

The swelling of interparticulate hydrogels in soil and their contribution to soil structural stability and soil-water interactions

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„Die Wissenschaft fängt eigentlich erst da an, interessant zu werden, wo sie aufhört“

Justus von Liebig (1803-1873)

DECLARATION

I declare that this PhD thesis, entitled “The swelling of interparticulate hydrogels in soil and their contribution to soil structural stability and soil-water interactions” was prepared and carried out by my own. All assistances, contributors and authors are declared and clearly indicated in this thesis. This thesis has never been submitted elsewhere for an exam, neither to any other university nor scientific institution.

Landau in der Pfalz,

Place, date
Buchmann)

signature (Christian

PARTS OF THE THESIS AND OWN CONTRIBUTIONS

This PhD thesis consists of five chapters, amongst the others, that represent four published research papers and parts of one published review article. The experiments were conducted at the Institute of Environmental Sciences, University Koblenz-Landau, Campus Landau as part of the DFG-funded project SOIL-H Relax (SCHA 849/5). My contribution to the scientific conception of the experiments was based on the objectives of the project and the results obtained from the research work. Hence, research priorities and research questions were further adapted and purposefully investigated in accordance with the findings gained during the project. However, conceptional designs of the experiments and data interpretation were in close collaboration with Prof. Dr. Schaumann and the co-authors.

Chapter 3 (Buchmann et al. 2015) is published in *Magnetic Resonance in Chemistry*:

Buchmann, C.; Meyer, M.; Schaumann, G.E. (2015): Characterization of wet-aggregate stability of soils by ¹H-NMR relaxometry. Magn. Res. Chem. 53: 694-703

My own contribution to this published research paper includes the development of the experimental design, all conducted laboratory measurements and data evaluation. Maximilian Meyer helped me with soil sampling and sample preparation. Data interpretation and paper publication writing was in close collaboration with the two co-authors.

Chapter 4 (Buchmann et al. 2015) is published in *Soil & Tillage Research*:

Buchmann, C.; Bentz, J.; Schaumann, G.E. (2015): Intrinsic and model polymer hydrogel-induced soil structural stability of a silty sand soil as affected by soil moisture dynamics. Soil Till Res 154: 22-33

Rheological and ¹H-NMR relaxometry measurements of soil samples were performed by Jonas Bentz during his Bachelor thesis under the supervision of Prof. Dr. Schaumann and me. The additionally conducted ¹H-NMR relaxometry measurements of the hydrogels and detailed data evaluation were done by myself. Data interpretation and publication paper writing in close collaboration with Prof. Dr. Schaumann.

Chapter 5 (Buchmann et al. 2016) is published in Plant and Soil:

Buchmann, C.; Schaumann, G.E. (2016). Effect of water entrapment by a hydrogel on the microstructural stability of artificial soils with various clay content. Plant Soil 414 (1-2): 491-198

Experimental design, laboratory measurements as well as data evaluation were predominantly performed by myself. The data interpretation and publication paper writing were done with the support of Prof. Dr. Schaumann.

Chapter 6 (Buchmann and Schaumann 2018) is published in the Journal of Plant Nutrition and Soil Science:

Buchmann, C.; Schaumann, G.E. (2018): The contribution of various organic matter fractions to soil-water interactions and structural stability of an agriculturally cultivated soil. J. Plant Nutr. Soil Sci. (Online early)

Experimental design, laboratory measurements as well as data evaluation were predominantly performed by myself. The data interpretation and publication paper writing were done with the support of Prof. Dr. Schaumann.

Chapter 7 includes certain sections within the review article of Brax et al. 2016 published in the Journal of Plant Nutrition and Soil Science:

Brax, M.; Buchmann, C.; Schaumann, G.E. (2017): Biohydrogel induced soil-water interactions: how to untangle the gel effect? - a review. Journal of Plant Nutrition and Soil Science 180 (2): 121-141

The following sections were written by myself and reflect my own contribution to the published paper and should be considered as part for this PhD thesis: Section 3.2 (“Rheometry as tool to measure soil microstructural stability”), section 3.3 (“Studying the impact of biohydrogels on soil rheology”), section 4.3.3 (“Entrapment of water in soils measured with ¹H-NMR relaxometry”), section 4.3.4 (“Swelling processes in soil measured with ¹H-NMR relaxometry”), section 4.4.2 (“Self diffusion coefficient of water in soil”) and section 4.5 (“Two-dimensional measurements to characterize the water entrapment in porous media”).

