Forward stepwise regression turned out to deliver smaller R^2 values than backward regression and thus was rejected. Previously, highly intercorrelated parameters were excluded from the model due to high values (> 0.6) within a covariance matrix scaled into the corresponding correlation matrix.

3.4 Results

Due to the relatively high number of different trials the results are split into two parts. The first part deals with those trials consisting of several different K level treatments. The second part includes those trials consisting only of two different K treatments, namely with and without K.

3.4.1 Trials with increasing K fertilization

The soils in this first part were collected at Bernburg, Halle, Forchheim, Pommritz and Spröda. As the rheological parameters are correlated significantly with each other only one parameter is discussed in detail, however, representing the other parameters, too. The chosen parameter is the maximum shear resistance of the soil samples τ_{max}, illustrating the maximum shear strength of the sample.

3.4.1.1 Experimental sites separately

3.4.1.1.1 K content generally

The influence of K content in the soil on the shear resistance at the micro scale differs distinctively between the various experimental sites. Two extremes are shown in Fig. 1 for the experimental sites of Pommritz and Spröda. While the samples from Pommritz exhibited a drop in τ_{max} with increasing K content (Fig. 3-1, top), those from Spröda showed a corresponding increase upon drying (Fig. 3-1, bottom). An overview of all investigated sites given in Fig. 3-2 gives evidence of the ambiguous effect of K fertilization. It is clearly visible that the Cambisol derived from Gneiss in Forchheim exhibits the highest shear resistance at all levels of drainage. The impact of matric potential is also strongly exhibited by the Haplic Phaeozem (site Halle) but at a lower level. The other site with a similar texture to Forchheim and Halle, Pommritz, is on a comparable level with Halle, and except from -6 kPa predesiccation the slope is similar to that of the Halle and Forchheim samples. The water saturated samples from the experimental field Bernburg do not differ distinctively in dependency of K content. With increasing drainage the values increase above average, and hence, the differences between Forchheim and Bernburg diminish with higher level of predesiccation (i.e. more negative matric potential) while at comparable matric potential the differences to Halle and Pommritz grew.

3.4.1.1.2 Matric potential

As the matric potential plays such an important role, the data were split into subsets of different levels of pre-desiccation. The matric potential interacted with the K content as with increasing drainage the slope of the linear regression became steeper for Halle, Forchheim and Pommritz soil samples (Fig. 3-1 and 3-2).

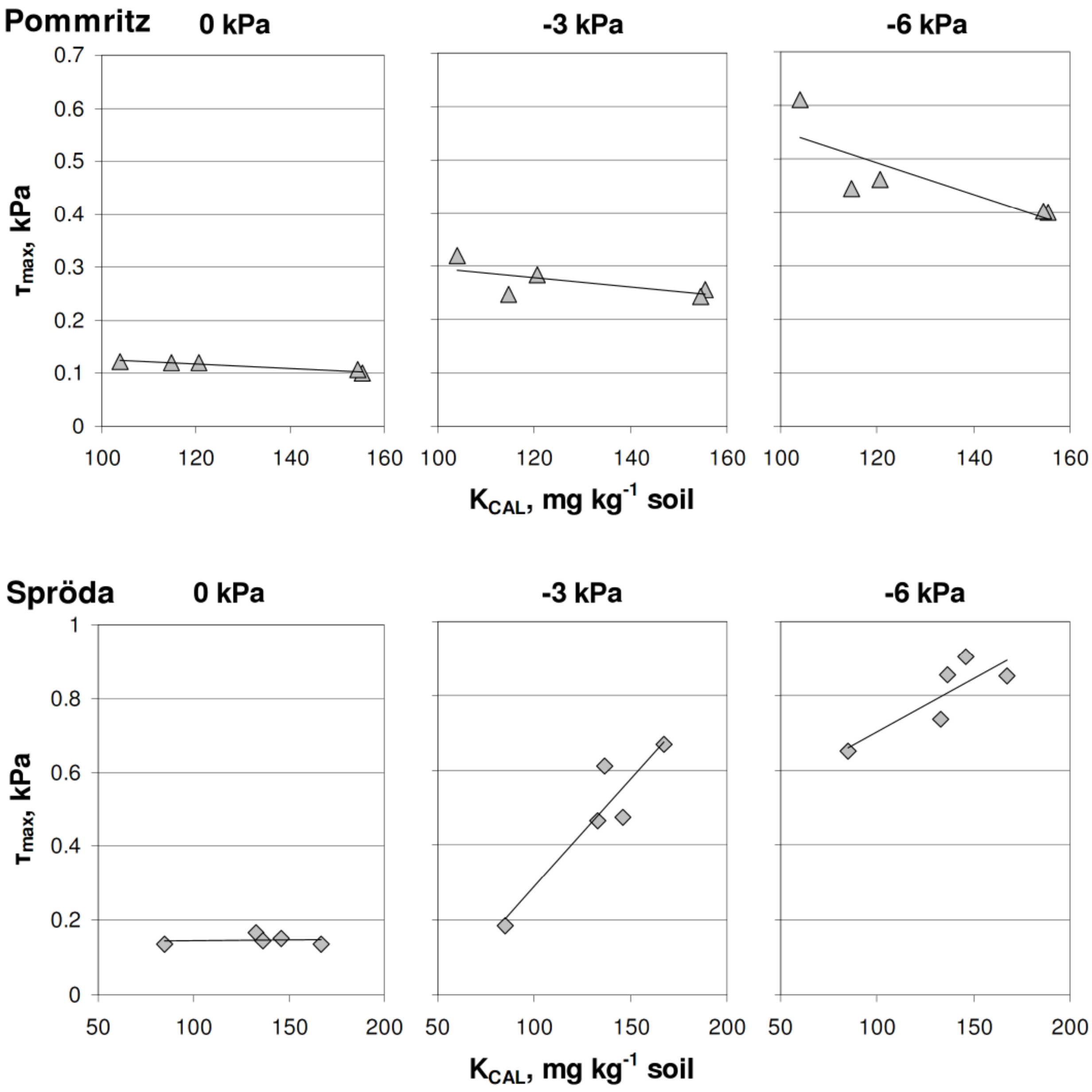

Figure 3-1: Maximum shear resistance τ_{max} as a function of K content in the soil at different matric potentials, experimental fields Pommritz (top) and Spröda (bottom), lines shows linear regression, n = 5, mean values

Obviously, further drainage fortified the destabilizing influence of K, independently of the differences in other soil parameters of those three experimental sites. Halle, Forchheim and Pommritz with comparable grain size distributions act in a similar way with increasing K content. However, Bernburg and Spröda are both pronouncedly different in texture from the other three sites, as Bernburg owns the smallest and Spröda the largest average particle size. At Bernburg, drainage to -3 and -6 kPa does not enhance the influence of K; instead the values of Bernburg samples tend to be more or less independent of K concentration and rose just due to lower water content (Fig. 3-2). The Spröda samples, however, showed the steepest slope at a matric potential of -3 kPa, while it declined from -3 to 0 kPa matric potential (Fig. 3-2).

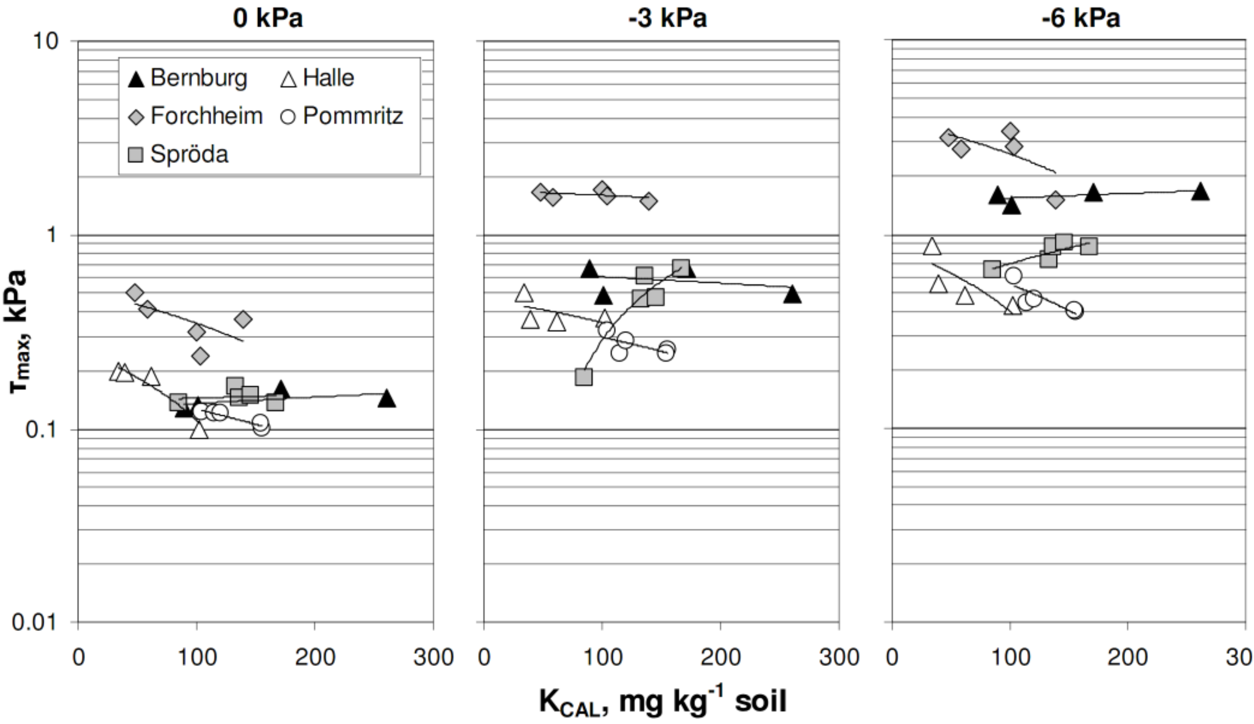

Figure 3-2: Maximum shear resistance τ_{max} as a function of K content in the soil at different experimental sites and at different matric potential, lines show linear regression, n = 5, mean values, axis of ordinates is log scaled

In most cases the dependency of τ_{max} showed a higher degree of correlation with a polynomial regression (Tab. 3-6). The latter resulted in some cases in an optimal K content in the soil indicating the highest shear resistance is not induced by the highest K content. Other data sets, however, showed the exact opposite with a minimum τ_{max} at a certain K content (K_{crit}) thus indicating higher shear strength with higher and lower K content than K_{crit}. This holds true for Forchheim (0 kPa), Pommritz (-3 and -6 kPa) and Halle (-3 and -6 kPa) while Bernburg (0 and -3 kPa), Forchheim (-3 and -6 kPa), Spröda (0 kPa) and Halle (0 kPa) exhibit an optimum K content. From this irregular pattern it can be seen that the appearance of the turning point either as maximum or minimum is not directly related to site or predesiccation level. Where the turning point denotes a maximum, the values vary with drainage level, i. e. at Bernburg site the highest shear strength is obtained at a K content of 191 and 158 mg per kg soil (at 0 and -3 kPa matric potential). At the experimental site Forchheim at -3 and -6 kPa matric potential, optimum K content would be 81 and 77 mg per kg soil, respectively.

Table 3-6: Coefficient of correlation r of linear (lin) and polynomial (poly) regressions between maximum shear stress τ_{max} and K_{CAL}, each as mean values (levels of significance: 0 '*' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1)**

Ψ_M, kPa	Bernburg		Halle		Forchheim		Pommritz		Spröda	
	lin	poly	lin	poly	lin	poly	lin	poly	lin	poly
0	0.588	0.988	0.952*	0.998.	0.711	0.991*	0.970**	0.981*	0.148	0.805
-3	0.336	0.558	0.507	0.745	0.418	0.670	0.676	0.799	0.930*	0.934
-6	0.620	0.637	0.736	0.859	0.667	0.916	0.813.	0.959.	0.832.	0.853

3.4.2 Trials with K depletion

The impact of a lack of K fertilization interacts intensely with the experimental site itself but also with predrainage as well as liming (Fig. 3-3). At Bad Lauchstädt site only those samples without liming showed a significant impact of K, expressed as destabilization irrespective of the existing matric potential. Still, also the limed samples showed a tendency of destabilization with K fertilization. On the contrary, the Bonn samples exhibited no significant differences, neither at 0 nor at -6 kPa. The most distinct differences can be seen for the Thyrow samples where the samples with K depletion exhibit a weaker structure at all levels of pre-desiccation with the differences being significant at 0 and -6 kPa.

Additional comparison of the samples at the experimental site Bad Lauchstädt with and without liming, respectively, showed a significant stabilizing influence of Ca for the K fertilized samples but not for the samples with K depletion. Obviously, the destabilizing effect of K at this site is strengthened by the lack of $CaCO_3$.

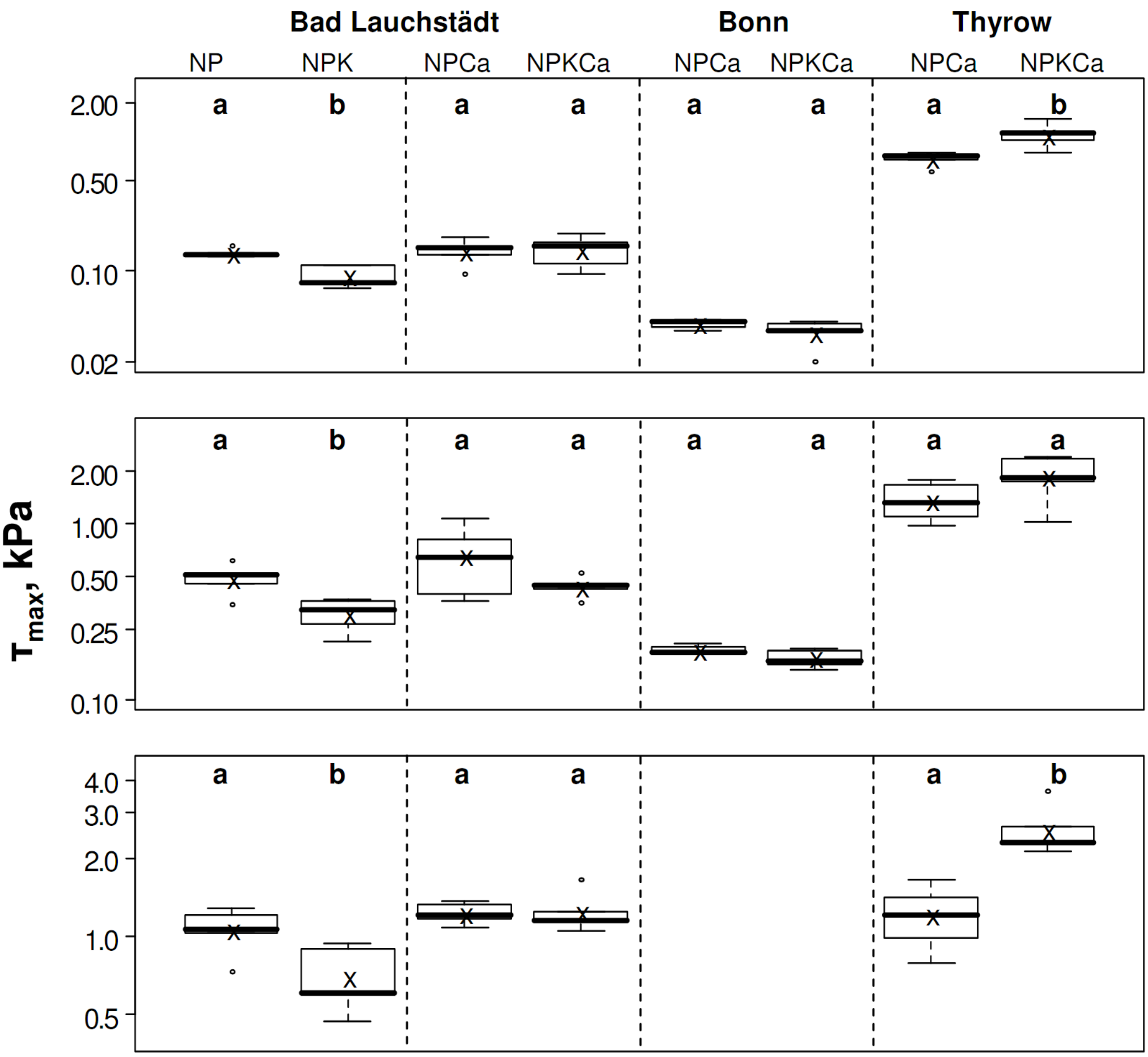

Figure 3-3: Maximum shear resistance τ_{max} as a function of K depletion in different soils at different levels of predesiccation (0, -3 and -6 kPa), boxplots shown with median (—) and mean (x). Different letters indicate significant differences ($p < 0.05$). N = nitrogen, P = phosphorous, K = potassium, Ca = lime; n = 5

3.4.3 Determination of shear strength by other parameters

Besides K content several other parameters were determined as described in Tab. 4. To compare the effect of K fertilization with the influence of other factors, a correlation matrix informs about the coefficients of correlation according to Pearson with τ_{max} (Tab. 3-7).

Depending on data subset according to the different matric potential values the Pearson correlation coefficient attained different absolute values and also different directions of correlation. Some factors had a negative impact in all subsets, namely K in the soil (derived by CAL method as well as at exchange sites) but also the lack of K, i. e. a higher K depletion with respect to recommended contents, led to increasing τ_{max} values. Exchangeable Na had a similar influence, so had silt. A stabilizing effect, however, can be expected if the samples have increasing amounts of most of the oxides except Si_o and Si_d, but also of P content, sand particles and a higher C/N ratio.

Table 3-7: Coefficients of correlation r for correlations between τ_{max} and different influencing parameters, positive and negative relationships denoted by algebraic signs, shown are only significant coefficients ($r \leq 0.098$, $p \leq 0.05$), n = 454, columns represent different subsets of samples by matric potential Ψ_M.

Ψ_M /parameters	all	0 kPa	-3 kPa	-6 kPa
Al/Fe	0.289	0.511	0.467	0.263
Al_d	0.470	0.232	0.671	0.671
Al_o	0.375	0.122	0.505	0.575
AP	0.357	0.185	0.532	0.517
C/N	0.259	0.743	0.419	0.168
Ca_{ex}		-0.329	-0.162	
CEC	0.118	-0.201		0.259
Clay	-	-0.420	-0.226	
$EC_{2.5}$	0.346	0.168	0.526	0.451
Fe_d	0.295		0.404	0.486
Fe_o	0.175		0.268	0.292
$Fe_{o/d}$		0.320		-0.163
h	0.414	0.178	0.599	0.584
K_{CAL}		-0.281	-0.125	-0.107
K_{diff}				-0.172
K_{ex}	-0.135	-0.426	-0.256	-0.105
K_{input}		-0.106		

Ψ_M /parameters	all	0 kPa	-3 kPa	-6 kPa
K_{sat}	-0.262	-0.456	-0.370	-0.322
MAT	-0.557	-0.408	-0.782	-0.764
Mg_{ex}	0.101	-0.219		0.237
Mn_d	0.281		0.307	0.595
Mn_o	0.196		0.163	0.499
N	0.239	-0.217	0.287	0.444
Na_{ex}	-0.164	-0.254	-0.276	-0.185
SOC	0.230	-0.207	0.266	0.429
P_{CAL}	0.353	0.223	0.473	0.520
pH		-0.277	-0.101	0.177
Sand	0.255	0.563	0.459	0.167
Si_d		-0.177		0.123
Silt	-0.293	-0.579	-0.507	-0.230
Si_o		-0.291		0.244
θ_{grav}	-0.118	-0.318		0.231
Ψ_M	-0.559			

Some parameters showed different relationships depending on the drainage level, e. g. organic carbon SOC had small values of correlation with τ_{max} when saturated but gained more and more increasing effect the dryer the samples were. A parameter similar in this regard is Mg_{ex}, being destabilizing at 0 kPa while stabilizing at -6 kPa. Differently, the direction of the influence of K in the soil does not change, instead the intensity is diminished. Obviously, the K content loses impact with higher drainage level (r of K_{CAL} with τ_{max} -0.281, -0.125, and -0.107 at 0, -3 and -6 kPa, respectively). Regarding the absolute values, the matric potential had the highest impact; however, if this parameter was excluded, the highest absolute r values were found for MAT both at -3 and -6 kPa drainage (-0.782 and -0.764), while at a matric potential of 0 kPa i.e. at complete saturation, the C/N ratio reaches the maximum absolute value r of 0.743. In general, the r values are relatively low, thus indicating none of them alone can fully explain the variation in τ_{max}.

3.4.4 Reciprocal effects of other soil parameters

The previous chapter showed ambiguous influence of K fertilization on soil microstructure. Hence, there must be other factors interacting with K content of the soil on its mechanical strength. To determine these interactions of different soil parameters on rheological behaviour stepwise regression was done. The used data consisted of the samples with increasing K fertilization as well as of those with K depletion. The parameters tested for their contribution to a suitable model were excluded upon collinearity, e. g. soil organic matter corresponded well with carbon content, so did pH measured in water with pH measured in $CaCl_2$. Hence, for the modelling, the following parameters were eliminated from the range of parameters (Tab. 3-2): Sand and water content, pH in water, total carbon TC. As already detected by preliminary linear regression, the different rheological parameters correlate well with each other, therefore, one parameter representing the others was chosen, namely the maximum shear resistance, τ_{max}.

A first approach included the matric potential and excluded climate and altitude as influencing factors. The simple linear model had an adjusted $R^2 = 0.731$. Addition of climate (MAT, AP) and altitude h enhanced the multiple R^2 value slightly but did not change the adjusted R^2, the latter being more important when comparing different models. Nonetheless, the coefficients of determination, multiple as well as adjusted, for the simple linear model with matric potential as a factor are very high compared to the single correlation coefficient between τ_{max} and the different parameters. Hence, this indicates the considerable degree of interaction between the parameters and their joined impact on soil structure.

After stepwise regression, the model included the following parameters: Ψ_M, K_{input}, silt and clay content, AP, MAT, K_{CAL}, P_{CAL}, Si_d, Mn_d, Al/Fe ratio, Si_o, Mn_o, Fe_o, Al_o, $Fe_{o/d}$, N, CEC, Na_{ex}, K_{ex}, Ca_{ex}, Mg_{ex}, K_{sat}. Almost all of the coefficients in this model were significant except $EC_{2.5}$ and Ca_{ex}. The corresponding R^2 values were, however, similar to those without stepwise regression: 0.747 (multiple R^2), 0.734 (adjusted R^2) ($p << 0.05$). Analysis of residuals confirmed the weakness of the model as the residuals were not normally distributed, and especially high values of τ_{max} were only poorly modelled.

As a consequence, it was decided to apply the stepwise regression separately for each matric potential level. The resulting models are summarised in Tab. 3-8. As backward regression eliminates the parameters contributing least to the model quality each step separately, the sequence of excluded parameters represents a range of least important factors while there is no statement about the most important factors in backward regression in the sequence of the remaining parameters in the table.

Table 3-8: Results of simple linear models before and after stepwise regression (level of significance of coefficients for remaining parameters: 0 '*' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1)**

Ψ_M, kPa	R² (before) - multiple - adjusted	R² (after) - multiple - adjusted	Removed parameters		Remaining parameters (+/- represents algebraic signs of coefficients)		
0	0.9406	0.9386	h	P_{CAL}	$+K_{input}$***	$+Mn_d$**	$+Fe_{o/d}$***
	0.9261	0.9288	Si_d	K_{sat}	$-EC_{2.5}$***	$+Fe_d$***	-SOC***
			N	Si_o	+silt	$-Al_d$***	-C/N.
			AP	pH	-clay**	-Al/Fe*	+CEC***
			Ca_{ex}		-MAT***	$-Mn_o$***	$+Na_{ex}$**
					$+K_{CAL}$**	$-Fe_o$***	$-K_{ex}$***
					$-K_{diff}$*	$+Al_o$***	$-Mg_{ex}$***
-3	0.8807	0.8749	AP	Mg_{ex}	$+K_{input}$*	$+Si_d$*	-SOC**
	0.8518	0.8573	N	C/N	+pH.	$+Al_d$***	+CEC***
			Mn_d	K_{CAL}	+silt*	-Al/Fe***	$-K_{ex}$***
			Fe_d	$EC_{2.5}$	+clay***	$-Mn_o$***	$-Ca_{ex}$**
			K_{diff}	Si_o	-h***	$-Fe_o$***	$+K_{sat}$***
			Na_{ex}		-MAT***	$+Al_o$***	
					+P***	$+Fe_{o/d}$***	
-6	0.8938	0.8935	K_{sat}	silt	$+EC_{2.5}$***	$+Si_d$***	$+Al_o$***
	0.8681	0.8733	Mg_{ex}	pH	+clay***	$+Mn_d$*	$+Fe_{o/d}$***
			K_{input}	Ca_{ex}	-h***	$-Fe_d$***	-N***
			K_{ex}		+AP***	$+Al_d$***	+SOC***
					+MAT***	-Al/Fe***	-C/N***
					$+K_{CAL}$*	$-Si_o$***	-CEC***
					$-K_{diff}$*	$-Mn_o$***	$+Na_{ex}$
					$+P_{CAL}$***	$-Fe_o$***	

First of all, the separation obviously improved the model distinctively, as R² of each single matric potential model is higher than that of the model with combined matric potential effects. But regarding the multiple R² values the stepwise regression decreased the model performance for all matric potentials slightly. Nonetheless, the adjusted R² increased gently and the models were simplified comprehensively. The highest coefficient of determination was found for the undrained samples with R² (adjusted)= 0.9288, while the samples drained to -3 kPa exhibited the lowest degree of correlation with R² (adjusted) = 0.8573. The analysis of residuals endorsed the improvements described above as the values were more equally distributed although high shear stress values still lack a perfect fit.

If we assume a positive sign of a coefficient marks positive relationship and a negative sign a negative one, the influence of a parameter strongly depends on the predrainage as already observed at the simple linear correlation analysis in Tab. 7. The parameter K_{input}, though not equivalent to the K amount actually present in the soil, is rather important for the modelling as can be derived from the fact that it was only once eliminated by stepwise regression at -6 kPa. At 0 and -3 kPa it increases τ_{max}, so did silt content and CEC. Compared to the single correlation shown in Tab. 3-7, especially K_{input} did not have a significant effect on τ_{max} at -3 and -6 kPa. Furthermore, at 0 kPa K_{input} decreased the shear resistance. Single coefficients of correlation of pH and CEC indicated a destabilizing influence at 0 kPa, but the influence changed into a stabilizing one at -6 kPa. Generally, the results proved the interdependency of the investigated parameters on the maximum shear resistance with some exceptions: soil organic carbon SOC exhibits a similar influence regardless of single or combined regression: While with a negative algebraic sign at 0 and -3 kPa, it contributes to soil strength at -6 kPa. Similar results hold true for clay content as a higher clay amount in a saturated sample leads to less micro structural strength but enhances it at drained samples.

With regard to the dithionite and oxalate soluble oxides a rather consistent behaviour can be observed. The ratio of Al_d to Fe_d tends to be destabilizing with excessive Al amounts at all drainage levels. On the other hand, the ratio between Fe_o and Fe_d acts in the opposite way; disproportionate amounts of Fe_o compared to Fe_d help to strengthen the soil. Destabilization occurs the more oxalate soluble Mn and Fe oxides are present. On the contrary, Al_o was assigned to a positive coefficient in stepwise regression for saturated and drained samples. Less consistent relationships can be observed for other oxides as some are at some drainage levels eliminated, and sometimes they act in the same direction, e. g. Al_d being destabilizing at 0 kPa but stabilizing at -3 and -6 kPa.

3.5 Discussion

3.5.1 Lack of shear strength prediction with K content as the single predictor

The K content of soils alone is not sufficient to explain decrease or increase in microstructural stability. Besides, the data set proved that the fertilization input does not correspond directly to the K content of the soil. This is mostly due to leaching, especially with low clay or soil organic matter content as both are able to store K (Jalali and Kolahchi, 2008). On the other hand, several authors (among others Burkart and Amberger 1978; Kuhlmann and Wehrmann, 1984) reported that high K fertilization rates did not show up in the soil but in the yield. Furthermore, the K content of a soil derived by the calcium acetate lactate (CAL) method does not represent the whole K capacity of a soil especially if the amount of easily available K is low as Finck (1957) showed among others. Instead, clay minerals can release interlayer K which contributes to the plant K uptake for up to 100 % (Hinsinger, 2002). For the results, therefore, one has to bear in mind that soil microstructural strength was considered as a function of easily available K and not of the total K present (that might also include the interlayer K). Nonetheless, the stepwise regression showed the importance of the difference between actual and recommended K content in the soil K_{diff}, as this value showed a negative relationship in the single parameter correlation analysis at a predessication of -6 kPa, i. e. K surplus resulted in an decrease in shear strength. The stepwise regression, however, led to the elimination of K_{diff} for those samples drained to -3 kPa. Exceptions were found at Spröda and Bernburg, the first being positively influenced, while the latter was widely independent of K_{diff}. Regarding the K depleted soils, Thyrow exhibited a similar behaviour. In the following different aspects of the presence of K in the soil changing the flow and deformation behaviour defined by maximum shear resistance during amplitude sweep test τ_{max} will be discussed.

3.5.2 K as dispersive agent

Most of the soils exhibited decreasing soil strength at the microscale with increasing K content. The dispersive character of K was already found by Wolkewitz (1960) and Walter (1965) who both defined K as a cation causing aggregate breakdown though to a lesser extent than Na. In excessive amounts together with its thin and easy to dehydrate hydrate shell K is adsorbed preferentially. If sufficient K cations have been adsorbed the interlayer space is reduced to less than 1 nm and transforms the clay mineral to illites (Scheffer and Schachtschabel, 2002). But Bohn et al. (2001) point out that it is uneconomical to fill all exchange sites of expandable clay minerals and thereby fixing K as it takes relatively high amounts of K fertilizer. Also the K release to the solution is assumed to be slow compared to exchangeable K. Nonetheless, especially in grassland management, high amounts of K are common in farmyard manure and slurry and are supposed to increase erodibility (Auerswald et al., 1996). The underlying mechanism is that K on the outer surfaces may increase dispersion which in turn results in a more dense packing with low hydraulic conductivity and infiltration rate (Auerswald et al., 1996).

In our investigations, the soils showing decreasing stability with increasing K content generally have appreciable amounts of clay possibly susceptible to dispersion. However, those soils lack K for a sustainable management (with regards to the recommended K content of the soil). Therefore, it is presumable that K input is delivered to exchanges sites both at clay surfaces and clay interlayers. While the first induces dispersion the latter leads to a mid-term transformation of clay minerals. If we assume both processes happen simultaneously, increased K input leads to a shift of smectites (highly dispersible but high structural stability) to illites (less dispersible but brittle structure) (Greene et al., 2002; Laribi et al., 2005). As maximum shear stress values decrease, the reduction in structural stability due to illite formation seems to be predominant.

3.5.3 Influence of decreasing matric potential

The level of predesiccation strongly influenced the maximum shear stress of the soil as with a more negative matric potential τ_{max} increased. The stabilizing effect of increased matric potential is well-known and described in literature many times (e. g. Horn and Fleige, 2003; Baumgartl and Köck, 2004; Bönsch and Lempp, 2007). Therefore, this aspect will not be discussed any further than with respect to interference with other soil parameters, e. g. the increase of salt concentration in remaining soil solution after drainage.

3.5.4 Salts as cementing substances

In general, salts can enhance particle-particle linkages due to precipitation at the areas of contact. This is a consequence of a soil solution containing salts, preferably with comparatively low solubility or in relatively high concentrations. Due to drainage, cohesive bridges between particles evolve at the areas of contact. The salt concentration of the remaining soil solution increases and results in salt precipitation as soon as the solubility is exceeded (Fig. 3-4). In doing so at the water-air surface, salt crystals build up a much stronger linkage than cohesion can. Soulié et al (2007) examined this phenomenon with glass beads in NaCl solution of different concentrations. With higher ratio of crystallized to dissolved salts the compressibility of glass beads compound increased, which is expressed in a steep rise in maximal force needed for compression at 80 % of the salt being precipitated. However, the initial concentration of the salt brine had no influence. This is of importance for our results as in general the drainage to -3 or -6 kPa does not lead to saturated salt brine. However, Alaily (1979) found P content in soil solution to change with pore size; it increased the smaller the pores were. Thus, freshly dug samples showed an increase of 4 mg P L^{-1} when pF increased from 1.6 to 3.7.

Both the experimental sites Spröda (increasing K fertilization) and Thyrow (K depletion) showed a clear increase in maximum shear stress with increasing K content in the soil. Although K content in this case is not identical with K content of the solution, precipitation of salts at the contact areas between particles may help explain the stabilizing influence of K. Spröda and Thyrow have the highest sand content of all investigated soils. Therefore, apparent cohesion is weak, as reported also by Soulié et al (2007) for glass beads, and shear resistance can only be increased by true cohesion via cementation, and is further enhanced by decreasing matric potential. Additionally, these are the only soils showing an increase in τ_{max} with increasing K_{diff} values. As reported previously, K is first distributed to clay interlayers and then to exchange sites at the outer surface and edges of the clay minerals. Therefore, a K surplus enhances the dispersive character of K but can also increase mutual attraction between particles due to the electrical double layer theory (Van Olphen, 1977) Thus, K can also act as a stabilizing agent. Similar effects were detected by Chen et al. (1990) who found increased yield stresses (comparable to higher structural stability) for Na-montmorillonite suspensions with higher salt concentrations in the suspending solution. In addition, the effects described above are more likely the more K is on the exchange sites and thereby prone to enter the solution.

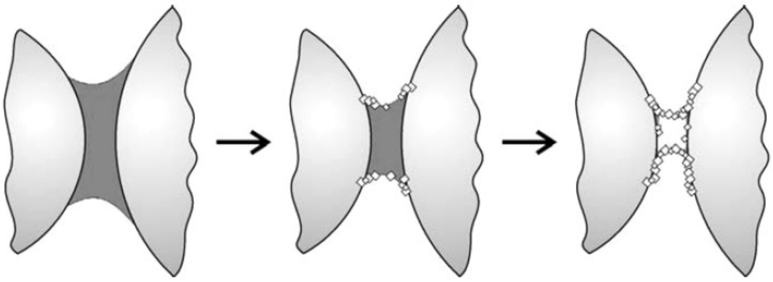

Figure 3-4: Schematic representation of the evolution of saturated brine bridge (Soulié et al., 2007)

Even so, Rodriguez-Navarro and Doehne (1999) found not all salts to crystallize at the air/solution interface, instead, some tend to precipitate within the solution, e. g. $NaSO_4$. Additionally, depending on other salts and chemicals in the solution, the crystallization pattern changes (Yamaguchi et al., 1998; Guo et al., 2010). Location and habit of crystallization in turn can damage soil particle bonds due to a high crystallization pressure, and thereby reduce soil strength (Rodriguez-Navarro and Doehne, 1999).

Another stabilizing effect of salts occurs in saline and sodic soils, namely via hard-setting due to drying while the soils are soft when wet. According to Mullins et al. (1987) hard-setting happens when bridging clay and silt material fails to connect adjacent sand grains. Failure takes place e. g. upon high water content meaning lack of cohesion. Furthermore, Dexter and Chan (1991) found the highest stability in dry soils with the highest rate of dispersion in wet state. They concluded that the occupancy of exchange sites with cations strongly influences the repulsion between particles as dispersive cations like e. g. Na improve particle arrangement and thereby enable denser packing and lead to higher soil strength. As K is said to be of dispersive character, too, it can also enhance the hard-setting of soils while drying upon sieving in the laboratory. This holds true especially for sandy soils as beside cohesion the bonding through fine material is the main source of structure. This is confirmed by the data obtained from Spröda and Thyrow. Additionally, hard-setting depends on the clay mineral according to Greene et al. (2002) who found illite/smectite interstratified materials to be more susceptible to dispersion than pure kaolinites or illites, therewith tending to hard-setting more likely. However, Ruiz-Vera and Wu (2006) discovered kaolinite to be most prone to dispersion, while soil containing mainly smectites was most vulnerable to slaking, and aggregates from a vermiculite dominated soil mainly broke down because of differential swelling.

3.5.5 Influence of additional soil solution components

Cl delivered with K fertilization to the soil is known to leach easily and therefore does not account for a change in soil structure presumably. Garz et al. (1993) mention for the experimental site Halle an accumulation of Cl in the subsoil in dry years, but only temporarily. Instead, the development of gypsum due to sulphuric depositions from adjacent industrial plants is possible at the experimental site of Bad Lauchstädt.

3.5.6 Interaction with pH

Soils with a low pH tend to have a higher amount of Al placed on the charged surface of clay minerals, bonding them in a stronger way than Ca ever can. This may hold true for the sandy soils at Spröda and Thyrow although Forcheim and Halle also have pH values below 6 (but bearing in mind that, according to Torrance (1999), trivalent Al ions are present only below pH 5). High K supply, however, is supposed to replace even Al cations and thereby destroy those bonds, hence resulting in lower soil stability. Nontheless, the sites with a low pH, namely Spröda and Thyrow were the ones also being stabilized by K. At both sites the replacement of polyvalent cations as reflected by the increasing value of K_{sat} did not result in less stability.

Another aspect of pH is the change in the edge charge. As the clay mineral edges change their charge depending on the pH, at low pH the edges are positively charged. This enhances edge-to-face bonds and thereby easily creates a cardhouse or stake structure. Ramos-Tejada et al. (2001) detected such a stabilizing influence of a low pH on Na montmorillonite suspensions by increasing yield stresses, determining the transition to flow, i. e. the transition from elastic to plastic deformation and thereby structural breakdown at a higher shear stress.

It is not quite clear how K interacts with pH and its effect on edge charge. K cations might replace protons at the edges thus impeding the charge reversal due to pH and also the cardhouse structure developing otherwise. On the other hand, a higher K amount enables plants to take up more K. This, in turn, leads to an additional release of protons by the plants, as a substitute for the K cations. In any case, promoted plant and hence root growth due to a higher K fertilization cause an increase in root exudates that can bind particles immediately (Morel et al., 1991).

3.5.7 Influence of particle size and shape

Obviously, texture is an important factor for microstructural stability. In their numerical case study, Kock and Huhn (2007) found silt-like-particles to have a higher friction than those similar to clay-like-particles. However, silt particles were expected to have less friction as generally rolling friction is smaller than kinetic friction. But perfectly spherical particles tend to develop dilatancy (shear-thickening, i. e. higher shear resistance with higher shear rate) while platy particles align in a parallel way and hence reduce friction. Regarding the K depleted sites, this holds true as the maximum shear stress is the higher the less clay is present in the soil. But Kock and Huhn (2007) did not consider water and its interference with solids and air. Therefore, the Bernburg samples, comparably rich in clay, showed increasing structural stability with higher predrainage as menisci developed at the areas of contact and stabilized the structure as can be derived from the effective stress equation. According to Terzaghi's concept of effective stress, supplemented by Bishop for unsaturated and structured soils (Eq. 3.6) the effective stress depends on the degree of saturation (Mitchell, 1993):

$$\sigma' = (\sigma - u_a) + \chi\,(u_a - u_w) \qquad (3.6)$$

σ' denotes the effective stress, depending on the normal stress σ minus the pore-air pressure u_a and the difference between pore-air pressure and pore-water pressure u_w, weighted by the χ factor, denoting the degree of saturation. In sandy soils χ decreases steeply with decreasing matric potential, hence the stabilizing influence of the menisci soon disappears as their total amount is decreased distinctively. On the contrary, in clayey soils the strength of the menisci is raised in a similar way by a decreasing matric potential but the total number of menisic is reduced to a lesser extent, hence they can exert more contracting forces on particles. Due to its high clay content, Bernburg is predestinated to exhibit a strong impact of a negative matric potential.

However, investigations done with soils depleted of phyllosilicates and natural clayey soils showed a dramatic decrease in yield stress (i. e. shear rate that causes transition from elastic to plastic behaviour, namely flow), denoting a decrease in stability with less phyllosilicates (Torrance, 1999). In previous works, Torrance (1985) already stated that the yield stress increased with decreasing silt content. This aspect of Torrance's works is opponent to the results of Kock and Huhn (2007) who found less friction for their model particles imitating phyllosilicates. However, Torrance (1999) observed also a shear-thickening behaviour of the phyllosiliate depleted soil samples which he ascribes only to the physical interference among particles. Hence, the high maximum shear resistance of the Thyrow samples compared to other less coarse-textured samples is mainly a result of an apparent cohesion caused by irregular and non-platey particle geometry (Mitchell, 1993).

Surprisingly is the high level of the site Forchheim that exceeds Bernburg even at a matric potential of -6 kPa. With respect to texture and other soil properties Forchheim is similar to Halle and Pommritz, thus for an explanation of this phenomenon further research is needed although the organic carbon contents might help explain the performance of the Forchheim samples as they are the highest of all investigated sites.

3.5.8 Influence of organic matter and metal oxides

Apart from soils derived from sediments, normal soil development takes place unaffected of organic matter, and thus soil is structured by shrinkage processes mainly. Consquently, the amount of particle-particle contacts increases and causes an apparent mechanical cohesion that is based only on physical interference as well as friction between particles (Mitchell, 1993). Organic matter, however, is the most effective agent to transform those solely on physical strength basing bonds to sustainable and also chemically strengthened linkages that grant soil flexiblity during shear and resilience after compression.

Soils with a good K supply provide better conditions for plants to grow. Unless they do not lack other elements, higher K fertilization rates therefore enhance plant and especially root growth. This in turn increases the amount of organic matter in the soil.

However, in our data set no noticeable relationship between K amount in the soil and organic carbon was observed. Instead SOC influenced water content and was correlated well to CEC and clay content. As SOC acts as a water reservoir, increasing SOC amounts are able to store water. The relationship to clay content may be based on the higher fertility of clay-rich soils as well as enhanced development of microaggregates that capture and preserve organic matter in intra-aggregate pores (organo-mineral complexes). Due to the reactive surface of clays and the higher amount of plant available water, the formation of SOC is enhanced in those soils. The interaction with other parameters appears e. g. with regard to temperature which reduces storage of SOC the higher it is (Conen et al., 2006) as reflected in the lower SOC content at the sites with highest mean annual temperature (Bonn and Halle with 9.7 and 9.2° C) and the highest SOC content at the site of Forchheim, where the lowest mean annual temperature of 6.9° C was found (albeit similar clay content). Additionally, the coefficient of single correlation with MAT was negative at all matric potentials and reached rather high values. On the contrary, enhanced decomposition of fresh organic matter, in turn, may result in increased soil strength. A hierarchical order of aggregate development due to organic matter was postulated first by Tisdall and Oades (1982), modified by Oades (1984): The first step of aggregation is considered to be caused by roots and fungal hyphae that bond particles into macroaggregates (> 250 µm) of only temporary existence. Fragmentation of those macroaggregates due to decomposition of plant and fungal residues leaves microaggregates (20-250 µm) coated with mucilages and encrusted with clays. Hence, fresh organic matter (roots and fungal hyphae) can only temporarily stabilize soil, and only their decomposition enhances microaggregation strongly. However, to bring this in accordance with the results it can be assumed that the organic carbon represents the already decomposed organic matter that stabilizes the soil and not the fresh organic matter, which is presumably lost due to sieving to 630 µm diameter anyhow. The organic matter hence stabilizes the remaining microstructure (as microaggregates are mostly unaffected by homogenization and sieving) according to Wierzchos et al. (1992) who determined the effect of removal of organic matter and found a change from a honeycomb structure to turbostratic domain structure with predominantly face-to-face contacts between the microaggregates. This is in accordance with the fact, that the highest SOC values were found for the Forchheim site, which exhibited also the highest maximum shear resistance though, e. g. the grain size distribution is very similar to that of the Halle samples whose microstructural stability, in turn, was pronouncedly lower.