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TABLE OF CONTENTS

1	INTRODUCTION	1
1.1	SOIL STRUCTURE AND SOIL STRUCTURAL STABILITY	1
1.2	SOIL-WATER INTERACTIONS REVEALED BY ¹ H-NMR RELAXOMETRY	4
2	OBJECTIVES AND HYPOTHESES	8
3	CHARACTERIZATION OF WET-AGGREGATE STABILITY OF SOILS BY ¹H-NMR RELAXOMETRY	10
4	INTRINSIC AND MODEL POLYMER HYDROGEL-INDUCED SOIL STRUCTURAL STABILITY OF A SILTY SAND SOIL AS AFFECTED BY SOIL MOISTURE DYNAMICS	11
5	EFFECT OF WATER ENTRAPMENT BY A HYDROGEL ON THE MICROSTRUCTURAL STABILITY OF ARTIFICIAL SOILS WITH VARIOUS CLAY CONTENT	12
6	THE CONTRIBUTION OF VARIOUS ORGANIC MATTER FRACTIONS TO SOIL-WATER INTERACTIONS AND STRUCTURAL STABILITY OF AN AGRICULTURALLY CULTIVATED SOIL	13
7	BIOHYDROGEL INDUCED SOIL-WATER INTERACTIONS: HOW TO UNTANGLE THE GEL EFFECT? - A REVIEW	14
8	SYNTHESIS AND GENERAL CONCLUSIONS	15
8.1	SCHEMATIC MODEL OF SOIL STRUCTURAL STABILITY AND SOIL-WATER INTERACTIONS INDUCED BY HYDROGEL SWELLING AND PARTICLE-PARTICLE INTERACTIONS.....	15
8.2	FINAL CONCLUSION AND OUTLOOK.....	21
9	REFERENCES.....	24
10	ANNEX	33
10.1	LIST OF ABBREVIATIONS.....	33
10.2	LIST OF TABLES.....	34
10.3	LIST OF FIGURES	34
10.4	LIST OF ATTACHED FILES ON CD-ROM.....	34
10.5	CURRICULUM VITAE	35
10.6	PUBLICATIONS	36

ABSTRACT

Organic substances play an essential role for the formation of stable soil structures. In this context, their physico-chemical properties, interactions with mineral soil constituents and soil-water interactions are particularly important. However, the underlying mechanisms contributing to soil particle cementation by swollen organic substances (hydrogels) remains unclear. Up to now, no mechanistic model is available which explains the mechanisms of interparticulate hydrogel swelling and its contribution to soil-water interactions and soil structural stability. This mainly results from the lack of appropriate testing methods to study hydrogel swelling in soil as well as from the difficulties of adapting available methods to the system soil/hydrogel.

In this thesis, ^1H proton nuclear magnetic resonance (NMR) relaxometry was combined with various soil micro- and macrostructural stability testing methods in order to identify the contribution of hydrogel swelling-induced soil-water interactions to the structural stability of water-saturated and unsaturated soils. In the first part, the potentials and limitations of ^1H -NMR relaxometry to enlighten soil structural stabilization mechanism and various water populations were investigated. In the second part, ^1H -NMR relaxometry was combined with rheological measurements of soil to assess the contribution of interparticulate hydrogel swelling and various polymer-clay interactions on soil-water interactions and soil structural stability in an isolated manner. Finally, the effects of various organic and mineral soil fractions on soil-water interactions and soil structural stability was assessed in more detail for a natural, agriculturally cultivated soil by soil density fractionation and on the basis of the experiences gained from the previous experiments.

The increased experiment complexity in the course of this thesis enabled to link physico-chemical properties of interparticulate hydrogel structures with soil structural stability on various scales. The established mechanistic model explains the contribution of interparticulate hydrogels to the structural stability of water-saturated and unsaturated soils: While swollen clay particles reduce soil structural stability by acting as lubricant between soil particles, interparticulate hydrogel structures increase soil structural stability by forming a flexible polymeric network which interconnects mineral particles more effectively than soil pore- or capillary water. It was apparent that soil structural stability increases with increasing viscosity of the interparticulate hydrogel in dependence on incubation time, soil texture, soil solution composition and external factors in terms of moisture dynamics and agricultural management practices. The stabilizing effect of interparticulate hydrogel structures further increase in the presence of clay particles which is attributed to additional polymer-clay interactions and the incorporation of clay particles into the three-dimensional interparticulate hydrogel network. Furthermore, the simultaneous swelling of clay particles and hydrogel structures results in the competition for water and thus in a mutual restriction of their swelling in the interparticle space. Thus, polymer-clay interactions not only increase the viscosity of the interparticulate hydrogel and thus its ability to stabilize soil structures but further reduce the swelling of clay particles and consequently their negative effects on soil structural stability. The knowledge on these underlying mechanisms enhance the knowledge on the formation of stable soil structures and enable to take appropriate management practices in order to maintain a sustainable soil structure. The additionally outlined limitations and challenges of the mechanistic model should provide information on areas with optimization and research potential, respectively.