However, not only the amount but also the composition of organic matter is of interest. While particulate organic matter enhances soil structure mostly mechanically due to refinement of particle size distribution, other components like polysaccharides produced by microaggregates or exudated by roots are only transient binding agents (Martens, 2000). Furthermore, in dependence of the above described processes of aggregation development Chenu and Plante (2006) found organic matter bound to primary mineral particles to be more resistant to biodegradation in comparison to free organic matter. Additionally, a recent literature review by Abiven et al. (2009) could prove a concept postulated by Monnier in 1965 (cited in Abiven et al., 2009): While easily decomposable components have an intense though only temporary effect, the impact of more recalcitrant components is less strong but long-lasting.

Organic matter in general can influence soil structure furthermore by a reduction in the wettability and hence diminish the impact of swelling leading to slaking otherwise. This phenomenon of hydrophobicity develops due to drying of soils containing organic matter. Once hydrophobic, organic matter acts rather different and reduces e. g. wetting rate of aggregates. The mechanisms of hydrophobicity of organic matter on aggregate stability were described by Zhang and Hartge (1992), Hallett and Young (1999) and Chenu et al. (2000). Previously, Zhang and Hartge (1989) showed that organic matter interacted with matric potential. While having no impact in a saturated soil, the stabilizing effect of strongly humified organic matter increased with increasing drainage. This is well reflected in the changes of algebraic signs of the coefficient of correlation in Tab. 3-7 (separate linear regression) where organic matter decreased maximum shear strength in saturated soils but increased it in drained soils, r being the higher the more drained the soils were.

The reduction in friction due to organic matter is also a consequence of its ability to increase maximum water capacity as observed by Asmus (1990) in a long-term field experiment. Increasing water retention equals increased water content at the same matric potential thus reducing friction via a water film between particles and consequently lower shear resistance. Furthermore, organic matter in wet state can further reduce friction, e. g. Zhang et al. (2005) found peat amendment to decrease shear strength and increase compressibility (the latter being influenced also by less friction). This is reflected by the negative impact of organic matter in saturated state as revealed by the negative coefficient of correlation. Similar results were found by Ekwue (1990) who investigated the effect of different kinds of organic matter on different soil physical parameters. The addition of different organic matter here also increased water retention, however, stabilizing effects could only be observed for organic matter from grass treatment while peat reduced shear strength and aggregate stability. Although particulate SOC (peat material) acts as a friction-reducing agent in saturated state, it multiplies the amount of menisci as described by Zhang and Hartge (1990) in drained state according to the concept of effective stress (see Eq. 3.6).

Additionally, Edwards and Bremner (1967) and Tisdall and Oades (1982) found organic matter to be involved in clay-polyvalent metal-clay associations as well as in bonds of organic matter-polyvalent metal-organic matter thus stabilizing the soil. Compared to other organic materials acting only temporarily (polysaccharides, roots and fungal hyphae), Tisdall and Oades (1982) classified those aromatic components linked with polyvalent metal ions as persistent. Addition of acetyl-acetone led to the destruction of those bonds but as long as organic matter was not removed, the microstructure did not collapse completely and some re-structuring took place (Wierzchos et al., 1992). However, the extraction of organically bonded metals led to a more pronounced destruction of microstructure and hence deflocculation. Opponent in those observations, the stepwise regression done in this paper revealed a destabilizing impact of amorphous (oxalate soluble) Al and Fe oxides by trend while the single regression showed a stabilizing influence of most of the oxides, most distinctively for Al and Fe, but also for Mn. Si oxides had a negative sign in saturated state and a positive at -6 kPa matric potential. Furthermore, the dithionite soluble oxides, M_d, always attained higher r values in single regression analysis. On the one hand, this is a consequence of the method as the M_d fraction contains both the amorphous *and* the crystallized oxides, thus the relationship improves if both groups are observed. On the other hand, the bonding of particles might have become even more effective with aging. Furthermore, due to sieving, some bonds by crystal oxides were presumably destroyed. The amorphous oxides then can contribute to some re-bonding and thus create new bonds. In this regard, the Forchheim samples do not only contain high organic carbon contents but also the largest amounts of Fe_d and Al_d, both stabilizing the soil distinctively, as the comparison with the site Halle, similar in grain size distribution, reveals.

In this context, the $Fe_{o/d}$ ratio is used to determine how much of the Fe oxides are non-crystalline (equal to the difference between Fe_d and Fe_o). The higher the value and the nearer to 1, respectively, the more dominant are the oxalate soluble, i. e. the amorphous Fe oxides in the soil. As those Fe oxides are mostly ferrihydrites, soils with high $Fe_{o/d}$ ratios are said to have been exposed to heavy weathering (Childs, 1992). Although ferrihydrites are said to contribute to nutrient and carbon storage due to their large surface area and many vacancies (Childs, 1992), this is not reflected in our results as the coefficient of correlation between SOC and $Fe_{o/d}$ is negative, indicating less organic carbon the higher the amount of Fe_o in relation to Fe_d. But it may be assumed that a soil strongly weathered (with a narrow ratio) lacks fertility and thereby the ability to accumulate organic carbon.

3.5.9 Influence of liming

At the experimental site Bad Lauchstädt liming had a significantly stabilizing effect on microstructural stability. Similar results were reported by Beese et al. (1979) at the mesoscale where they found higher shear resistance as well as reduced compressibility with increasing lime addition to artificial soil samples. Obviously, lime promoted flocculation of the clay fraction, especially at the points of contact of silt grains and thereby enhanced structural stability. Similar effects were previously reported by Czeratzki in 1972 when investigating aggregate stability with respect to the addition of calcium hydroxide to several soils. Besides, the samples enriched in calcium showed a shift in soil plasticity towards higher soil water contents

3.5.10 Changes in microstructural stability due to changes in clay mineralogy

Investigations of the K content at the experimental site of Halle done by Garz et al. in 1993 revealed a distinct differentiation in the different treatments that reached its equilibrium already after 40 years. The differences mainly resulted from a decrease in exchangeable K in the treatments with K depletion rather than from an increase in treatments with a K surplus. HCl extracted K does not account for the missing K considering the difference between plant uptake and exchangeable K, although it exceeded the exchangeable K by far. So Garz et al. concluded that some of the K supply origins in the clay mineral interlayer, visible also in the changes of cation exchange capacity (CEC). The K depleted soils had a higher CEC than the soils with K surplus, presumeable due to more exchange sites in expanded clays that have released K (e. g. smectites, vermiculites). Also, the differences in K content do not derive from a uptake (K fixation) but from a K release, as the comparison of K content at highest fertilization level with the initial value (that are both very similar) shows. Furthermore, the K fixation was increased in soils with K depletion indicating an increase in K fixing clay minerals, namely illites. Thereby, Garz et al. (1993) confirmed the process of clay mineral transformation not by X-ray diffractometry but by logical conclusions. Although further information about the clay mineralogy of the investigated soils is missing, a transformation seems possible as several authors observed clay mineralogy to be a function of K content of the soil solution or the K removal by crops, respectively and hence proved the transformation of non-expandable, K-containing illites to expanded K-depleted smectites and vice versa (Niederbudde and Fischer, 1980; Tributh, 1981; Tributh et al, 1987; Srinivaso Rao and Khera, 1994; Barré et al., 2007). Others did not detect this effect, e. g. Dreibrodt et al., (2002) who found no change between the fully fertilized and the completely unfertilized plot at the long-term experimental site of Bad

Lauchstädt. However, the uptake of K into clay interlayers is a short-term phenomenon (Jungk and Claassen, 1986), and hence should be visible in a clay mineral shift if it took place. Nonetheless, Dreibrodt et al. (2002) admit, that nearby industrial plants could have caused atmospheric input and thus balanced the nutrient supply. Furthermore, Simonsson et al. (2009) generally found clay minerals to transform according to K supply but not for all examined soils: With low pH the K release from clay interlayers was irreversible which seemed to be correlated to the occurrence of hydroxy-aluminium interlayers in the 2:1 minerals that hampered K fixation. Another reason for omitted clay mineral change was mentioned by Brümmer and Schroeder (1976) who could verify a transformation in laboratory experiments but not when investigating the clay mineralogy of North Sea sediments that are assumed to contain strongly weathered clay minerals. But the attempt of K to enter interlayers and get fixed there is rather low as the concentration gradient between interlayer and seawater was very low, and also the competition with other cations dissolved in the water was too high. With respect to the observations by Garz et al. (1993), decreasing CEC values with increasing K fertilization (as a hint for clay mineral transformation) is exhibited at the sites of Spröda, Pommritz, Bad Lauchstädt (without lime) and Bonn. However, at least for Spröda and Pommritz the differences are very small and need further investigation to verify a relationship to clay mineral transformation.

3.5.11 Stability as function of clay mineral

Different types of clay minerals go along with different impacts on soil strength and stability. Hence, Laribi et al (2005) found interstratified illite-smectite clays to exhibit distinctly lower yield stresses and thereby shear stresses as pure smectite clays. They explained their observation with different rheological properties of the different clay minerals as pure smectite clay is able to swell and organise in water, thereby creating three-dimensional structures. But once illites are present the soil becomes brittle and the structure collapses more easily under stress. In another work the impact of different types of clay minerals on tensile strength were tested (Barzegar et al., 1995). The authors found decreasing tensile strength with the following sequence of predominant clay minerals in the investigated soils: smectites, illites, kaolinites. Thus, clay minerals weathered or expanded more intensely, respectively contribute more to soil and aggregate stabilization than non-swelling and non-expandable clay minerals.

3.6 Conclusions

The investigation of K fertilization on different soils revealed either increasing or decreasing effects of K. The latter occurred at soils poor in clay, while the first happened to the soils with average clay content in the range of soils in this paper. The soil with highest clay amount was apparently not influenced by K fertilization. In some treatments (e. g. Spröda) drainage to -3 kPa increased the impact of K, others only reacted at the drainage level of -6 kPa with amplification (e. g. Pommritz). The comparison of K depleted and well-supplied treatments had similar results. The soil with highest amount of sand, Thyrow, exhibited a significant increase of shear strength with K addition, while the samples from Bonn at were not affected by K depletion albeit having distinctly higher clay and silt amounts. The third site, Bad Lauchstädt, was found to have a more brittle structure with K, the differences being more pronounced, i. e. significant, without liming.

Thus, the impact of potassium fertilization on rheological soil parameters was ambiguous and showed interference with several other parameters. This is first of all reflected in the comparably small coefficients of correlation when considering the parameters separately while a combination in a simple multilinear model increased the coefficient of determination R^2 between observed and modelled values to at least 0.743. Stepwise regression enhanced this model to an adjusted R^2 of up to 0.923. Depending on matric potential, different parameters were eliminated during stepwise regression to create the best fit, thus revealing the strong impact of matric potential that can lead to a completely different influence at different levels of drainage. The present work proved that soil strength is a rather complex matter even on the miroscale, and it depends on a multiplicity of parameters that, in turn, interact with each other manifold.

3.7 References

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4 PHYSICO-CHEMICAL PROPERTIES OF A LUVISOL AT THE MESO- AND MICROSCALE DUE TO DIFFERENT FARMYARD MANURE APPLICATIONS AND DIFFERENT K FERTILIZATION TREATMENTS

4.1 Abstract

This paper deals with the physico-chemical properties of a Luvisol derived from Loess near Bonn, Germany, under different long-term fertilization treatments. In 1904, an experimental trial was set up to determine the impacts of depletion of the main nutrients nitrogen (N), phosphor (P) and potassium (K) as well as the amendment of farmyard manure (FYM) and liming on 24 plots in total.

For the investigation of the impact of FYM, undisturbed samples were taken from selected plots samples in two different depths, namely with no fertilization at all (0), with full mineral fertilization (NPKCa), with farmyard manure only (0-FYM) and with both mineral and organic fertilization (NPKCa-FYM). Saturated hydraulic conductivity, air conductivity at several matric potential values, pore size distribution, as well as precompression stress, cyclic compressibility were investigated and related to rheological data at the microscale. Furthermore, chemical properties as well as rheological behaviour of homogenized samples were determined in order to quantify the structure effects on mechanical strength. Furthermore, samples from K depleted and K supplied plots under various FYM treatments were taken and measured in an amplitude sweep test in oscillating modus at matric potentials of 0 and -6 kPa. Additionally, the same material was tested after air-drying and remoulding at 0, -1, -2 and -3 kPa matric potential, respectively.

With respect to the organic fertilization a pronounced effect could be determined as for the FYM treated plots soil pores were increased and improved in their functionality which were attributed to the increase in organic matter and the consequently enhanced soil fauna creating well-connected pores. Though less dense, the structure was less prone to compression as the precompression stress was higher than in unfertilized plots. The mineral fertilization also increased pore volume but not pore functionality. The subsoil was rather unaffected by fertilization, instead it was influenced by texture. The rheological behaviour was related to cyclic compressibility and revealed a relationship between micro- and mesoscale. Homogenization could not eliminate the stabilizing effect of organic matter that was the more pronounced the more negative matric potential was.

K was found to increase microstructural stability but only if considered as actual K content of the soil, while K input was not well correlated to actual K content.

Homogenization of the samples led to distinctively different behaviour. However, further investigations of the soil particle surfaces and soil solution are needed in order to fully explain these interrelations.

4.2 Introduction

In the last century several long-term fertilization trials were set up as listed comprehensively by Debreczeni and Körschens (2003), the most known ones in Germany certainly being the trials on the Julius-Kühn Field in Halle (described in detail by Merbach and Deubel, 2007), the static experiment in Bad Lauchstädt (see e. g. Altermann et al., 2005) but also the trials in Thyrow initiated 1937 and 1938 by Opitz (described recently by Ellmer and Baumecker, 2005). Their originally intended purpose was to determine the effect of different amounts, kinds and combinations of fertilizers on crop yield in a long-term range, e. g. the effect of mineral versus organic fertilization or the depletion of single nutrients. Hence, the effect of farmyard manure versus mineral fertilization as well as nutrient depletion on crop yield was investigated many times, e. g. in the works mentioned beforehand.

Although designed to reveal the impact on yield and plant properties in general, those long-term trials also allow us nowadays after several decades with different fertilization to determine its influence on soil physical properties. According to Finck (1982), organic fertilizer either act on physical or on chemical properties. With regard to soil physics, the humic substances of organic fertilizers improve soil structure directly by loosening it with large humus particles and indirectly by the production of humates or cementing substances like bacterial residues. Several studies revealed that long-term organic fertilization increased number and biomass of microorganisms (Dick, 1992; Iovieno et al, 2009; Ge et al., 2010), accumulated bacterial residues (Jörgensen et al., 2010) and increased enzyme activity (Saha et al., 2008). Furthermore, humic substances increase the water storage capacity due to their inherent water storing structure and also by creation of medium and narrow coarse pores, which coincides also with better aeration. As a consequence of the darker color, humic substances raise soil temperature, enhanced by a structure in favour of better drainage. Soil chemistry is enhanced by the nutrient storing capacity of humic substances, contributing to the cation exchange capacity of a soil, and furthermore the provision of nutrients from the organic matter itself. Additionally, the decomposition of humic substances decreases pH and redox potential and thereby mobilizes some nutrients otherwise unavailable. But Finck (1982) also reports detrimental effects of organic matter. The less dense the soil structure the relatively weaker it is, while fixation of nutrients by humic substances occurs at a short-term range when microbes store ingested nutrients in their biomass and is even more pronounced at a long-term range when the transformation of humic substance leads to permanent humus which is hardly decomposable. Another negative effect of organic fertilization is reported by Haynes and Naidu (1998) as it can lead to water repellent soil that, in turn, exhibit lower water holding capacities and a reduced infiltration rate. Furthermore, at the microscale, small amounts of humic acids were found to increase clay dispersion due to their pH lowering impact, which, in turn, leads to edge-charge reversal (Tarchitzky and Chen, 2002a; Ramos-Tejada et al., 2003). As the positively charged edges are then occupied by humic substances of anionic character, the otherwise possible edge to face associations between clay platelets are blocked.

Occurrence and intensity of nutrient depletion strongly depend on the general fertility of the soil. The higher the initial resources of nutrients and the subsequent delivery from the soil the longer it takes to note remarkable differences. The most important fertilizer elements are nitrogen (N), phosphor (P) and potassium (K). With respect to the other elements, K is present in the soil in high amounts but only seldom easily available. Due to the role of K in plants K deficiency causes severe damage and reduces yield pronouncedly, especially of legumes as it inhibits N fixation (Prabhu and Fageria, 2007). Due to its mobility in the plant, symptoms of K deficiency appear first on older leaves, like stunting with little or no reduction in tillering but also dark leafs that appear withered, accompanied by chlorosis of interveinal areas and margins of lower leaves (Prabhu and Fageria, 2007). Tisdale et al. (1985) also found changes in root morphology, like reduced branching and less lateral roots.

The effect of K on soil, however, is ambiguous. Markgraf and Horn (2006) found a positive influence of K on microstructural stability, presumably due to a decrease in electrostatical repulsion and hence a net increase in attractive forces according to the double layer theory. Besides those investigations on differently fertilized soil samples, a recent work on remoulded soil samples from glacial till detected stabilizing effects of increased K concentration in soil solution (Holthusen et al., 2010). Similar results for other monovalent cations were found by Abend and Lagaly (2000) and Ramos-Tejada et al. (2001). Besides its flocculating impact due to high soil solution concentrations, K can stabilize particles directly via precipitation as described in Soulié et al. (2007) when crystallized along the menisci between particles. Indirectly it enhances plant growth and thereby, as mentioned above, e. g. the root system. Higher amounts of well-distributed roots, in turn, help develop soil structure due to wet-dry cycles, enmesh particles and release substances acting similar to humic substances, e. g. polysaccharides, which glue particles together (Bronick and Lal, 2005). Furthermore, K depletion was sometimes associated with clay mineral transformation from smectites to illites in the wake of K fixation (Tributh et al., 1987, Barré et al, 2007). While clay mineral transformation can not be related explicitly to either stabilizing or destabilizing impacts, other studies found a distinctively dispersing effect of K, equaling and even exceeding that of Na (Zalba et al., 1995). Especially if present in the soil in excessive amounts due to liquid manure (mainly dairy manure), K is said to enhance soil erodibility (Auerswald et al., 1996).

The aim of our investigations was to determine the impact of organic versus mineral fertilization as well as the effect of K depletion on soil physical properties. Due to the long time period of differentiated fertilization, pronounced effects may be expected as especially fertile loess soils like those found in the experimental area take a lot of time to be truly depleted of single nutrients. Investigations were done at the mesocale but also at the micro scale to determine and to compare the impact on both scales and possibly detect relationships between them. Besides the impact of different fertilizer treatments on the development of structure, namely the aggregation processes in the soil, the rheological investigation of homogenized soil also enabled us to reveal the impact of fertilization on the soil components themselves without the superimposing characteristics of structure.

4.3 Materials and methods

4.3.1 Investigated site and experimental trial

Among the many long-term fertilization trials in Germany, the experiment on the Dikop farm near Bonn started in 1904, designed to determine the depletion of the main nutrients nitrogen, phosphor and potassium as well as lime but also the effect of organic versus mineral fertilization. The farm is situated in the southern part of the Köln-Aachen bay on the intermediate terraces of the Rhine at 62 m. a. s. l. Due to the maritime climate the mean annual temperature is 9.9° C and the annual precipitation 633 mm. The general soil type was classified as a Luvisol derived from loess above sand (below 160 cm depth). The clay-deriched Al horizon is concordant with the ploughed Ap horizon (0-30 cm), followed by a illuvial Bt horizont until a depth of about 80 cm. The subsequent cambic horizon reaches until about 100 cm depth, while underneath a layer of parent loess, about 60 cm thick, is present until the parent sand and gravel layer starts beyond 160 cm depth.

Due to different fertilization for each of the main crop rotation fields 24 subplots were established and treated differently for more than 100 years. The following fertilizers were used: ammonium sulphate nitrate for N fertilization, triple superphosphate for P fertilization, muriate of potash (60 % K_2O) for K fertilization and calcium oxide for liming. The investigations in this work only deal with a subset of those plots, varying in K fertilization and in mineral and organic fertilization. The difference between K depleted and K supplied plots resulted in an annual input of 116 kg K per ha and year. Detailed information about the trial setup, fertilizer amounts subject to the crop and fertilizer as well as yield for selected treatments can be found in Schellberg and Hüging (1997).

An overview of the different treatments and the abbreviations that will be used in the following text is given in Tab. 4-1. Main soil properties of the investigated treatments are given in Tab. 4-2 and Tab. 4-3 for topsoil and subsoil, respectively. The amounts of extractable P and K were determined according to Schüller (1969) by calcium-acetate-lactate (CAL) extraction.

Table 4-1: Overview of different treatments in the long-term experiment at Dikop farm, Bonn (Germany), treatments with a * denote those plots investigated at the mesoscale and rheologically for determination of impact of organic vs. mineral fertilization while last two rows contain plots investigated rheologically for determination of impact of K depletion in interaction with different organic fertilization treatments

	No amendments	**Farmyard manure**	**Mineral fertilization equivalent to farmyard manure**	**Farmyard manure + mineral fertilization equivalent to farmyard manure**
No fertilization	0*	0-FYM*		
No potassium (= -K)	NPCa	NPCa-FYM	NPCa-mFYM	NPCa-2xFYM
Full fertilization (= +K)	NPKCa*	NPKCa-FYM*	NPKCa-mFYM	NPKCa-2xFYM

Table 4-2: Selected topsoil properties of the investigated treatments (in 10 cm depth): electrical conductivity EC[1], pH in $CaCl_2$[2], CAL soluble P and K content[2], soil organic carbon SOC[1], C/N ratio[1], cation exchange capacity CEC[1], sand (S), silt (U), and clay (T) content, n. d. = not determined

Treatment	$EC_{2.5}$	pH	P	K	SOC	C/N	CEC	S	U	T
	µS · cm^{-1}	-	mg 10^{-2} g^{-1}		%	-	mmol$_c$ · kg^{-1}		%	
0	31	5.36	2.7	3.9	0.67	11.2	187	14.3	72.5	13.2
0-FYM	58	5.67	6.9	12.4	1.03	11.9	93	14.4	74.2	11.3
NPKCa (+K)	59	6.24	7.9	8.4	0.86	11.6	88	14.5	73.9	11.6
NPCa (-K)	49	6.14	6.8	3.3	0.81	11.6	119	14.5	73.7	11.8
NPKCa-FYM (+K)	88	6.38	15.5	20.0	1.21	11.7	122	15.2	71.7	13.1
NPCa-FYM (-K)	88	6.26	16.2	10.4	1.21	11.6	108	n. d.	n. d.	n. d.
NPKCa-mFYM (+K)	61	6.21	10.3	8.8	0.89	11.2	94	14.7	72.7	12.6
NPCa-mFYM (-K)	57	6.50	10.6	4.4	0.80	11.8	100	n. d.	n. d.	n. d.
NPKCa-2xFYM (+K)	112	6.42	20.9	25.4	1.25	11.4	122	12.8	76.2	10.9
NPCa-2xFYM (-K)	96	6.38	20.6	13.9	1.30	11.7	116	n. d.	n. d.	n. d.

[1] Jahn et al., unpublished

[2] Schubert et al., unpublished

Table 4-3: Selected subsoil properties of the investigated treatments (in 40 cm depth): electrical conductivity EC[1], pH in $CaCl_2$[2], CAL soluble P and K content[2], soil organic carbon SOC[1], C/N ratio[1], cation exchange capacity CEC[1], sand (S), silt (U), and clay (T) content, n. d. = not determined

Treatment	$EC_{2.5}$	pH	P	K	SOC	C/N	CEC	S	U	T
	µS · cm^{-1}	-	mg 10^{-2} g^{-1}		%	-	mmol$_c$ · kg^{-1}		%	
0	28	6.05	0.25	3.66	0.35	8.7	n. d.	6.8	67.3	25.9
0-FYM	44	6.12	0.78	2.96	0.29	8.8	76	9.1	74.8	16.1
NPKCa	106	6.49	0.49	2.45	0.28	10.9	103	7.9	73.1	19.0
NPKCa-FYM	87	6.47	0.81	5.99	0.31	7.7	145	7.4	70.1	22.5

[1] Jahn et al., unpublished

[2] Schubert et al., unpublished

4.3.2 Sampling design

Undisturbed samples were taken in cylinders of 100 and 236 cm³ volume from four treatments (0, 0-FYM, NPKCa and NPKCa-FYM) for the determination of saturated hydraulic conductivity k_s, air conductivity k_l as a function of matric potential, pore size distribution as well as precompression stress P_c at -6 kPa matric potential, and coefficient of cyclic compressibility c_n at the same predrying intensity. Furthermore, changes in bulk density and air conductivity after predrying at -6 kPa due to static and cyclic loading were investigated.

For the investigation of rheological properties, undisturbed samples were collected from the topsoil (0-30 cm) of all treatments and prepared into specimen of about 2.8 cm height and 3.6 cm diameter. Disturbed samples from the same plots were air-dried at 20° C. Afterwards, they were sieved up to 2 mm and prepared for rheometry by filling them into small cylinders of about 2.8 cm height and 3.6 cm diameter at a bulk density of 1.5 g cm^{-3}. After saturation for two days both the undisturbed and remoulded samples were either measured in that state or drained to subsequent levels of matric potential (-6 kPa for undisturbed samples, -1, -2 and -3 kPa for remoulded samples). Immediately before the measurement, all samples were trimmed to a height of 4.5 mm and a diameter of 2.5 cm to match the plate-plate measuring system of the rheometer perfectly.

4.3.3 Rheometry

For the rheological measurements a rheometer MCR 300 (Anton Paar, Stuttgart, Germany) with a parallel-plate measuring system of 25 mm diameter was used. According to Markgraf et al (2006) amplitude sweep test was conducted with a deformation range of $\gamma = 0.0001 - 100$ %, a constant frequency of $f = 0.5$ Hz and 30 measuring points. In an amplitude sweep test the soil is placed between the two profiled plates after trimming it to a height that will guarantee contact between plate and soil surface but not cause any unnecessary pre-deformation of the sample. During the test, the upper plate oscillates due to a sigmoidal course with increasing amplitudes, characterized by the deformation γ as the ratio of the distance s that is covered by an imaginary point at the outer rim of the upper plate during oscillation, and the gap h between the plates (Eq. 4.1). 100 % of deformation therefore is reached when s equals h.

$$\gamma = s \cdot h^{-1} \tag{4.1}$$

It is: γ = deformation (%), s = distance (m), h = gap (m)

From the torque M needed for the movement and the radius r of the plate the corresponding shear stress τ of the soil is calculated (Eq. 4.2).

$$\tau(t, M) = (2 \cdot M) \cdot (\pi \cdot r^3)^{-1} \tag{4.2}$$

It is: τ = shear stress (Pa) as function of time and torque, M = torque (Nm), r = radius (m).

The particular advantage of the amplitude sweep test is that two raw parameters are derived instead of one like in rotational measurements. One of those parameters is the torque which can be converted to shear stress. The other one is the phase or loss angle δ denoting the delay between the presetted (γ) and the resulting (τ) curve. It is best described by two extreme examples: A loss angle of 0° (with regard to the sigmoidal course of the deformation and the resulting shear stress) is caused by perfectly elastic materials like for instance a spring, i.e. the highest deflection of the plate coincides with highest shear resistance. Perfectly viscous materials, in turn, exhibit the highest delay of 90° as maximum deflection is accompanied by zero shear resistance, like e. g. water.

Generally, the flow and deformation behaviour of each material features both of the two characters, namely elastic and viscous (also called plastic) behaviour. Therefore, the shear modulus used for a one-way movement according to Hooke's law is transformed into a complex shear modulus (Eq. 4.3).

$$G^* = \tau \cdot \gamma^{-1} \qquad (4.3)$$

It is: G* = complex shear modulus (Pa)

G' and G" represent the storage and the loss modulus. Both characterize either the stored energy and thereby the elastic deformation or the lost energy and the plastic deformation, respectively (Eq. 4.4). With tan δ being the ratio of G" to G', storage and loss modulus themselves are calculated in dependence of G* and δ (Eq. 4.5 and 4.6).

$$G^* = (G'^2 + G''^2)^{1/2} \qquad (4.4)$$

$$G' = G^* \cdot \cos\delta \qquad (4.5)$$

$$G'' = G^* \cdot \sin\delta \qquad (4.6)$$

It is: G' = storage modulus (Pa), G" = loss modulus (Pa)

Investigations of correlations proved that there is strong relationship between the different rheological parameters deduced from the amplitude sweep test. In the following, therefore only one parameter will be shown, namely the maximum shear resistance τ_{max}, which enables us to compare rheological behaviour at the microscale more easily to that on the mesoscale.

For more comprehensive information about rheology see the introductory works by Keedwell (1984), Vyalov (1986) and Mezger (2006) while detailed description of the used amplitude sweep test is given in Markgraf et al. (2006), Markgraf and Horn (2006 and 2007), as well as in Holthusen et al. (2010).

4.3.4 Pore functions

Saturated hydraulic conductivity k_s was measured with the falling head method described in detail by Hartge and Horn (2009).

While hydraulic conductivity was measured only for saturated soils, air conductivity k_l was measured at different stages of drainage as well as before and after static and cyclic loading according to the method described by Vossbrink and Horn (2004).

While k_l is dependent on soil and fluid properties, air permeability k_a depends exclusively on the pore geometry of the soil (Hillel, 1998). Hence, it was calculated as follows from k_l according to Upadhyaya et al. (1994) (Eq. 4.7).

$$k_a = k_l \cdot \eta_a \cdot \rho_l^{-1} \cdot g^{-1} \quad (4.7)$$

It is: k_a = air permeability (µm²), k_l = air conductivity (m s^{-1}), η_a = viscosity of air (Pa s^{-1}), ρ_l = density of air (kg m^{-3}), g = gravitational acceleration (m s^{-2})

To determine pore continuity two indices were used as proposed by Groenevelt et al. (1984) and termed them according to Ball et al. (1988) as C_2 (µm²) and C_3 (µm²). Both are calculated from air permeability k_a and air-filled porosity ε_A (Eq. 4.8 and 4.9), ε_A being the difference between total porosity and volumetric water content at a certain matric potential.

$$C_2 = k_a \cdot \varepsilon_A^{-1} \quad (4.8)$$

$$C_3 = k_a \cdot \varepsilon_A^{-2} \quad (4.9)$$

Similar pore size distributions and pore continuities can be derived from similar values of C_2, while similar C_3 values indicate *only* similar pore size distribution, thereby enabling us to detect differences in pore continuity by differences in C_2 and C_3 (Groenevelt et al., 1984). Ball et al. (1988) found a relationship between k_a and ε_A as follows (Eq. 4.10), that includes two empirical parameters, M and N, derived from linear regression.

$$k_a = M \cdot \varepsilon_A^{N} \quad (4.10)$$

In a log-log relationship Eq. 4.10 is converted to Eq. 4.11

$$\log k_a = \log M + N \cdot \log \varepsilon_A \quad (4.11)$$

The parameter N resembles the compressibility index c_n (described in 4.3.6 Static and cyclic loading), as both indicate the increase or decrease of void ratio e or air-filled porosity ε_A due to the influencing parameter number of cycles or air permeability k_a, respectively, equivalent to the slope in a linear regression. Consequently, N reflects the decrease of pore tortuosity and surface area with increasing air-filled pore volume (Ahuja et al., 1984).

4.3.5 Water retention curve

For each treatment eight soil cores of 100 cm³ volume were saturated for two days by capillary rise and afterwards drained at decreasing matric potentials of -3, -6, -15, -30 and -50 kPa on ceramic plates. After equilibration for each drainage step, the samples were weighed. Eventually, bulk density was determined after drying the cores in the oven at 105° C for 16 h. Total porosity TP as well as air capacity AC and plant-available water PAW were calculated according to Hartge and Horn (2009), assuming a particle density similar to that of quartz, namely 2.65 g cm^{-3}.

4.3.6 Static and cyclic loading

Static and cyclic loading was performed with a programmable pneumatic oedometer in combination with a software enabling specific stress paths, as described in Peth et al. (2010). To determine precompression stress P_c different stresses were applied subsequently on samples drained to -6 kPa with a pneumatic piston under confined compression while sinter metal plates on top of and underneath the samples allowed excessive water to drain off freely. The load steps 20, 30, 40, 50, 70, 100, 120, 150, 200, 300 and 400 kPa were applied each for 10 min. From the settlement recorded meanwhile, the precompression stress can be computed according to the method by Casagrande (1936).

Cyclic loading measurements were executed like those described in Peth and Horn (2006) and Peth et al. (2010), but with a load of 30 kPa, applied for 100 cycles of 30 s loading and 30 s unloading time. Similar to static loading, the settlement is recorded constantly, hereby enabling us to calculate changes in void ratio during the test.

The coefficient of compressibility c_n was derived according to Peth and Horn (2006) from the relationship between void ratio and the log-transformed number of cycles with the help of linear regression (Eq. 4.12).

$$e = e_u^1 + c_n \cdot \log N \tag{4.12}$$

It is: e = void ratio (-), e_u^1 = interpolated void ratio after the first unloading event, (-), c_n = coefficient of cyclic compressibility, N = number of load cycles.

4.3.7 Statistical analyses

For the statistical analyses the statistical software R, version 2.11.1 (R Development Core Team, 2010), was used. A correlation matrix according to Pearson was calculated with the help of the cor command in the stats package. To determine significant differences between treatments either one-way analysis of variance with a Tukey post hoc test or Kruskal-Wallis test with a post hoc test of multiple comparison according to Siegel and Castellan (1988) were performed for normally and not-normally distributed data sets, respectively. The commands used for those procedures were aov and kruskal.test (both in package stats), glht (package: multcomp) and for the post hoc test after performing Kruskal-Wallis test the command kruskalmc from the package pgirmess.

As values of saturated hydraulic conductivity k_s, air conductivity k_l as well as of air permeability k_a and the values derived from k_a, C_2 and C_3, are not-normally distributed, geometrical mean values were calculated and if necessary, visualization was done with the help of boxplots, enabling us to show within one graph median, 25 % and 75 % quartiles as well as whiskers with 1.5 times the interquartile range. Outliers are displayed as empty circles, for details see also McGill et al. (1978). No conversion to log values is needed, therefore, as median and geometrical mean do not differ significantly.

4.4 Results

4.4.1 Pore capacities

Total porosity (TP) in 10 cm depth was significantly increased due to farmyard manure (Tab. 4-4). However, with regard to plant available water (PAW), it made no difference if the fertilization was of mineral or organic kind (20.8 vs. 20.4 % PAW). Consequently, the combination of both of the fertilizer led to the highest amount of PAW, 21.3 %, in the topsoil. All those differences were significantly different from the unfertilized plot. The impact of farmyard manure on air capacity (AC) was less consistent and acted only at 0-FYM significantly increasing while at other treatments the differences were comparatively small.

In the subsoil (40 cm depth) the least TP was found for the fully fertilized plot, while the only organically treated plot had the highest TP with 39.7 %. AC was increased significantly either due to mineral or organic fertilization while NPKCa-FYM showed no significant difference to the unfertilized plot. Similar to the topsoil, the effect of treatment on PAW was little, and, hence, fertilization increased the values of fertilized plots only gently.

TP and AC were smaller in the deeper horizon, while the PAW values were rather similar. The differences in TP were 2-6 %, albeit AC values in 40 cm depth are reduced to one third up to half of the values from 10 cm.

With regard to the variation, a trend can be detected: Standard deviation is higher the more fertilizer is added. FYM enhances this effect, e. g. visible at the TP, AC and PAW values in the topsoil.

Table 4-4: Pore capacity values for total porosity TP, air capacity AC and plant available water PAW, mean plus/minus standard deviation, different letters indicate significant differences ($p \leq 0.05$)

Depth	Treatment	TP	AC	PAW
cm		------------------------------	% v/v	--------------------------
10	**0**	39.5±1.6 a	10.1±2.4 a	18.3±0.9 a
	0-FYM	44.6±1.6 b	14.4±2.6 b	20.4±1.2 b
	NPKCa	42.0±1.8 ab	11.4±2.1 ab	20.8±0.6 b
	NPKCa-FYM	43.4±3.0 b	11.6±4.5 ab	21.3±1.5 b
40	**0**	38.0±1.2 ab	3.1±2.2 a	19.4±1.4 a
	0-FYM	39.7±1.7 a	7.7±2.1 b	20.8±0.8 a
	NPKCa	39.4±1.8 ab	7.2±2.3 b	20.6±0.6 a
	NPKCa-FYM	37.1±2.5 b	3.3±3.5 a	20.3±1.2 a

4.4.2 Impact of organic versus mineral fertilization on pore functionality

4.4.2.1 Saturated hydraulic conductivity

The range of saturated hydraulic conductivity values comprises average to extremely high values according to the German guidelines for soil description (AG Boden, 2005) (Fig. 4-1). Classes range from ks1 to ks6: ks1 (very low) < 1 cm d^{-1}, ks2 (low) = 1-10 cm d^{-1}, ks3 (average) = 10-40 cm d^{-1}, ks4 (high) = 40-100 cm d^{-1}, ks5 (very high) = 100-300 cm d^{-1}, ks6 (extremely high) > 300 cm d^{-1}. Furthermore, the samples from FYM treatments (0-FYM, NPKCa-FYM) exhibited the highest variation, displayed in the length of the whiskers and hinges. The topsoil showed slightly higher values than the subsoil and different dependence on the kind of fertilization treatment. While in the topsoil the smallest conductivity was found for the minerally fertilized samples and the highest for the samples with organic and mineral fertilization, k_s in the subsoil increased significantly from zero to organic or mineral fertilization, respectively, and decreased when both fertilizer groups were added (NPKCa-FYM).

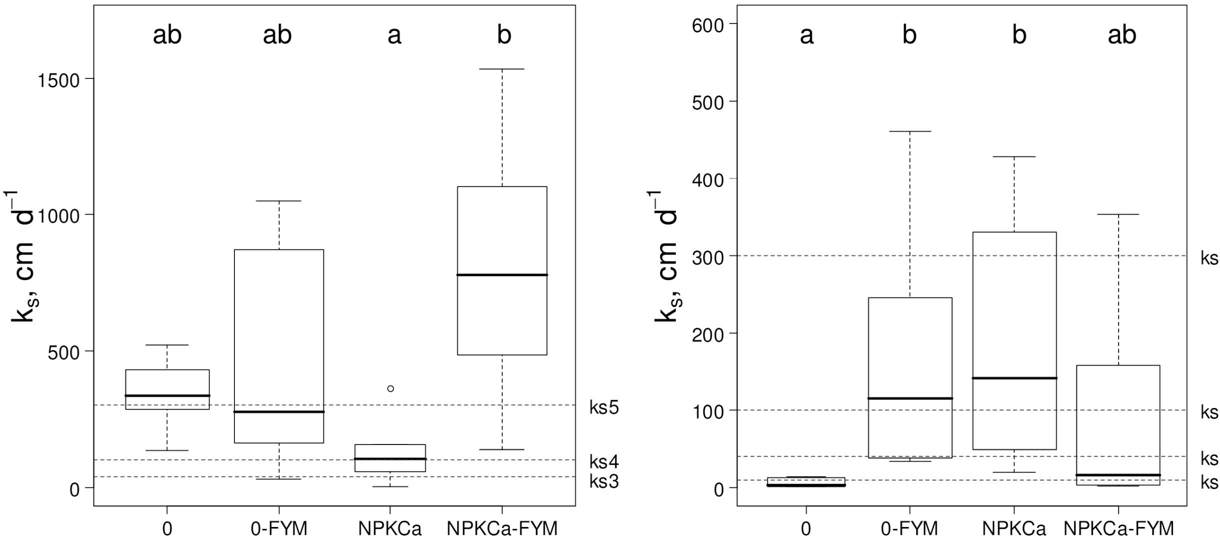

Figure 4-1: Boxplot of saturated hydraulic conductivity k_s in dependence of different fertilization treatments, for topsoil (left) and subsoil (right). n = 5-8 (box width represents n), dashed lines mark classes for k_s assessment, for explanation see text, labels are placed at the upper boundary of each class. Different letters indicate significant differences ($p \leq 0.05$)

The relationship between the saturated hydraulic conductivity k_s and matric potential dependent air conductivity k_l generally became the stronger the higher the desiccation (Tab. 4-5). The coefficient of correlation was always higher at 40 cm depth compared to 10 cm depth. Furthermore, the value increased with drainage level, hence r equals 0.90 for k_l samples at a matric potential of -50 kPa.

Table 4-5: Pearson coefficient of correlation r between k_s and k_l at different matric potentials, n = 4, significant values when $r > 0.95$ ($p < 0.05$)

	k_l at ψ_M =	-3 kPa	-6 kPa	-15 kPa	-30 kPa	-50 kPa
Depth	10 cm	-0.20	0.38	0.41	0.43	0.50
	40 cm	0.65	0.74	0.70	0.82	0.90

Analysis of linear regression showed that k_s is also closely related to precompression stress. The relationship was more pronounced in 10 cm depth compared to 40 cm depth. However, while in 10 cm depth increasing precompression stress is accompanied by decreasing conductivity values (r = -0.82), the opposite was true for the data in 40 cm depth (r = 0.61).

4.4.2.2 Air conductivity and pore continuity indices

To determine the effect of mechanical stress on air conductivity, Fig. 4-2 informs about the reduction of k_l during cyclic (30 kPa) and static loading (400 kPa), respectively. The air conductivity decreased the more the higher the load. This held true for both depths. In dependence of the load itself, the reaction of differently fertilized soil samples changed, too. While at 10 cm depth during cyclic loading with 30 kPa the highest reduction was observed for the 0-FYM treatment and the lowest for the control treatment, the distribution changed with high load and kind of loading. Under static loading conditions, now NPKCa was most susceptible to loading, even significantly different from the unfertilized treatment. In 40 cm depth, no significant differences were observed; however, a trend was displayed: At the low load level under cyclic load application, the loss in k_l increased from 0 via 0-FYM and NPKCa to NPKCa-FYM, while at 400 kPa, the sequence was reversed.

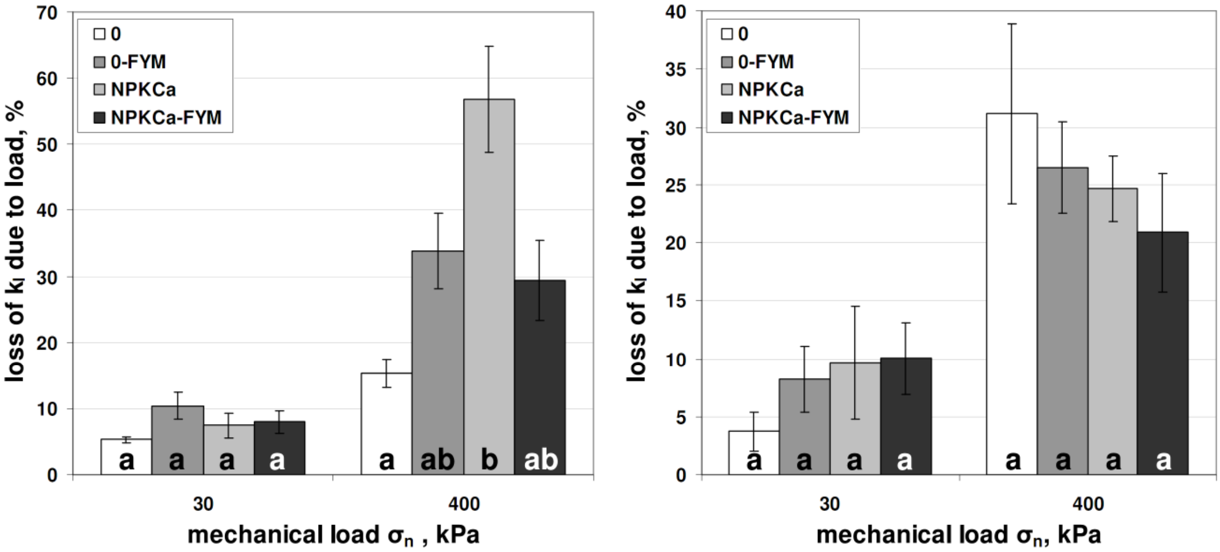

Figure 4-2: Loss of air conductivity k_l due to different mechanical stresses σ_n during cyclic (30 kPa) and static (400 kPa) loading for topsoil (10 cm depth, left) and subsoil (40 cm depth, right), error bars show standard error, different letters indicate significant differences ($p \leq 0.05$)

A closer look at the scales in Fig. 4-2 informs about the differences between top- and subsoil. In the topsoil the losses reached almost 60 % (NPKCa after loading with 400 kPa) while the highest reduction in subsoil was found at the unfertilized plot with an average value of about 30 % after loading with 400 kPa. In contrast to these differences, the values are similar in both depths, ranging from 5 to 10 % due to 30 kPa stress application.