ZUSAMMENFASSUNG

Organische Substanzen spielen eine wichtige Rolle bei der Bildung von stabilen Bodenstrukturen. Dabei sind maßgeblich deren physikochemischen Eigenschaften, Wechselwirkungen mit der mineralischen Bodenphase und die daraus resultierende Boden-Wasser Interaktionen von Bedeutung. Dennoch weiß man nur wenig über zugrunde liegenden Mechanismen der Partikelvermittlung durch organische Substanzen und inwieweit deren Quellung unter Bildung von interpartikulären Hydrogelen die bodenstrukturelle Stabilität beeinflusst. Bis heute existiert kein mechanistisches Model, das deren Quellung im Boden beschreibt und daraus resultierende Boden-Wasser Interaktionen in Zusammenhang mit bodenstruktureller Stabilität bringt. Dies ist maßgeblich auf das Fehlen bzw. eine unzureichende Adaptierung geeigneter Testmethoden zur Erfassung von Quellungsprozessen interpartikulärer Hydrogele in Böden zurückzuführen.

In der vorliegenden Dissertation wurde die $^1\text{H-NMR}$ Relaxometrie mit mikro- und makrostrukturellen Bodenstabilitätstests kombiniert um Boden-Wasser Interaktionen mit der strukturellen Stabilität wassergesättigter und ungesättigter, feuchter Böden zu verknüpfen. Der Erste Teil der Arbeit erfasste Potential und Grenzen der $^1\text{H-NMR}$ Relaxometrie zur Erfassung unterschiedlicher Wasserpopulationen und struktureller Stabilisierungsmechanismen Boden. Im zweiten Teil der Arbeit wurde die $^1\text{H-NMR}$ Relaxometrie zur Untersuchung von Quellungsprozessen einer hydrogelbildenden organischen Modellschubstanz in Modelböden unterschiedlicher Komplexität eingesetzt. Mittels der Kombination mit Bodenrheologie sollten die zugrundeliegenden Mechanismen identifiziert werden, die im Zusammenhang mit der strukturellen Bodenstabilität stehen. Im letzten Teil der Arbeit wurden die zuvor gesammelten Erkenntnisse auf einen humosen, landwirtschaftlichen Boden übertragen und die Effekte einzelner organischer und mineralischer Bodenbestandteile auf Boden-Wasser-Interaktionen und bodenstrukturelle Stabilität mittels Dichtefraktionierung noch detaillierter erfasst.

Die zunehmende Komplexität der Experimente ermöglichten eine Brücke zwischen den physikochemischen Eigenschaften interpartikulären Hydrogels und bodenstruktureller Stabilität zu schlagen und ein Modell für die zugrunde liegenden Prozesse für wassergesättigte und ungesättigte, feuchte Böden abzuleiten: Während gequollene Tonpartikel die Reibung zwischen Bodenpartikeln erniedrigen und somit die bodenstrukturelle Stabilität herabsetzen, zeigen gequollen Hydrogelstrukturen den gegenteiligen Effekt und erhöhen die bodenstrukturelle Stabilität. Dies ist zurückzuführen auf die Bildung eines flexiblen und viskosen Polymernetzwerkes, welches mineralische Bodenpartikel über weite Bereiche verbindet und eine deutlich höhere Stabilität als Poren- oder Kapillarwasser aufweist. Es zeigte sich zudem, dass die bodenstrukturelle Stabilität mit steigender Viskosität des interpartikulären Hydrogels zunimmt und dabei von der Inkubationszeit, Bodentextur, Zusammensetzung der Bodenlösung und externen Faktoren wie Bodenfeuchtedynamik und landwirtschaftliche Bewirtschaftungsweisen abhängt. Die stabilisierende Wirkung von interpartikulärem Hydrogel wird zusätzlich durch Tonpartikeln verstärkt, was maßgeblich aus Polymer-Ton-Interaktionen und der Aufnahme von Tonpartikeln in das Hydrogelnetzwerk resultiert. Zusätzlich konnte gezeigt werden, dass die gleichzeitige Quellung von Hydrogelstrukturen und Tonpartikeln und der dabei vorhandenen Konkurrenz um verfügbares Wasser und freien Raum zu einer gegenseitigen Quellungshemmung führen. Somit erhöhen Polymer-Ton-Interaktionen nicht nur die Viskosität des interpartikulären Hydrogels und damit dessen Stabilisierungspotential, sondern erniedrigen zudem die Quellung von Tonpartikeln und damit deren negativen Effekte auf die bodenstrukturelle Stabilität. Das Wissen um diese zugrunde liegenden Prozesse erweitert das Verständnis zur Bildung stabiler Bodenstrukturen und ermöglicht das Ergreifen geeigneter, nachhaltiger Bodenbewirtschaftungsmaßnahmen. Die zudem aufgezeigten Limitierungen des mechanistischen Modells sollen Ansatzpunkte für weitere Forschungs- und Optimierungspotentiale aufzeigen.