To assess the impact of load, the absolute values before loading are given in Tab. 4-6. In the topsoil, the treatments 0-FYM as well as NPKCa attain very high values while the other plots reach only one third of those values. The difference is significant at a probability level of 5 %. In the subsoil k_l also increases with increasing fertilization. Compared to the control treatment, the difference is significant for the NPKCa-FYM treatment.

With regard to the loss of k_l shown in Fig. 4-2, the reduction in k_l found for NPKCa is more pronounced than for 0-FYM as they had initially a similar conductivity. On the other hand, NKPCa-FYM had a low k_l already prior to loading and lost additionally 30 % of it. In the subsoil a higher initial k_l coincided with a small reduction, i. e. the highest reduction and the lowest k_l were both found at the control treatment.

Table 4-6: Air conductivity k_l at a matric potential of -6 kPa of samples prior to loading in dependence of different fertilization treatments, either in log transformed values with standard deviation or as not-normally distributed values, n = 8, different letters indicate significant differences ($p \leq 0.05$)

Depth cm	Treatment	log k_l $cm \cdot s^{-1}$	k_l $cm \cdot s^{-1}$
10	0	-2.49±0.38 a	$3.3 \cdot 10^{-4}$
	0-FYM	-1.96±0.29 b	$10.9 \cdot 10^{-4}$
	NPKCa	-1.98±0.27 bc	$10.5 \cdot 10^{-4}$
	NPKCa-FYM	-2.36±0.39 ac	$4.3 \cdot 10^{-4}$
40	0	-2.68±0.33 a	$2.1 \cdot 10^{-4}$
	0-FYM	-2.48±0.30 ab	$3.3 \cdot 10^{-4}$
	NPKCa	-2.47±0.31 ab	$3.4 \cdot 10^{-4}$
	NPKCa-FYM	-2.35±0.29 b	$4.4 \cdot 10^{-4}$

In order to quantify the structure effect on pore continuity the relation between the air permeability and the corresponding air filled porosity was calculated. The idea of C_2 and C_3 is that if C_2 values of different sites or treatments are not significantly different from each other, they have similar pore size distribution and pore continuity. If C_3 values differ, however, this indicates different pore continuity values only. In the topsoil significant differences were found mostly between NPKCa and FYM treated plots, at -30 kPa also to the control treatment (Tab. 4-7). The subsoil samples showed no significant differences at all although, e. g. the air capacity values in Tab. 4-4 cover a huge range. Hence, despite a different pore size distribution the pore continuity is assumedly not different. The same holds true for C_3 values; the differences are similar to those of C_2.

At all drainage levels, the soils from 40 cm depth with the combined fertilization, NPKCa-FYM, exhibit the highest C_2 values indicating a high continuity or small tortuosity, respectively (Schjønning et al., 1999). At 10 cm depth the differences are not that persistent, instead the highest C_2 value can be found at the 0-FYM treatment at all drainage levels. At -3, -6 and -50 kPa the other FYM treated plot, NPKCa-FYM, attains the second highest value, but at the other levels 0 has higher C_2 values than NPKCa-FYM. Generally, C_2 and C_3 in the topsoil decrease with drainage from -3 to -6 kPa and increased again with further drainage while in the subsoil this holds true only for 0-FYM. The other plots showed steady decrease with increasing drainage. Furthermore, the C_2 values in the topsoil are generally higher than those of the subsoil except from the NPKCa treatment.

Table 4-7: Pore continuity indices at different matric potentials for two depths and four treatments, n = 8, different letters indicate significant different medians, p ≤ 0.05)

Depth	Treatment	at -3 kPa		at -6 kPa		at -15 kPa		at -30 kPa		at -50 kPa	
		C_2	C_3	C_2	C_3	C_2	C_3	C_2	C_3	C_2	C_3
cm		---------- $\mu m^2 \cdot 10^2$ ----------									
10	0	3.6 ab	38.2 ab	3.1 ab	29.9 ab	4.0 ab	35.7 ab	5.9 a	46.2 a	5.6 ab	33.9 a
	0-FYM	9.1 a	80.8 a	7.9 a	54.1 a	8.8 a	56.6 a	11.1 a	64.5 a	13.6 a	72.9 a
	NPKCa	1.7 b	17.2 b	1.7 b	14.2 b	1.7 b	12.9 b	1.7 b	11.2 b	1.9 b	9.9 b
	NPKCa-FYM	7.6 a	115.2 a	3.6 ab	32.2 ab	3.9 ab	31.1 ab	4.5 ab	32.4 ab	6.7 a	42.4 a
40	0	0.6 a	27.5 a	0.7 a	25.9 a	0.3 a	8.8 a	1.0 a	17.4 a	0.6 a	6.4 a
	0-FYM	1.4 a	23.2 a	0.6 a	7.8 a	0.5 a	5.7 a	0.8 a	6.7 a	1.2 a	8.6 a
	NPKCa	2.6 a	45.1 a	2.1 a	28.7 a	1.7 a	12.9 a	1.3 a	11.2 a	1.4 a	7.8 a
	NPKCa-FYM	1.7 a	32.4 a	2.0 a	89.5 a	1.0 a	24.8 a	0.9 a	12.5 a	0.8 a	8.5 a

4.4.2.3 Precompression stress and cyclic compressibility

No significant differences were found for the precompression stress P_c (Fig. 4-3). Samples from the topsoil had low to medium P_c values according to DVWK (German Association of Hydrology and Engineering, 1995).

Nonetheless, there is a trend for the samples from 10 cm depth. Fertilization increases P_c, independently of the character. But if both fertilizers were added, the soil was weaker (NPKCa-FYM). The visualization as boxplots also displays that the fully fertilized samples are skewed while for the other treatments the upper and lower hinges have roughly the same distance to the median.

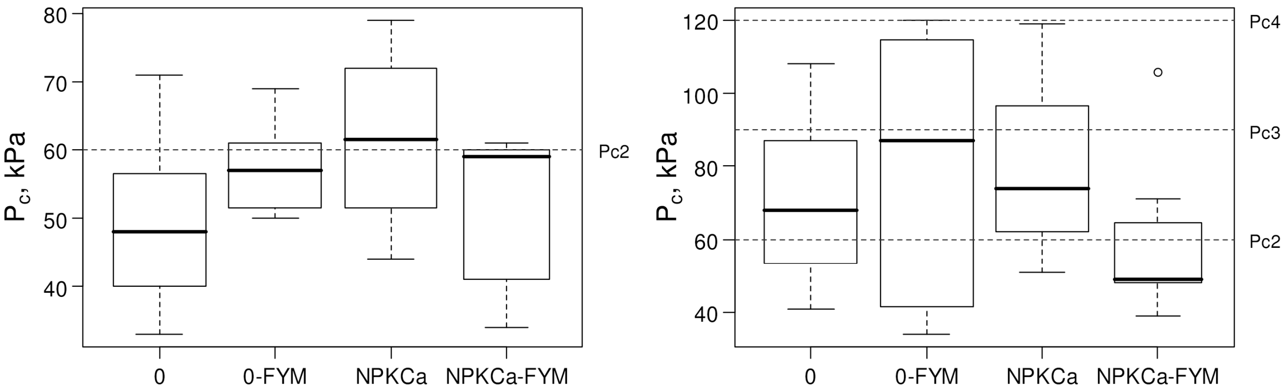

Figure 4-3: Precompression stress P_c in dependence of different fertilization treatments, for topsoil (left) and subsoil (right), n = 8 (box width represents n), dashed lines mark class borders of P_c assessment, for explanation see text, labels are placed at the upper boundary of each class, no significant differences at a probability level of $p \leq 0.05$

In subsoil FYM increased the mean value but also the variation, while mineral amendment increased P_c slightly without a noticeable change in variation. The soil was weakened by the combination of fertilizers, therefore, NPKCa-FYM exhibits the lowest P_c values of all treatments.

While P_c commonly is defined as the inner bearing capacity of a soil, the coefficient of compressibility (short: cyclic compressibility) c_n represents the ability of a soil to withstand repeated loading at a level within the range of precompression stress. A stress of 30 kPa is assumed to cause no plastic deformation of the soil because the precompression stress is always higher (Fig. 4-3). However, even this recompression is different for the examined plots, although differences were not significant (Fig. 4-4). The higher c_n the more susceptible is the soil to reduction in void ratio due to applied stresses (in this case to stresses even below P_c). Hence, fertilization weakened the topsoil compared to the control treatment. Combination of both fertilizers, in turn, resulted in a small increase of c_n only. In the subsoil a sequence appeared from zero amendment via organic and mineral to fully fertilized soil samples. In this case, a higher nutrient supply resulted in a higher compressibility and thereby a weaker soil structure.

Special attention must be paid to the opponent results for P_c and c_n of the samples from 10 cm depth: While having a high P_c, some treatments displayed a very high susceptibility to further recompression within this high P_c. For the topsoil, a linear coefficient of correlation of $r = 0.847$ was calculated, while in the subsoil $r = -0.635$.

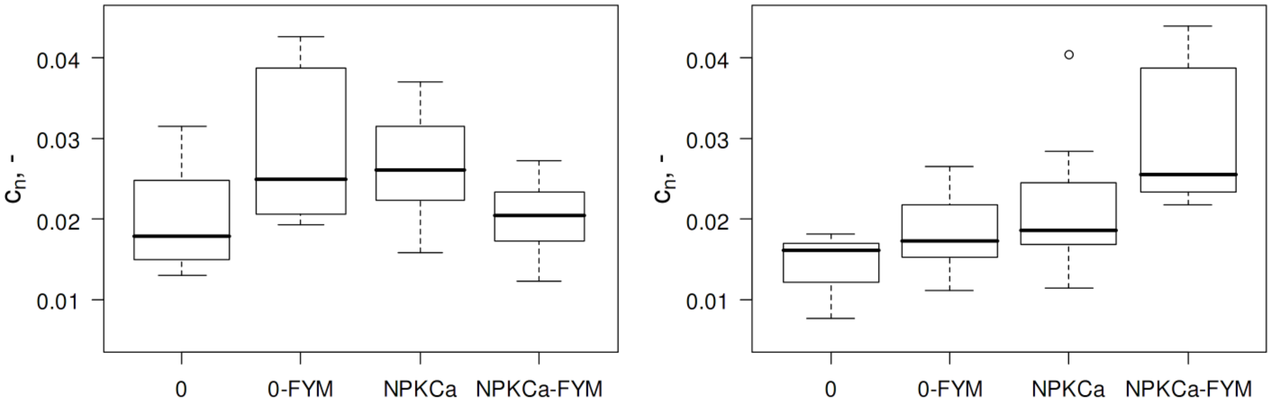

Figure 4-4: Coefficient of cyclic compressibility c_n in dependence of different fertilization treatments, for topsoil (left) and subsoil (right), $n = 8$, no significant differences at a probability level of $p \leq 0.05$

4.4.3 Rheometry

4.4.3.1 Impact of organic versus mineral fertilization

The results of the rheological measurement showed no significant differences for the saturated structured samples (Fig. 4-5, left). The samples, however, exhibited a tendency towards less shear strength with FYM or mineral nutrition while the combination of both fertilizers seemed to have no pronounced effect on τ_{max}. Drainage to -6 kPa (Fig. 4-5, right) enforced the tendency; hence the addition of fertilizer reduced the microstructural strength. The reduction became significant for the mineral amendment, while NPKCa-FYM had a slightly lower shear strength than the unfertilized plot. The microstructural samples are correlated well to bulk density ρ_B (1.81, 1.65, 1.60, 1.61 g cm^{-3} in 0, 0-FYM, NPKCa and NPKCa-FYM treatment, $r = 0.75$). Compared to the bulk density of the larger core samples, the small rheometry samples have larger bulk densities albeit the relationship remained the same.

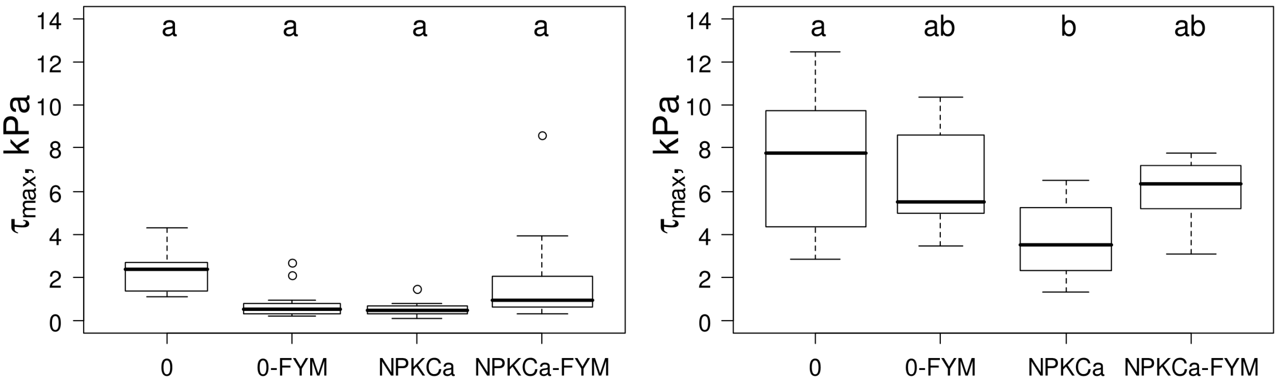

Figure 4-5: Maximum shear stress τ_{max} of structured soil samples in dependence of different fertilization treatments, at 0 kPa matric potential (left) and at -6 kPa matric potential (right), n = 8-12 (box width represents n), different letters indicate significant differences ($p \leq 0.05$)

Besides structured samples, also the rheological behaviour of remoulded samples was investigated after drying to defined matric potential values. Fig. 4-6 illustrated the results for four drainage levels, that apparently enhanced differences. While the saturated samples (Fig. 4-6, at the very left margin) show no significant differences and apart from that, similar tendencies as already found for the structured samples, drainage to -1 kPa revealed increase of shear strength with FYM (Fig. 4-6, left of centre). Drainage to -2 kPa in turn allows the not organically fertilized soil samples to catch up with the FYM treated plots. At the most negative matric potential the differences are very pronounced because the FYM treatments are intensely strengthened. The plot amended with NPKCa, however, did not gain any further strength due to developing menisci. Also the shear strength of the control treatment was only slightly increased.

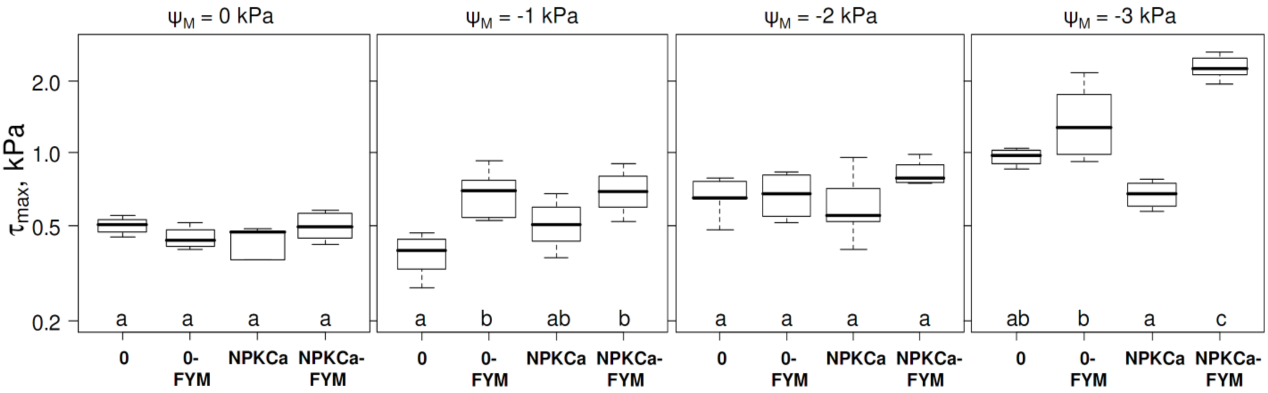

Figure 4-6: Maximum shear stress τ_{max} of remoulded soil samples (after sieving to 2 mm) in dependence of different fertilization treatments and at different matric potentials (from left to right

0, -1, -2 and -3 kPa), n = 5, different letters indicate significant differences ($p \leq 0.05$). For the sake of comparability, the ordinate is log-scaled.

4.4.3.2 Impact of K depletion and its interaction with organic and mineral fertilization

The setup of the experimental trial allowed us to determine the impact of K depletion in dependence of organic vs. mineral fertilization. The effect of omitted K fertilization on the structured samples was quite consistent (Fig. 4-7). At all levels of FYM application (no FYM, FYM, mineral nutrition equivalent to FYM and combination of both) the K depleted plot showed higher shear strength than the fully supplied plot. This held true for 0 and -6 kPa matric potential and the differences were mostly significant after more intense drying. Obviously, it made no difference whether organic or mineral fertilizers were applied, because FYM and mFYM samples showed rather similar values. The highest shear strength was found for the fully supplied samples with K depletion (2xFYM, -K), being significantly different from all other treatments at -6 kPa.

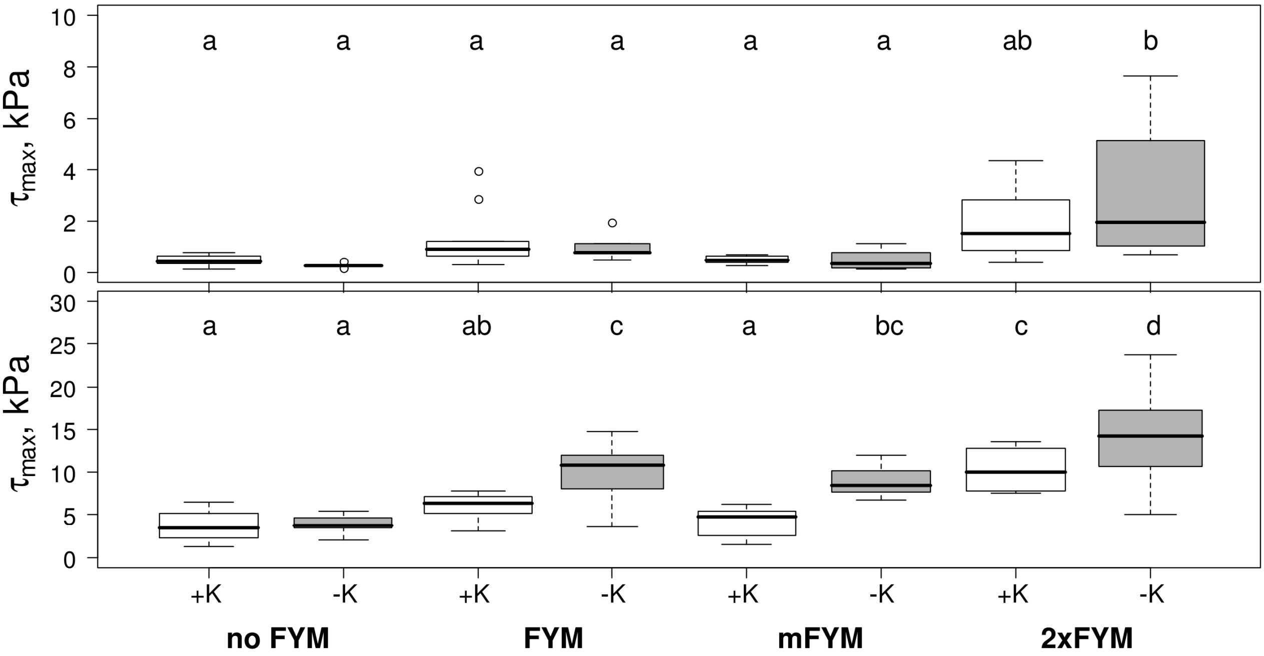

Figure 4-7: Maximum shear stress τ_{max} of structured soil samples in dependence of different fertilization treatments and at different matric potentials (0 kPa at the top, -6 kPa at the bottom). +K = fully K supplied, -K = K depleted, no FYM = no farmyard manure, FYM = farmyard manure, mFYM = mineral fertilization equivalent to FYM, 2xFYM = FYM plus mFYM. n = 5-12 (box width represents n), different letters indicate significant differences ($p \leq 0.05$)

Nonetheless, the K input does not fit perfectly with the K content of the soil. Hence, different results are gained when maximum shear stress is plotted against the actual K content of the soil (Fig. 4-8). Though negatively correlated to K input, τ_{max} of saturated samples is a linear function of K content with a coefficient of determination of $R^2 = 0.8497$ and positive slope, i. e. the higher the K content, the higher the maximum shear resistance (Fig. 4-8, top). This relationship is much more pronounced for saturated samples as R^2 of samples drained to -6 kPa is reduced to only 0.1501. But if the data set was divided into samples with and without K depletion and linear regression analysis conducted again for each data subset separately, the fit was pronouncedly improved to R^2 values of more than 0.8 (Fig. 4-8, bottom). If we consider the value of the K depleted plot without FYM ("none NPCa") as an outlier and therefore disregard it for a linear regression analysis, R^2 is even slightly enhanced (from 0.8223 to 0.852).

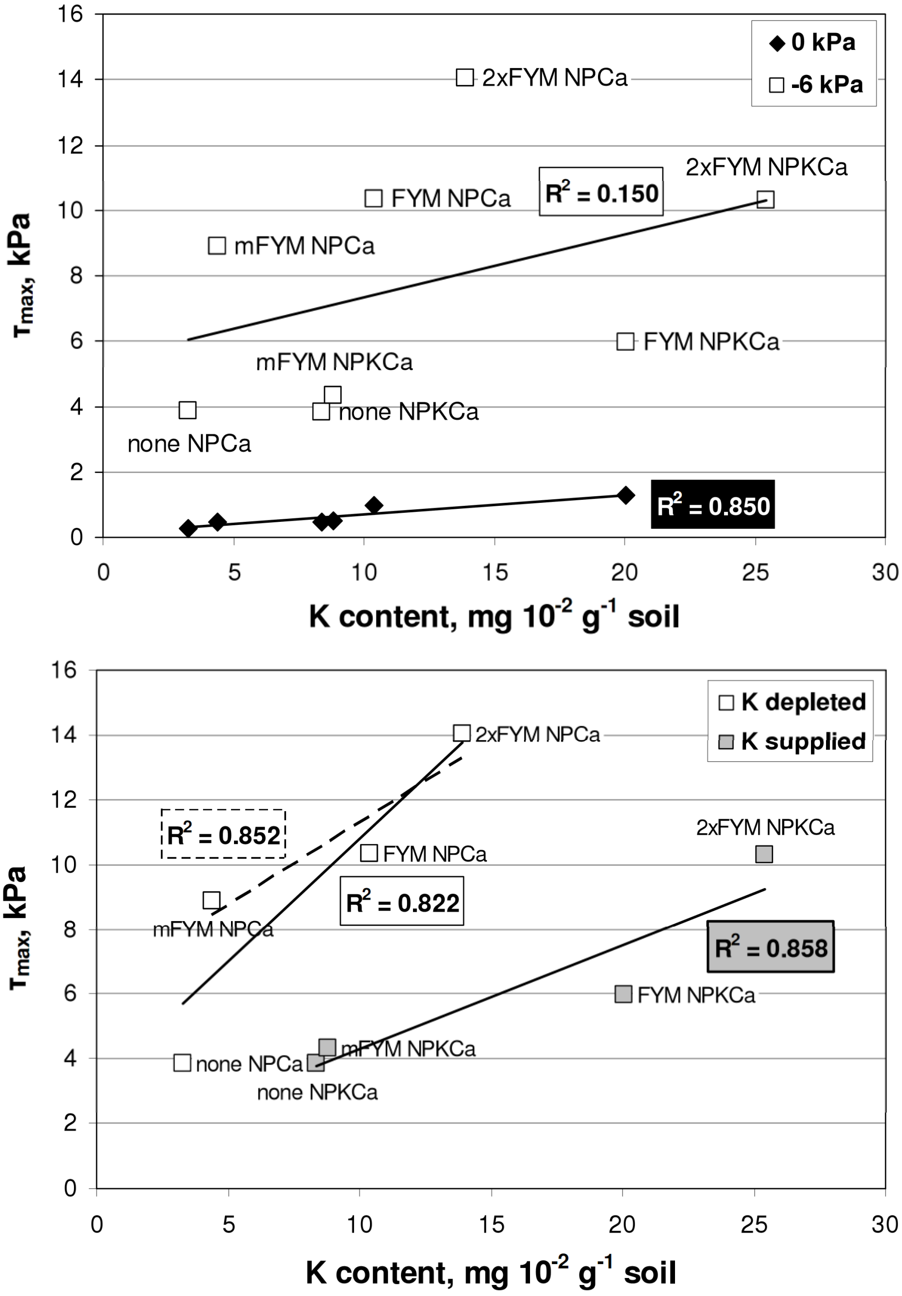

Figure 4-8: Maximum shear resistance as a function of K content of the soil in mg per 100 g of soil for different treatments (none = no FYM, FYM = FYM, mFYM = mineral fertilization equivalent to FYM, 2xFYM = FYM plus mFYM, N = nitrogen, P = phosphor, K = potassium, Ca = lime), different levels of drainage (top) and subsets of data with and without K fertilization, measured at -6 kPa (bottom)

Corresponding bulk density values for the samples shown in Fig. 4-7 are given in Tab. 4-8. It is visible that generally, higher values of τ_{max} coincide with higher values of ρ_B. Only the samples under 2xFYM treatment show lower bulk density in the K depleted plot albeit the values are rather similar.

Table 4-8: Bulk density ρ_B of structured samples used for rheological measurements after drainage to -6 kPa. Absolute values are probably overestimated due to drainage and resulting shrinkage

Treatment		ρ_B
FYM	K	g cm^{-3}
0	**+K**	1.60 ± 0.07
	-K	1.70 ± 0.06
FYM	**+K**	1.61 ± 0.07
	-K	1.75 ± 0.11
mFYM	**+K**	1.64 ± 0.04
	-K	1.74 ± 0.06
2xFYM	**+K**	1.72 ± 0.17
	-K	1.69 ± 0.11

The observations made at homogenized samples were in some cases opponent to the results of structured samples (Fig. 4-9). First of all, some treatment pairs of +K and -K exhibited increase in τ_{max} with K depletion like in Fig. 4-7 but other also showed the contrariwise behaviour. Samples without any FYM amendment showed a different trend as structured samples although the differences were not pronounced but weakened by drainage. With FYM addition the K depleted sample turned out to be significantly more stable at 0 and -1 kPa, but the difference was diminished at -2 kPa and disappeared at -3 kPa. On the other hand, the samples treated with nutrients equivalent to those of FYM but in a mineral form, displayed a tendency of decreased maximum shear stress when K depleted. But only at -3 kPa the difference became significant. Furthermore, the 2xFYM treatments added another pattern to the observations as at low drainage levels the K depleted sample is the weaker one. The more the soil is drained, however, the more the relationship changes until eventually at -3 kPa the K depleted samples are significantly more stable than the K supplied ones.

To determine whether the actual K content influences rheology stronger than K input, coefficients of correlations were determined for τ_{max} for each drainage level separately: 0.00 at 0 kPa, -0.15 at -1 kPa, -0.05 at -2 kPa and -0.18 at -3 kPa. Obviously, the main differences cannot be ascribed to actual K content, as well. Splitting the data in two groups of +K and –K increased r, but seldom to more than 0.3. The samples showed furthermore decreasing r with more negative matric potential.

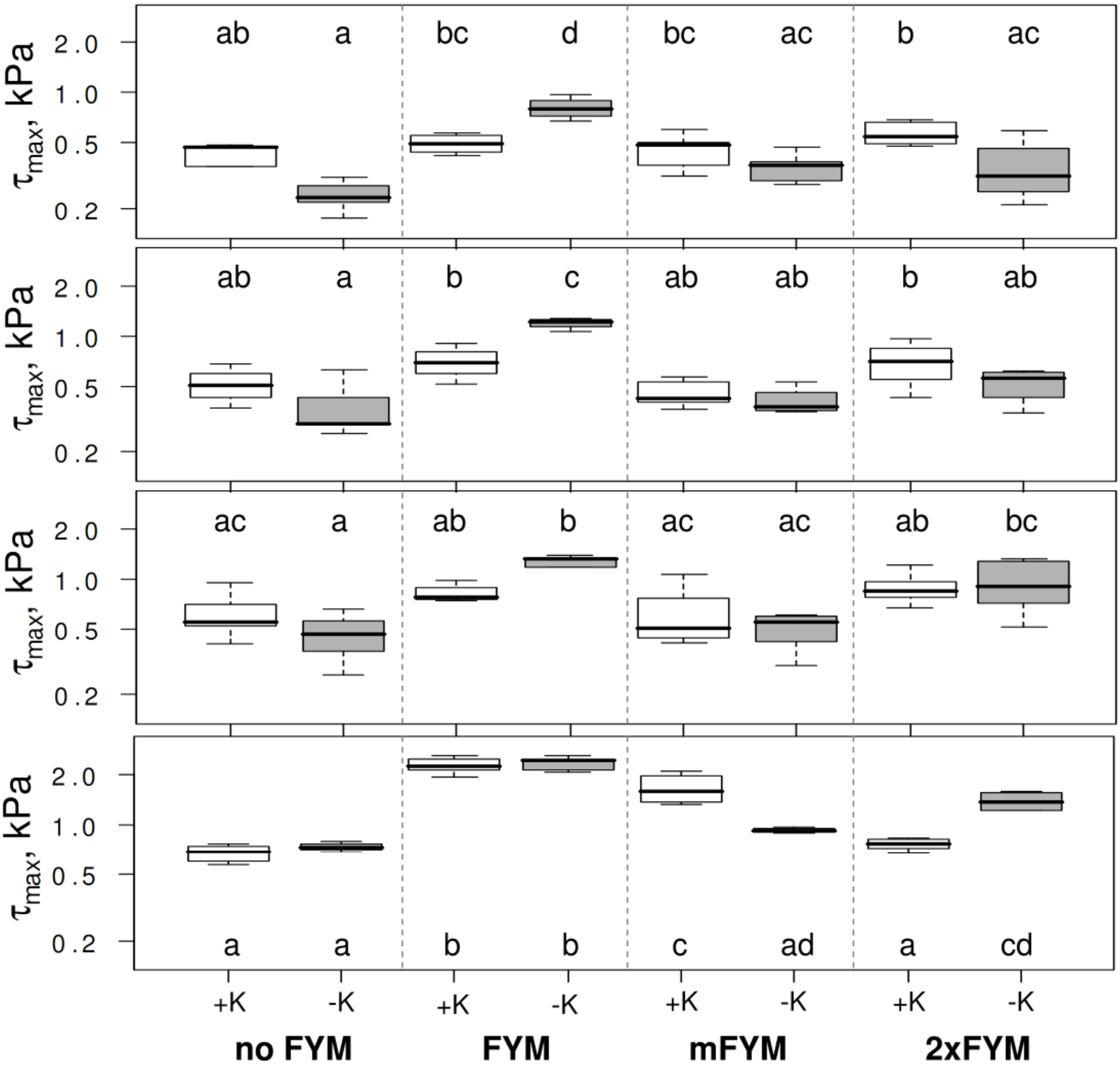

Figure 4-9: Maximum shear stress τ_{max} of remoulded soil samples (after sieving to 2 mm) in dependence of different fertilization treatments and at different matric potentials (from top to bottom 0, -1, -2 and -3 kPa), n = 5, different letters indicate significant differences ($p \leq 0.05$). For the sake of comparability, the ordinate is log-scaled.

4.5 Discussion

4.5.1 Impact of organic versus mineral fertilization

4.5.1.1 Macromechanical aspects

The different FYM treatments had a distinct effect on the physical properties which was different at meso- and microscale. The pore capacity and functionality was generally improved by farmyard manure as reflected e. g. by porosity and saturated hydraulic conductivity. Finck (1982) listed the pore volume creating ability as one of the advantageous effects of organic fertilization, increasing both microporosity (≈ 10 µm) due to elongated micropores and macroporosity (50-500 µm) (Pagliai and Antisari, 1993). Besides organic matter itself can storage water thus increasing plant available water (PAW). Salter and Williams (1963) found an increase in PAW of almost 75 % with the addition of 20 tons on sandy loam over a 6-year period, while Asmus (1990) determined an increase in maximum water capacity of 0.72 Vol. % per 0.1 % increase of organic matter content on an Albic Luvisol. Although the other parameters showed that it does matter whether the fertilization was carried out in mineral or organic mode, plant available water remained constant. However, the impact of FYM on air capacity (AC) was more pronounced and lost its impact in NPKCa-FYM probably due to a crumb-like structure that is softer and creates pores smaller in size, therefore enhancing directly PAW. However, organic matter can change generally hydrophilic mineral surfaces to be hydrophobic and thus decrease field capacity, causing severe water shortage (Hallett, 2008).

In the subsoil the impact of fertilization on pore size distribution can be neglected and is superimposed by texture as the clay-rich samples (0 and NPKCa-FYM) show lower TP and AC but similar PAW. As the higher TP equals less particle-particle contacts the samples are more prone to compression as is reflected in precompression stress values.

In our results the higher TP on FYM treated plots led to higher mean k_s while the variation was increased due to the enhanced earthworm activity as described by Edwards et al. (1990): When passing through the soil they create large pores compressing the surrounding bulk soil. Hence, Schrader et al. (2007) found an increase of 11 % in bulk density around earthworm burrows, distributed to an area with a total radius of up to 2.2 cm (including burrow). This can help explain high values as well as high variation of k_s as well as of k_l in FYM treated plots. Although the plots are ploughed regularly and thereby partly homogenized, the differences remain visible due to the ability of earthworms to outlast this process in the subsoil and to re-immigrate into the topsoil. Besides creating pores, earthworms create well-connected microaggregates through gut passage, but their quality strongly depends on the original soil properties (Schrader and Zhang, 1997). Compared to naturally aggregated soil, the aggregate stability of the earthworm cast was low, as the ingestion also destroyed existing bonds (Zhang and Schrader, 1993). Hence, the most advantageous effect of gut passage is the creation of hydrophobicity upon drying (Dekker et al., 1998) and thereby higher resistance towards slaking because the water infiltration rate is distinctively reduced (Zhang and Hartge, 1992), accounting also for high k_s.

The low values of k_s on the NPKCa plot presumably resulted from the orientation of pores mainly in horizontal direction. Although the total porosity is not distinctively smaller, these pores do not contribute to flow as reflected in the C_2 values that were the lowest for NPKCa treatment and did not increase with drainage. Predominance of horizontal pores is also reflected by the fact that the NPKCa samples were most susceptible to loading (400 kPa) with regard to air conductivity although the P_c was the highest of all treatments in the topsoil thus indicating a rigid pore system. One reason might have been a lack of root stabilization as generally aggregation is enhanced strongly by roots and hyphae that enmesh particles and induce wet-dry cycles due to transpiration (Angers and Caron, 1998; Bronick and Lal, 2005). On the NPKCa plot, however, the root system is presumably smaller because the overall availability of nutrients is high and thus the plant can satisfy its demand with less roots. As due to Bronick and Lal (2005) the main factors for soil aggregation are soil organic carbon (SOC), biota, ionic bridging, clay and carbonates, the impact of SOC increases in the absence of carbonates and at a similar clay content. SOC of the examined soil was increased by increasing fertilizer rates thus explaining the higher precompression stress albeit higher total porosity TP which is normally expected to accompany a loose and thus weak soil structure. So here the capacity parameters like bulk density are not reliable parameters to deduce intensity parameters like fluxes or strength as pointed out by Horn and Kutilek (2009).

In the wake of organic fertilization organic matter pools consist of the farmyard manure itself but soon also the plant growth as well as soil organisms (fungi, earthworms, microorganisms) add and change the composition of this pool. Earthworms enhance organic matter creation as according to Zhang and Schrader (1993) the ingestion by earthworms increased SOC by 4 to 21 % for burrow-wall material and by 21 to 43 % for casts depending on the species. Besides, ingestion also adds polysaccharides, which are strong but only short-term binding agents (Bronick and Lal, 2005). In 0-FYM and NPKCa-FYM plot polysaccharides exudated by plants as well as humic acids agglutinate particles allowing them a less dense packing and therefore higher k_l and k_s. Enhanced by the impact of earthworms, the gluing processes might be so pronounced that they create a structure of many small colloids instead of larger aggregates (Stott et al., 1999; Six et al., 2004) or even a homogenized soil due to mixing processes (Horn and Smucker, 2005), that results in a low absolute k_l as in NPKCa-FYM at -6 kPa albeit a high saturated conductivity k_s. At a matric potential of -6 kPa water locks pores smaller than 50 µm, but also larger pores can be excluded from flow when they are poorly-connected e. g. by narrow and thus still water-filled passages (bottlenecks, cf. Hamamoto et al., 2009). Such a structure, additionally, is very susceptible to compression as can be seen by low P_c.

With further drainage, k_l and k_s are better correlated as the pore volumes available for flow converge (Springer et al., 1998). Nonetheless, the relationships were always better in the subsoil, probably due to the overlying effect of fertilization in interaction with ploughing at the topsoil. Ploughing creates artificial chunks of soil with a high pore tortuosity in inter-aggregate pores (but still comparatively high continuity in the intra-aggregate pores). Because the different fertilization treatments enhance or impede the re-structuring of the soil, the pore continuity is heterogeneous in the topsoil while the subsoil structure is widely unaffected or at least to a lesser extent. Therefore, the existing pore capacities in the subsoil fit well with pore continuity, independent of drainage level, reflected both in the high coefficients of correlation of k_s with k_l as well as with TP, AC and PAW. Consequently, the differences in pore functionality in the subsoil rather depend on soil inherent properties than on fertilization. For instance, k_s is low in 0 and NPKCa-FYM treatments, where also the clay content is high, while the other two subsoils have less clay and higher k_s, as reflected by lower TP and AC. Nonetheless, the fertilized plots exhibit higher variations compared to the unfertilized plot, proving the existence of larger pores in an otherwise dense bulk soil. With regard to depth, Francis et al (2001) did not find earthworms to create significant porosity below 20 cm in a laboratory experiment. This stresses the assumption that the subsoil in our investigations remained widely unaffected by the fertilization treatments and did not significantly benefit from increased earthworm activity at the topsoil. However, Wierman et al. (2000) detected in 30 to 40 cm depth still fragments of channels in computer tomography images while Fazekas (2005) even found increasing percentage of earthworm burrows in a cross sectional area with depth, independently of soil management.

Contrary to our results, Haynes and Naidu (1998) found organic fertilization to decrease soil structural stability due to excessive amounts of monovalent cations like Na^+ and K^+ that lead to dispersion when they exceed the amount of polyvalent cations. Also NH_4^+ is said to favour dispersion if present in excessive amounts, which is likely to occur on the experimental trial on the Dikop farm as the applied N fertilizer contains NH_4^+. However, the influence is time-limited as NH_4^+ is nitrified to NO_3^- quickly when the conditions are advantageous (high soil pH, low levels of accumulated NH_4^+ and well aerated conditions). Excessive amounts of N and therewith NH_4^+ are only to be expected on the NPKCa-FYM treatment. As pore capacities as well as pore functionality is high on this plot, the dispersing effect of ammonium fertilizers seems not predominant. Furthermore, investigations of plots treated with different NH_4^+ fertilizers as well as without any N fertilization for 10 years revealed no significant differences in soil physical parameters like k_s and ρ_B (Intrawech et al., 1982).

The persistence of flow parameters is a suitable parameter for determining the soil's susceptibility to mechanical stresses as it enables e. g. the detection of changes in pore functions although the capacity parameters like bulk density and porosity are the same (Horn and Kutilek, 2009). In this respect, McCarthy and Brown (1992) found different relationships between air permeability and air-filled porosity depending on vertical or horizontal orientation albeit the same air-filled porosity. Thus, for their concept of risk assessment of subsoil compaction, Horn and Fleige (2009) recommend soil functions like air conductivity rather than e. g. penetration resistance and bulk density because only the first had a high ability to verify soil structure degradation. In our results, hydraulic stress generally had an impact on pore continuity which was consequently high for those plots with a supposedly high activity of soil organisms, namely in the FYM treatments. However, a general trend of decreasing C_2 values from -3 to -6 kPa might be explained by the changing composition of pores contributing to air flow. These coarse pores are mostly created by worms and roots. Further drainage does thereafter not enhance air permeability in the same intensity as the air filled porosity increases because additional air-filled pores are less continuous and smaller in diameter which intensely reduces the air or water fluxes. Instead, their structure is far from being regular and tube-shaped as some of them are relicts of ploughing. Although large parts of such pores are already emptied, the air flow is not increased in the same way because bottlenecks let water lock the pores. Only further drainage opens those pores and enables air flow. Moreover, the intra-aggregate pores that were spared from destruction by ploughing presumably have a low tortuosity, therewith increasing air flow above average. This is also the reason for the improvement of coefficients of correlation between k_s and k_l and, additionally, for the rising C_2 values. Instead, in the subsoil further drainage does not open pores with higher connectivity and, therefore, C_2 mostly remains the same. However, a constant C_2 value is not an indicator of constant air permeability - instead it characterizes an higher air permeability the higher the corresponding air filled porosity is (Reszkowska et al., 2010).

Loading destroys existing pores and increases pore water stress so the water disperses glued particles instead of contracting them. This is the more enhanced the shorter the duration of loading as water cannot exhaust, especially in poorly-structured soil (cf. Janßen, 2008; Zink, 2009). k_l is also reduced most where pores are not vertical and locked by extruding water (like in FYM treated plots as well as in NPKCa plot). While the impacts on k_l persistence in the topsoil were already discussed, the subsoil shows higher reduction of load the lower the initial air conductivity. Presumably, vertical and hence air conducting pores that were created by earthworms act as pillars due to the increased density of the burrow walls (Schrader et al., 2007). Therefore, the higher their amount, the less susceptible is the soil to deformation. The absolutely lower values of the subsoil are then mainly derived from the long-term structure development causing higher soil strength.

The similar absolute values of k_l loss due to cyclic loading show that c_n is strongly dependent on bulk density that is rather similar for the different horizons. As reported by Hartge and Sommer (1982), a similar reduction in void ratio is accompanied by similar increase in number of particle-particle contacts mainly independent of texture and aggregation. Though during cyclic loading the internal stress is not exceeded we observed a decline in pore properties as the repeated loading had a cumulative effect (O'Sullivan and Robertson, 1996; Alakukku et al., 2003). In this respect, Jorajuria and Draghi (1997) and Jorajuria et al. (1997) observed as much or even greater compaction due to many passes of a lighter tractor than due to fewer passes of a heavier tractor. Horn et al. (2003) stated that static loading led to a mainly vertical displacement while particles were aligned perpendicular to the stress during repeated wheeling. Dexter (1988) concluded, that externally applied stresses destroy the highest hierarchical order of aggregates present, leaving aggregates of the next hierarchical level with a higher internal strength. Thus, the relationship of void ratio and number of cycles follows a linear regression line if plotted in log-log-scales: The destruction of one aggregate level exposes the next, more rigid level to the stress, which was observed also by Peth et al. (2010) who found stepwise decrease in void ratio with increasig number of load cycles. During this process, aggregate fragments fill pores and thereby reduce conductivity which is often confirmed in the literature. What however is seldom dealt with is the effect of cyclic loading on changes in pore functionalities. Reszkowska et al. (2010) found well-structured soils to maintain air conductivity during a larger number of repeated loadings compared to soils affected by grazing and trampling. Air conductivity is furthermore reduced by a particle rearrangement as observed by Cetin (2004) who found particle orientations to become perpendicular to the maximum principal stress direction once the precompression of artificial soil cores was exceeded. This rearrangement surely is impeded by an already dense structure thus allowing the soil to keep more of the initial particle and hence pore arrangements as can be seen at the low reduction in k_l of the unfertilized treatment with.

The behaviour of the topsoil samples differed pronouncedly under low transient or high static load as soils with a high resilience exhibited a totally low precompression stress. Obviously, those different reactions are caused by mechanisms acting opponently. The glueing effect of organic substances e. g. can cause a high resilience within the range of precompression stress albeit this range is very low, which is in accordance with the findings by Zhang et al. (2005) who found peat amendment to increase compressibility but also resilience. By contrast, the well-structured samples had a higher total bearing capacity but are very sensitive to repeated loading.

Unfortunately, the investigation of the impact of cyclic compressibility lacks the long-term behaviour. According to Dexter (1988) it would be expected, that settlement due to external stresses below the P_c is reversible, e. g. upon wetting. This effect should be the more pronounced the more water expandable organic matter is present, resulting in a large rebound. Hence, the high susceptibility of organically fertilized soil samples to repeated loading reveals only the short-term behaviour while recovery on the long-term range might be different, possibly higher for the soil samples richer in SOC as observed by Soane (1990), McBride and Watson (1990) and Zhang et al. (2005). In this respect, Gregory et al. (2009) found higher resilience not only due to high soil organic matter contents but also due to wet-dry or freeze-thaw cycles, however, only at clay contents beyond 26 %. Thus, the presence of organic matter induced short-term recovery while otherwise structure-affecting components like clay first needed hydraulic stresses. McBride and Watson (1990) report a time period of 15-20 min required for the total rebound after loading intact cores from different soils. In their attempt to find a simple model for the determination of rebound they found a high correlation to organic matter content ($r = 0.796$) but also to bulk density before compression ($r = -0.627$). Consequently, rebound of the investigated samples can be expected to be high for samples high in SOC content as well as low in bulk density, and consequently confirm our results for the FYM plots.

4.5.1.2 Micromechanical aspects

4.5.1.2.1 Structured samples

As the results of the rheological measurements revealed, cyclic compressibility of the samples is highly related to microstructural shear strength. Obviously, both c_n and τ_{max} are caused by short-term particle-particle responses at the microscale. Therefore, it seems possible to relate properties gained at the microscale to those derived from mesoscale samples. Due to the strong impact of mesoscale structure on micromechanical behaviour, Fig. 4-10 shows the relationship between c_n and τ_{max} with the help of median values. If we consider arithmetic mean, a linear regression exhibits slightly higher or distinctively lower R^2 values (-0.841 and -0.123 for 0 and -6 kPa matric potential, respectively).

The common origin might be bulk density, as both the parameters depend strongly on the number of contact points between particles. The more contacts the more elastic is the soil under transient loading but also the more shear resistance is made available as particles can support each other or distribute incoming stresses on other particles. However, the bulk density itself showed only very small differences which were not significant at all. Hence, either already a slight increase in number of contact points can increase soil stability at the microscale or within the range of precompression stress, respectively, or the capacity parameter bulk density is not capable alone for the prediction of cyclic compressibility and microstructural shear strength and must be supplemented by intensity parameters (cf. Horn and Kutilek, 2009). However, to verify the hypothesis that a linkage between micro- and mesoscale is possible via the relationship of c_n and τ_{max} more measurements and also the consideration of several different soils with regard to properties of the solid phase (e. g. texture, CEC, SOC, inorganic carbon) as well as the aggregation level are required.

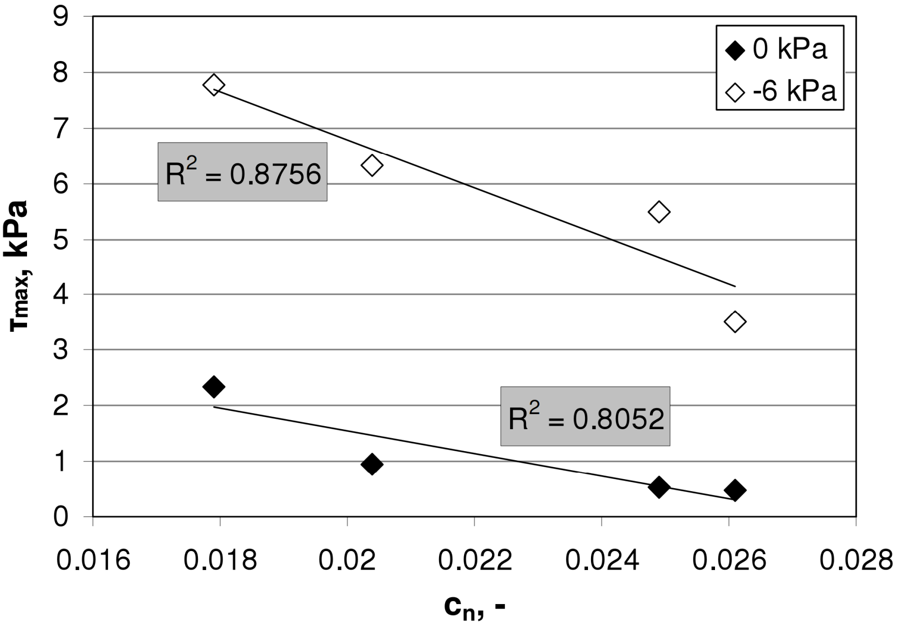

Figure 4-10: Relationship between cyclic compressibility c_n and maximum shear stress during amplitude sweep test τ_{max} in dependency of different matric potentials of τ_{max} (while c_n was determined at -6 kPa matric potential)

4.5.1.2.2 Remoulded samples

The homogenized samples enable us to detect mechanism formerly hidden by aggregation and eliminate the impact of bulk density. Although all samples reacted on increasing drainage with increasing shear resistance, the samples from the plots without FYM obviously were not stabilized by menisci at -3 kPa to the same extent as 0-FYM and NPKCa-FYM. The increasing content of organic matter was visible already at -1 kPa matric potential but became significant at -3 kPa eventually. This is in accordance to the observations Zhang and Hartge (1990) made when investigating the impact of organic matter on the cohesion of unsaturated sandy soils: The distinct increase in cohesion due to organic matter they explained by an higher water retention that enhances development of more menisci. This, in turn, increases the area on which the menisci can exert their contracting forces and thus, the effect of organic matter is brought out only after drainage and is not visible in saturated state. Furthermore, Zhang and Hartge (1989) found organic matter to increase the surface roughness which increases shear resistance, too (DeJong and Westgate, 2009).

4.5.1.3 Interim conclusions

In conclusion FYM amendment increased porosity and pore functionality in the topsoil. It lead to a higher amount of plant available water and enhanced the activity of soil organisms. Mineral fertilization also increased porosity but not pore functionality. A combination of both FYM and mineral fertilization improved microaggregation but weakened the structure, resulting in low P_c. Short-term loading revealed sensitivity of FYM treated plots although a higher rebound was expected. It can be hypothesized that further rebound can take place upon wetting the samples. The parallel observation of samples at meso- and microscale revealed a relationship between cyclic compressibility and maximum shear resistance during amplitude sweep test thus enabling upscaling to a certain extent.

4.5.2 Impact of K depletion and its interaction with organic and mineral fertilization

4.5.2.1 Impact of FYM treatment

The kind of FYM treatment generally influenced both the K depleted and the K supplied plot in a similar way resulting in increased shear strength with FYM as well as with mFYM while the highest fertilization (2xFYM) caused the highest microstructural shear strength. The effect of FYM treatment was pronouncedly stronger at -6 kPa matric potential but already visible under saturated conditions, while K depletion revealed its impact only after drainage. Furthermore, FYM and its mineral equivalent obviously could deploy their stabilizing impact better on K depleted samples as seen for the drained samples. Here, the +K plot was not enhanced at all by mFYM and sligthly by FYM whereas the -K plots were significantly strengthened. 2xFYM increased shear strength at both plots, but it was exhibited more pronouncedly the less K was present.

4.5.2.2 Impact of K depletion/K content

From the literature, it can be concluded that a lack of K can either result in a decrease or an increase of particle interactions, due to attractive or repulsive forces. If we assume the stabilizing effect to prevail, K supplied samples are supposed to own a more rigid structure than K depleted samples. Hence, the structure is less susceptible to slaking and either remains stable during ploughing or re-attains its rigidity after ploughing more easily. In contrast, K depleted samples are prone to compaction which causes an increase of grain-grain contacts and hence increased friction. The higher amount of particle contacts is well reflected by the higher bulk density on the K depleted plots. According to Carter (1990), Servadio et al. (2001) and Zhang et al. (2001) a higher bulk density increases shear strength at the mesoscale, hence a similar process at the microscale can be assumed, causing higher shear resistance for the K depleted plots. This effect was only exhibited after drainage to -6 kPa which can be attributed to increased number of contact points and hence increased number of menisci exerting contracting forces on the particles while in saturated state more contact points do affect shear strength to a lesser extent. Hence, to determine the impact of K and FYM itself on the particle interaction, the impact of bulk density has to be eliminated. As this was done by homogenizing the samples, those results will be discussed later.

With regard to K input, K addition seemed to result in an overall reduction of shear strength at the microscale. However, the K input does not always equal the K content of the soil (cf. Kuhlmann and Wehrmann, 1984). Hinsinger (2002) stated that the plant demand can be met to up to 100 % by interlayer K release of clay minerals. Additionally, investigations of Andrist-Rangel et al. (2006) revealed uncertainty about the representativeness of several methods to determine K content in soil. As the CAL soluble K is defined as the amount of K easily available for plants the main focus will be on this amount but neglect those K pools accessible only beyond exhaustion of easily available resources in the following. This distinguishment is necessary because of the very different impact of K input versus actual content, as our results revealed. The difference between each pair of +K and -K plots resulted in a shear strength increase with K depletion which can be explained by the microstructure collapse as described above.

It could be proved that the maximum shear resistance during amplitude sweep test increased with increasing actual K content, expressed by a linear regression line where more than 80 % of the shear stress variation of saturated samples was explained by K content. This positive relation is mostly influenced by the FYM treatments as the corresponding +K and -K plots of each FYM treatment are rather similar. Drying required the splitting of the dataset to reveal the stabilizing effect of K content. The least stability was found for the unfertilized samples and increased with the following sequence: mFYM, FYM and 2xFYM. Hence, mineral nutrition was less effective in stabilizing soil structure than organic matter, while the combination of both maximized shear resistance because of an increased proportion of humates, a higher ionic strength and possibly ion precipitations that, in turn, can cementate particle bonds (Soulié et al., 2007).

A special experiment was set up in 1929 in Versailles, France, where no crops were grown on the plots, therewith enabling the determination of the influence of fertilization on the soil without plant-induced changes. The manure treated plot was more water repellent than not organically fertilized plots but attained also the highest water retention and total porosity, while sodic and potassic plots had lowest values (Pernes-Debuyser and Tessier, 2004). Furthermore, the authors found K and Na to produce intense surface crusting followed by considerable water ponding after rain. Hence, they concluded, that K as a monovalent cation enhances soil dispersion and degradation. As the structured samples revealed, K stabilized the soil, but with regard to the results found by Pernes-Debuyser and Tessier (2004) this might be primarily ascribed to plants growing differently or releasing different substances.

4.5.2.3 Remoulded samples

4.5.2.3.1 Conservation of structure due to micoaggregates and organic matter

To eliminate the impact of bulk density remoulded samples were investigated. The variety of shear strength reactions on K depletion in combination with the predrying effects after homogenization is suggestive of the existence of other influencing parameters than K fertilization and matric potential. Obviously, the elimination of different bulk densities as the most important influencing factor unmasked other influences previously superimposed by structure. Like for the samples shown in Fig. 4-6 organic fertilization caused an increase in shear resistance if we neglect the K fertilization. However, the impact was more pronounced when the soil was K depleted as could be seen at the FYM treated samples compared to the plots having not received FYM at all. With regard to the bulk densities measured before homogenization, it can be hypothesized that the denser soil samples allowed also for the existence of particle clusters in the wake of more contact points. Where cementing substances were present (like e. g. polysaccharides, humic acids), the homogenization process possibly did not affect those clusters that again increased the roughness and hence shear strength (Zhang and Hartge, 1989) already in saturated state due to apparent mechanical cohesion (Mitchell, 1993). So the distribution of bulk density of structured samples is reflected by shear strength at 0 kPa matric potential for those samples with organic fertilization while in the unfertilizid plots as well as in the mFYM plots the binding agents were either less effective or not enough.

4.5.2.3.2 Salt impact

If no organic fertilizer is added, the water saturated K depleted soil was less stable. Drying to -3 kPa matric potential strengthened the -K samples identically as the +K samples. Thus, it can be stated that the shear strength of the -K samples is small with respect to the actual matric potential (as a pulling force) and hence drying resulted in a shrinkage which was more intense than that of the +K samples at the same matric potential as they were already stabilized by the presence of K. Moreover, this strengthening can be a result of crystallization as in accordance to Alaily (1979) the salt concentration increases with decreasing pore size. As with higher drainage subsequently smaller pores remain water filled their salt content hence might increase. This in turn can cause crystallization as described by Soulié et al. (2007). Albeit similar nutrient amounts, the effect on microstructural stability was distinctively different for FYM and mFYM samples. In a saturated state the mFYM samples exhibited a similar behaviour as the samples without FYM. However, at -3 kPa the +K samples gained strength above average (compared to the otherwise similar samples without FYM). Probably the higher salt content also led to the development of salt cementation as it can be also assumed for the +K treatment under FYM influence. However, in order to explain these strengthening processes more comprehensively both at the micro- but also at the mesoscale shrinkage tests and corresponding strain and rheometric measurements must be made in order to finally calculate the interparticle forces.

4.5.2.3.3 Interaction of K depletion with organic matter

For the homogenized samples the effect of K was not persistently dispersive but instead was related to FYM treatment and matric potential. Besides the conservation of structure due to organic matter as binding agent despite homogenization, another possible reason are interactions between organic matter in different stages of decomposition and humification with the solid soil phase as well as with K. The degree of humification can be assessed by CEC as of all organic matter only humus can noticeably enhance CEC, generally supplied by clay. Data in Tab. 4-2 reveal higher CEC of FYM amended +K plots compared to -K plots while in treatments that received none ore only mineral fertilization the CEC was higher in -K plots. It is assumed that the presence of K enhances the decomposition of fresh organic matter and hence the humification and therewith creation of persistent humus. However, the effect of differently humified organic matter and the general composition of the organic matter require further research with regard to the multiple influencing factors. Furthermore, special attention must be paid to the accessibility of structure-relevant agents as the work by Hartmann et al. (1998) proved: Well-structured soil samples exhibited pronounced differences in CEC if measured in homogenized or structured state, the later being much lower. Hence, some of the differences revealed by homogenized samples in the present work might originate in the improved accessibility of K thus revealing the lack of fit between capacity and intensity parameters (Horn and Kutilek, 2009).

Though SOC is only slightly lower in the K depleted plots, the effect might be emphasized by the different interactions of SOC with texture. Kay (1998) stated the less clay a soil has the more important is the clay type in determining aggregation. In general, high activity clays like smectites and other 2:1 clays have high cation exchange capacity, large surface areas and high SOC content, all of correlated to high levels of aggregation. However, their expandability can disrupt aggregates upon wetting and makes them more susceptible to dispersion compared to less reactive clays, e. g. kaolinites (Bronick and Lal, 2005). A clay mineral transformation as reported by (Tributh et al., 1987; Srinivasa Rao and Khera, 1994) in the wake of K depletion seems only possible in an noticable extent at the plots without FYM as FYM or its mineral equivalent possibly compensated for the lack of K. A hint for a clay mineral transformation can be found in CEC. As described in the previous paragraph, the organic treated plots had larger CEC where K was supplied. On the contrary, without FYM, CEC was higher in K depleted plots. As expanded clay minerals offer more exchange sites, a possible clay mineral transformation can be reflected by increasing CEC values with K depeletion. In FYM treated plots this phenomenon was then superimposed by an increase in CEC by organic matter that is assumedly enhanced by K. The resulting expanded smectites then could either enhance aggregation due to high surface activity or decrease shear resistance as they are said to have lower shear resistance than illites (Laribi et al., 2005). With regard to our own results, they are more in accordance with the observations made by Laribi et al. (2005). Assuming the dominant clay mineral in +K to be illit and in -K smectite, the convergency with drainage might be a consequence of a better interaction between menisci and expandable smectites than with non-expandable illites, leading to a reversal of differences.

4.5.2.3.4 Changes in the soil solution

Another impact of fertilization that can be revealed only by investigations of homogenized samples, is the induced change in soil solution properties which cause e. g. an increase in viscosity. Tarchitzky and Chen (2002b) examined the impact of polysaccharides as temporary binding agents that are produced by microbes degrading organic residues on the rheology of clay suspensions. Like humic acid (Tarchitzky and Chen, 2002a), the polysaccharides impede edge to face associations of clay platelets, however, they can act as binding agents themselves and link clay minerals in manifold constellations. The resulting flow curves showed, therefore, a decrease of shear strength at low polysaccharide contents and increasing resistance to deformation at high polysaccharide contents. On the other hand, Barré and Hallett (2009) found a root mucilage analogue (polygalacturonic acid, PGA) and a fungal polysaccharide (scleroglucan) to increase viscosity by up to 10-fold in 2:1 clay-dominated soil. In 1:1-(kaolinitic) dominated soils the viscosity was also increased but to a lesser extent and the impact of scleroglucan was higher than that of PGA, while a sandy soil was not influenced at all. At higher shear stresses, however, the artificial biological exudates caused shear thinning. Zhang et al. (2008) investigated the fracture toughness, indicating the ability of a material to resist the growth of a crack, as influenced by root exudates. They found an increase by PGA which was even enhanced by washing (for the simulation of weathering). The higher strength due to washing was explained by several processes, among them the elimination of excessive PGA otherwise keeping particles in a distance too large for Van der Waals forces to overcome. This might help explain the changing relationships in the FYM treated plots with drainage: with the removal of soil solution and probably excessive amounts of PGA or similar substances, the particles were able to approach and improve soil structure therewith. The plots fertilized with K (+K) should contain more PGA and thus exhibit higher stability with further drainage.

4.5.2.4 Interim conclusions and outlook

The highly fertilized plot 2xFYM exhibited different impacts of K depletion in dependence on matric potential as in moist state K acted stabilizing and at -3 kPa matric potential destabilizing. While the impact of K input at 0 kPa is similar to that on no FYM and mFYM, the K depleted samples gained strength above average with drainage while the +K treated samples are only slightly stabilized by menisci. Eventually, at -3 kPa the +K samples even lost strength while the -K samples remained the same. Without detailed knowledge of the fundamental processes, this change cannot be related satisfyingly to fertilization but has to consider also changes in plant growth and therewith induced soil changes that lead to the described interaction with matric potential. In order to fully understand the processes of strength gain or loss in combination with or because of the decomposition of FYM and its constituents detailed investigations of the microbiology and redox reactions are needed. Therefore, further investigations of the homogenized material and the change of properties of the soil solution with increasing matric potential at the microscale are suggested. One opportunity could be to determine the roughness of the surface attributed to different fertilization treatments as due to Heil and Sposito (1995) organic matter increased roughness of soil colloid surface as detected with the help of scanning force microscopy, which, in turn, can raise friction (Alshibli and Alsaleh, 2004). With regard to K amendments, Chen et al. (1983) found K to cause microaggregation and precipitate on sand grains, which can also increase surface roughness distinctively. A less smooth surface also could be derived by weathering, salt cementation and its interaction with matric potential and, therefore, help explain our results. Furthermore, the interaction between viscosity, salt concentration, and matric potential could help to get more insight in the strengthening or weakening processes at the particle to particle level, i.e. microscale.

4.6 Conclusions

Organic fertilization increased pore capacities and pore functionality in the topsoil. Furthermore, it supported the activity of earthworms that in turn created air and water conveying vertical pores, which were more resistant to loading. Neither was the so formed structure destroyed by ploughing completely nor the pore continuity in persistent inter-aggregate pores of the remaining soil chunks. Thus, pore continuity of the organically fertilized samples was high under wet conditions and further increased strongly when dried due to the opening of less tortuous and finer pores. Especially the high fertilization rate at the NPKCa-FYM plot led to a crumble-like structure that contained high pore volumes but because of negligible small pore continuity the structure mostly did not support intra-aggregate air and water flow.

The precompression stress and the cyclic compressibility values were both higher with farm yard manure application compared to minerally fertilized samples.

Mineral fertilization also increased pore volume compared to the unfertilized plot but obviously this pore volume owned a low pore functionality determined by a smaller saturated hydraulic conductivity lower than in the unfertilized plot. Despite the high precompression stress (presumably because of a more compressed soil structure), the loss in air conductivity was comparatively high. The pore continuity was the lowest of all observed plots.

In the subsoil, soil physical properties were mostly unaffected by fertilization.

Rheological investigations revealed similar results as obtained for cyclic compressibility and enabled a relationship between meso- and microscale. After homogenization, the predominant effect of organic matter persisted and was the more pronounced the drier the samples. The structure degrading effect of NPKCa was also more pronounced leading to the lowest shear resistance of remoulded samples at -3 kPa.

The impact of K depletion on rheological soil properties revealed both a destabilizing impact of K input but a stabilizing impact of the actual K content on the maximum shear stress during amplitude sweep stress. The interaction between the added or the “available or accessible/active“ K and the mineral particles depends on the actual K saturation and the clay mineralogical reactions. The higher the K content and the better it can be distributed within the soil particles the higher the strength. Homogenization of the samples removed the impact of structure, but less comprehensively for the samples with organic amendment as was exhibited by similar behaviour of homogenized saturated samples and structured samples. At comparable initial bulk density of the differently FYM treated samples some results are still unclear and deserve further investigation to unravel the intertwined influences of different fertilization treatments as well as the indirect changes in the soil due to differences in plant growth and exudation of biological exudates.

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5 CONCERTED DISCUSSION AND CONCLUSION

This work showed the impact of K on rheological properties of soil samples saturated with KCl solution in various concentrations in a short-term range as well as in a long-term range as exhibited by the investigation of soil from long-term fertilized plots. Furthermore, it revealed the manifold interactions with other soil components as well as with other factors like climate. It was shown that a simulation of shear strength in the soil needs a variety of different parameters for a good fit that, in turn, differs according to the superimposing impact of matric potential. Additionally observance of the effect of organic fertilization versus mineral fertilization revealed the aggregation-supportive impact of organic fertilization that enables the soil to provide good conditions for plant growth and to persist during mechanical stresses by keeping pore functionality. The investigations also gave evidence of a relationship between the deformation behaviour at micro- and mesoscale.

As proved by Or and Ghezzehei (2002), some of the post-tillage soil structural dynamics can be modelled very well with the help of rheometry, being either of steady or transient character. The steady stress is represented by the shear stress necessary to induce flow and hence can be described with the help of the Bingham model, namely by the parameters plasctic viscosity and yield stress (Or and Ghezzehei, 2002; Karmakar and Kushwaha, 2005, 2006; Czibulya et al., 2010). Or and Ghezzehei (2002) found two-parameter exponential equations to predict very well the yield stress τ_B and the plastic viscosity η_p with the help of matric potential and employed those findings to supplement previous model assumptions with regard to aggregate coalescence due to drying and wetting cycles. With the help of the results gained in this work, the change of structural dynamics under steady stress can be predicted also in dependence of existing K content of the soil. Though further research is needed for the determination of the short-term impact of K on other soil materials, this first approach presented in this work can add a term to the model dealing with steady stress during drying by Or and Ghezzehei (2002) as our results showed e. g. an increase in maximum shear resistance of sandy soils with increasing K content. The ambiguous effect of K revealed by the examination of long-term experiments, however, requires the consideration of the soil type itself, exchange capacity, pH and several other parameters.

The results of this work can contribute even more to the modelling of structural dynamics under transient stress as rheometry is a very powerful method to imitate even the stress exerted upon soil by the passage of tractor wheels or farm implements (Or and Ghezzehei, 2002). Although, generally, the maximum shear resistance was used, analysis of correlation revealed a high interdependence with the other parameters derived during the amplitude sweep test, which is in agreement with the findings by Ramos-Tejada et al. (2001) who established scaling laws between several rheological quantities (steady, oscillatory, or transient). Hence, an increase of maximum shear resistance indicates not only a simultaneous increase of e. g. storage modulus at the end of the linear viscoelastic range (G' (LVE) but can be also related to other rheological quantities, e. g. those determined by Or and Ghezzehei (2002). Or and Ghezzehei (2002) conducted a test similar to the amplitude sweep test used in this work but with a sinusoidal shear stress instead of a sinusoidal shear strain as presetting. Furthermore, different frequencies were used to simulate different velocities. The derived parameters phase shift angle δ as well as complex viscosity η^* enabled the distinguishment of viscous and elastic deformation as η^* describes both viscous and elastic strains whereas δ contains information about the relative contribution of each (Ghezzehei and Or, 2001). Therewith the simulation of single or repeated wheeling both as a function of shear stress and frequency (i. e. velocity of the passing tractor) could be modelled assuming that wheeling causes elastic and viscous strain (cf. Horn et al., 1998; Horn and Baumgartl, 2000). Despite its different design, the amplitude sweep test provides the relationship between shear and strain (deformation) as well as the phase shift angle δ during oscillation. Although plastic viscosity η_p is not available, the complex shear modulus G* can replace it as it represents both the elastic and viscous strain, given by storage modulus G' and loss modulus G". Consequently, for a range of deformation rates as well as shear rates a corresponding shear stress can be calculated for each level of K in the soil solution, thus enabling the prediction of change in soil structural dynamics due to K in the soil solution. This is in accordance to the request by Rosenqvist (1984) for an implementation of a term that deals with the pore water chemistry into Terzaghi's effective stress equation (1925, cited in Rosenqvist, 1984). In its simplest form, the equation considers the pore water pressure u_w and the principal stress σ to determine the effective stress σ' (Mitchell, 1993; Horn and Baumgartl, 2000) (Eq. 5.1):

$$\sigma' = \sigma - u_w \tag{5.1}$$

While Eq. 5.1 is valid for saturated soils, in unsaturated soils stresses are also transmitted by the gaseous phase, resulting in the addition of the pore air pressure u_a and the χ factor that indicates the degree of saturation (Bishop, 1960) (Eq. 5.2). χ ranges from 0 (dry soil, $u_w = -10^6$ kPa) to 1 (saturation, $u_w = 0$ kPa).

$$\sigma' = (\sigma - u_a) + \chi\,(u_a - u_w) \tag{5.2}$$

The combination of Terzaghi's with Coulomb's equation for the determination of shear strength of a soil hence can be written as in Eq. 5.3 (Rosenqvist, 1984):

$$\tau = c + \sigma' \cdot \tan\delta \tag{5.3}$$

It is: τ = shear stress (Pa), c = cohesion (Pa), δ = angle of internal friction (°).

Rheometry in general as well as the results gained in this work in special can contribute to the determination of a cohesion parameter reflecting the existence and consequences of cemented bonds and their fragmentation into nonreversible and reversible components. Following the recommendations by Denisov and Reltov (1961) who suggested the implementation of cementing bonds either via the cohesion or via the external stress, the impact of pore water chemistry can be incorporated by two parameters, c_c and f_c, as proposed in Eq. 5.4.

$$\tau = (c + c_c) + \sigma' \cdot (f_c \cdot \tan\delta) \tag{5.4}$$

On the one hand, the salt increases the overall cohesion, which is implemented via c_c. On the other hand, cemented bonds might be broken with increasing normal stress. Thus, the additional cohesion c_c is a function of stress which can be implemented by the factor f_c. This factor has an upper limit of 1 where cementing bonds are unaffected by normal stress and is the lower the more bonds are broken with increasing normal stress. In this way, also the ability of some bonds, especially of chemical nature, to re-develop after rupture is reflected in f_c. As the results of the present work proved an amplification of general trends with a more negative matric potential, the dependency of cohesion on water content can be incorporated by multiplying c_c also by the χ factor, thus resulting in an effective c_c' (Eq. 5.5).

$$\tau = (c + \chi \cdot c_c) + \sigma' \cdot (f_c \cdot \tan\delta) \Rightarrow (c + c_c') + \sigma' \cdot (f_c \cdot \tan\delta) \tag{5.5}$$

Both c_c and f_c are strongly influenced by soil inherent properties like texture, cation exchange capacity, soil organic carbon et cetera, which requires a multiple approach for the determination of c_c and f_c.

As the results showed, not the absolute input of a salt is the determining influencing factor, similar to the critics uttered by Horn and Kutilek (2009) with regard to a lack of relationship between soil physical capacity and intensity parameters. Hence, it was proved that more attention has to be paid to the actual content in the soil, but also to the prevailing interactions with other binding or dispersing agents that are present in a natural soil. This is either a consequence of pronounced changes of the soil due to fertilization or distinctively different reactions on the same fertilization due to the inherent differences of the present soil. Moreover, besides the chemical distinguishment of different K fractions in the soil which still lacks a uniformly definition, manifold interactions between physical and chemical processes have to be assumed. For instance, the availability of K is not only dependent on the strength of the bonds attaching K ions to mineral and organic surfaces and molecules but also the accessibility which in turn is strongly influenced by aggregation amongst others. This was confirmed by the completely different results of samples either structured or homogenized which stresses the need for further investigations of the interactions of K with the soil and its components generally and with the present structure as well as with the structure developing in the wake of K addition. Moreover, further investigation of the plant-soil-fertilizer system is necessary to distinguish between the yield-increasing processes originating from the plant, the soil and from the place of interaction between the two of them, because several authors examining the plant itself found distinct improvement of water use efficiency in plants well supplied with potassium due to a decrease in transpiration (e. g. Egilla et al., 2001; Huang, 2001). Furthermore, more research about the interactions between soil mineralogy and K addition has to be done as there are hints that the clay mineralogy is decisive for an either stabilizing or destabilizing impact of K (cf. Chen et al., 1983; Arienzo et al., 2009). Eventually, the microstructural stability of a soil can be related to the percentage of K at the exchange sites and thus become predictable by the Gapon equation albeit the restriction of comprehensive accessibility (Hartmann et al., 1998) and simple implementation of binary coefficients into ternary and quarternary cation-exchange-systems (Feigenbaum et al., 1991; Wada and Seki, 1994; Evangelou and Lumbanraja, 2002; Hannachi et al., 2009).

To sum up, a supplementation of nowadays valid recommendations for K fertilization is not possible yet because the processes and mechanisms that determine the impact of K addition in soils either to be dispersive or to support aggregation still need further investigation. Moreover, dispersion or aggregation in turn lead to different soil conditions, that in some cases might be in favour for or in other cases impeding the attainment of agricultural aims like higher yield, increased water and nutrient efficiency and sustainability as well as decreased environmental effects. However, it can be concluded, that sandy soils benefit much more from additional K fertilization than did soils with a higher clay and/or silt content where other aggregation-enhancing substances or mechanisms are prevailing. As described in the Pareto principle according to Juran (1941, inspired by the works of Vilfredo Pareto, 1848-1923), 20 % of effort are responsible for 80 % of the resulting benefits and vice versa. With regard to soil science and agriculture, the improvement of fertility and physical performance of well-structured and highly fertile soils by nature, like loamy soils, takes 80 % of effort to receive the remaining 20 % of obtainable soil fertility and performance. Yet on soils less fertile, like the sandy soils investigated in the present work, little effort can cause comparably high benefit. Hence, the results at hand might be implemented in K fertilization recommendations with respect to a re-valuation of texture impact and interaction with K fertilization.

As revealed by the other main focus of the present work, also organic fertilization influences soil structure pronouncedly and can help attenuate the negative impacts of soil compaction. In this regard, a clay loam was found to take 2 years for recovery, while a heavy clay took even 5 years in spite of annual ploughing and frost while in subsoils, depending only on natural processes like freeze-thaw, wet-dry cycles and biological activity, this takes even longer (Alakukku, 1996). Hence, it is inevitable to avoid compaction or to establish a soil less prone to compaction. Our results showed organic fertilization had a similar effect as mineral fertilization on the pore capacity, but the pore functionality was much more enhanced with farmyard manure and thus was more persistent. Hence, though generally the availability of mineral fertilizers, their reliability and rather easy management makes their usage very advantageous, the positive influences of organic fertilization on soil structure and soil persistence due to compaction should not be forgotten (Alakukku, 1996). Furthermore, as stated by Syers (1997), "[…] chemical fertilizers alone cannot achieve long-term productivity on many soils and organic material inputs are required to maintain soil organic matter". Especially with regard to the recent detachment of animal husbandry and the corresponding agricultural cultivation of arable land, one has to reconsider the usage of animal wastes that is nowadays mostly regarded as a disposal of wastes, while once liquid and farmyard manure served as a valuable source of nutrients as well as a soil conditioner free of charge and ready at hand.

By determining soil physical properties at different scales, a relationship between rheological parameters characterizing properties at the microscale and soil physical parameters at the mesoscale was established. Although a linear regression line revealed a high correlation this aspect needs further investigation. To make sure the observations are not coincedental, other soils and treatments have to be measured with both the methods to consolidate the hypothesis stated here. One possiblity is the comparison between shear tests at the microscale as conductable with rheometry and shear tests at the mesoscale as conductable with the shear frame test described e. g. in Dörner and Horn (2009). But also a change in deformation behaviour in dependency of scale can help to gain new insight into interactions between bulk soil and single components of the soil and thus reveal information about the different impact of e. g. fertilization at different scales. Thus, increasing contents of organic matter can enhance the association of single particles whereas it might not increase aggregation at a larger scale while roots enmesh particles especially in sandy soils to macro aggregates but do not affect the interparticle forces generally (Oades, 1984). Thus, investigating the different scales can also add information in the field of aggregate hierarchy and the processes influencing it. This could enable the determination of angle of internal friction as well as cohesion in-between particles themselves.

Another approach is the establishment of a relationship between rheological parameters at the microscale and the concept of precompression stress as a parameter for soil strength at the mesoscale (Horn, 2003). According to Ghezzehei and Or (2000) soil behaviour can be described by the Bingham model i. e. a certain yield stress, corresponding to a certain soil strength, has to be overcome by the capillary forces to cause aggregate coalescence (i. e. visous or plastic deformation). However, the process of aggregate mergence is not ceaseless; indeed it is restricted by increasing shear strength, finally exceeding the capillary forces and thus ending coalescence. In agreement with those findings, it seems possible to compare the yield stress of a given soil at a given matric potential with the precompression stress (in this case determined by means of hydraulic stresses). A similar approach was reported by Karmakar and Kushwaha (2007) who found a statistically significant positive relationship between soil compaction and yield stress. As postulated by Ghezzehei and Or (2001), rheometry is even more useful in simulating transient loadings. This is in accordance with the findings of this work as results gained with rheometry were highly correlated to results gained by cyclic (i. e. transient) loading.

The present work mainly focussed on amplitude sweep tests and revealed significant impact of e. g. K content of the soil on the maximum shear resistance. Hence, an impact on yield stress as determined in accordance to the Bingham model can be hypothesized. Future investigation thus could consider the impact of K and other stabilizing or dispersing agents, respectively) on yield stress in relation to precompression stress of a soil.

6 SUMMARY

The present work deals with the impact of fertilization on soil stability as it can be determined with the help of rheometry. The sensitivity of rheometry to detect differences in microstructural stability was proved in previous works but still there is a lack of knowledge with regard to the influencing factors, especially salts that occur in soils. Special attention was paid to potassium (K) as several studies revealed a positive impact of K fertilization on water use efficiency of plants. Besides the fact that K decreases the transpiration rate of plants, another explanation is the improvement of soil structure in the wake of K amendment as it might enhance microstructural stability and therewith increase plant available water. Thus, the general research objective was the impact of K, but also of organic versus mineral fertilization on microstructural stability by means of an amplitude sweep test to eventually allow for a comparison of fertilization impacts at different time and spatial scales.

The first attempt was to test how K influences the shearing resistance of a saturated sample at a short-term range. Samples from glacier till were saturated with KCl solutions of varying concentrations for three different time periods. It could be shown that the rheological parameters shear stress τ at the end of the linear viscoelastic range, maximum shear stress τ_{max} and storage modulus G' and loss modulus G", respectively, at the yield point were increased due to increasing K concentrations in the soil. Raising the time of exposure to the salt solution enhanced this effect, thus indicating that age-hardening is promoted by KCl. Additionally, the impact of drying was found to be related to shear strength as with decreasing matric potential the soil samples had higher values of rheological parameters, i. e. a higher strength.

To supplement the investigations of the impact of K with regard to the long-term range, the second attempt dealt with the observation of microstructural properties of samples from several long-term fertilization trials. Those plots were mainly designed to reveal the impact of different K fertilization rates on plant growth and yield but are also adequate for the investigation of soil properties. Hence, the shear resistance of soil samples was determined at several matric potential levels and afterwards related to the physico-chemical properties of the soil. Both the consideration of the impact of single or combined parameters revealed that soil physical parameters are not determined by a single factor but depend on a multiplicity of parameters that, in turn, interact with each other. With regard to K, both stabilizing and destabilizing effects were found, mostly related to soil texture: While soils with rather coarse texture were stabilized by K, soils with an average clay content revealed a destabilizing impact of K fertilization. Furthermore, the soil with the highest clay content was obviously unaffected. Generally, the observed differences were amplified by drainage to -3 and -6 kPa matric potential.

In the last part of this work, several plots of a long-term experiment at the Dikop farm near Bonn, Germany, were investigated for their physical properties at meso- and microscale. To determine the impact of organic versus mineral fertilization, undisturbed samples from plots with mineral and organic as well as combined fertilization were examined. Organic and mineral fertilization increased porosity of the soil similarly, but plots with organic amendment had a much better pore functionality that was also more persistent during mechanical stresses. The microstructural stability was significantly decreased by mineral fertilization but not enhanced by organic fertilization. Obviously, the microstructural stability was different than the stability measured at the mesoscale with one exception: Cyclic compressiblity c_n had a strong correlation with maximum shear resistance τ_{max}. Thus these two parameters may allow for the upscaling of rheological parameters to the mesoscale. After remoulding the samples, the previous organic fertilization led to increasing stability, either as single treatment or in combination with mineral fertilization, whereas mineral fertilization alone had destabilizing impact. K fertilization seemed to decrease shear resistance at the microscale but the actual K content of the soil was positively related to soil stability. Manifold interactions with organic fertilization treatments and matric potential of remoulded samples underline the need for further research. However, it can be assumed, that organic fertilization preserved the former structure partly.

In a nutshell, the impact of K on microstructural stability is rather ambiguous and always requires the additional consideration of the investigated soil itself as well as the time and spatial scale. Furthermore, the results present a first approach for the upscaling of rheological parameters to the mesoscale.

7 ZUSAMMENFASSUNG

Die vorliegende Arbeit befasst sich mit dem Einfluss von Düngung auf Bodenstabilität wie sie mit Hilfe der Rheometrie erfasst werden kann. Die Messmethode hat sich in früheren Untersuchungen als geeignet gezeigt für diese Aufgabe, nichtsdestotrotz bestehen Wissenslücken besonders hinsichtlich der Auswirkungen verschiedener Einflussfaktoren wie z. B. Salze. Besonderes Augenmerk gilt hierbei Kalium (K), das in diversen Studien einen positiven Einfluss auf die Wassernutzungseffizienz von Pflanzen gezeigt hat. Neben dem Sachverhalt, dass K in der Pflanze die Transpirationsrate senkt, basiert ein anderer Erklärungsansatz auf der Verbesserung der Struktur durch K, was durch erhöhte mikrostrukturelle Stabilität die Menge pflanzenverfügbaren Wassers erhöhen könnte. Daher wurde in der vorliegenden Arbeit der Einfluss von K, aber auch organischer versus mineralische Düngung auf mikrostrukturelle Stabilität mit Hilfe eines Amplitudentests analysiert, um schlussendlich einen Vergleich der Einflüsse von Düngern über verschiedene Zeit- und Raumskalen zu ermöglichen.

Der erste Ansatz war die kurzfristige Beeinflussung des Scherwiderstandes gesättigter Proben durch K. Dazu wurden Proben aus Geschiebemergel mit KCl-Lösungen unterschiedlicher Konzentrationen für unterschiedliche Zeiträume aufgesättigt. Die rheologischen Parameter Scherwiderstand τ am Ende des linearviskoelastischen Bereichs, maximaler Scherwiderstand τ_{max}, Speichermodul G' und Verlustmodul G" an der Fließgrenze erreichten mit zunehmender K-Konzentration höhere Werte, was durch die längere Einwirkzeit der Lösung noch verstärkt wurde und zeigt, dass „age-hardening“ stattgefunden hat. Des Weiteren konnte festgestellt werden, dass ein abnehmendes Matrixpotential die rheologischen Parameter ebenfalls erhöht, also die Scherfestigkeit durch höhere Entwässerung zunahm.

Für die Erfassung des Langzeiteffektes von K wurden Proben verschiedener Dauerdüngungsversuche untersucht. Obwohl ursprünglich für die Untersuchung des Einflusses auf Pflanzenwachstum und -ertrag erstellt, eignen sie sich auch für die Betrachtung bodenkundlicher Fragestellungen. Die Scherfestigkeit wurde nach verschiedenen Vorentwässerungsstufen gemessen und dann mit physikalisch-chemischen Eigenschaften der Böden vernetzt. Sowohl die Betrachtung der Einzelparameter als auch ihre Kombination in multipler linearer Regression und anschließender schrittweiser Modellanpassung zeigt, dass bodenphysikalische Parameter nicht nur von Einzelfaktoren bestimmt werden, sondern von einer Vielzahl an interagierenden Parametern abhängen. Hinsichtlich der K-

Düngung wurden sowohl stabilisierende als auch destabilisierende Einflüsse beobachtet. Während Böden mit gröberer Textur durch K stabilisiert wurden, verhielt es sich umgekehrt bei Böden mit mittlerem Tongehalt. Der feinkörnigste Boden hingegen zeigte keinerlei Einfluss durch K. Im Allgemeinen wurden die beobachteten Unterschiede durch Entwässerung auf -3 und -6 kPa verstärkt.

Im letzten Teil dieser Arbeit wurden einige Varianten eines Dauerdüngungsversuches des Dikopshofes in der Nähe von Bonn auf ihre physikalischen Eigenschaften auf Mikro- und Mesoebene untersucht. Für die Erfassung des Einflusses von organischer versus mineralischer Düngung erfolgte die Entnahme von ungestörten Proben mit mineralischer, organischer sowie kombinierter Düngung. Sowohl organische als auch mineralische Düngung erhöhten die Porosität des Bodens, jedoch war die Porenfunktionalität bei den organisch gedüngten Böden deutlich besser und auch persistent bei mechanischer Belastung. Die mikrostrukturelle Stabilität wurde durch mineralische Düngung signifikant verringert, aber durch organische Düngung erhöht. Offensichtlich gab es skalenbasierte Unterschiede in der Bodenstabilität mit einer Ausnahme: Die zyklische Kompressibilität c_n war eng korreliert mit dem maximalen Scherwiderstand τ_{max}, was die Übertragung von rheologischen Parametern auf die Mesoskala ermöglicht. Nach Homogenisierung der Proben hatte die organische Düngung eindeutig stabilisierenden Einfluss, sowohl in alleiniger Gabe als auch in Kombination mit mineralischer Düngung. Die Scherfestigkeit wurde scheinbar durch K-Düngung verringert, war jedoch positiv korreliert mit dem tatsächlichen K-Gehalt im Boden. Hier führte das Homogenisieren zu vielfältigen Interaktionen mit organischer Düngung und Matrixpotential, deren umfassende Erklärung weitere Untersuchungen erfordert. Es kann jedoch davon ausgegangen werden, dass die vorherige Struktur durch organische Düngung zum Teil konserviert wurde.

Zusammenfassend lässt sich sagen, dass der Einfluss von K-Düngung auf die mikrostrukturelle Stabilität vielfältig ist und immer der zusätzlichen Betrachtung der weiteren bodenspezifischen Eigenschaften sowie des Zeit- und Skaleneffektes bedarf. Darüberhinaus bieten die Ergebnisse einen ersten Ansatz zur Aufskalierung rheologischer Parameter auf die Mesoskala.

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