1 INTRODUCTION

1.1 SOIL STRUCTURE AND SOIL STRUCTURAL STABILITY

Soil is formed from parent rock material by physical, chemical and biological weathering processes, followed by its disintegration, decomposition and re-composition towards various soil constituents of different hierarchical orders. The fragmented rock material typically consists of primary soil particles comprising clay (<2 μm), silt (2-50 μm) and sand (50-2000 μm) which is transmuted into a stable ordered soil structure over time (Hillel, 2003). The term “soil structure” covers the spatial arrangement of soil constituents with the resulting pore system in terms of pore size distribution, porosity and interconnectivity (Santamarina, 2003; Bronick & Lal, 2005). Depending on soil type and stabilization mechanism, soil structure can either consist of loose and unstable arrangements of randomly distributed primary soil particles or of well-structured particle associates (soil aggregates) as summarized in Figure 1 (Gregorich *et al.*, 2001; Peng *et al.*, 2015).

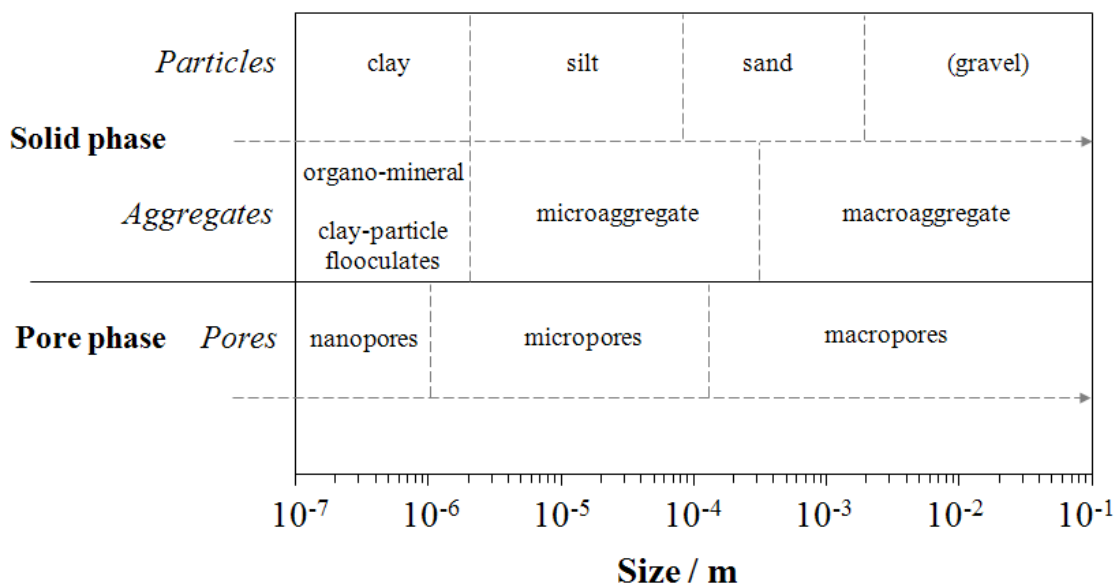


Figure 1: Classification of typical soil mineral particles with a vast scale of formed aggregates and pore types in terms of size and designation (redrawn after Peng *et al.*, 2015 and modified).

In early years, researchers have already identified the essential role of aggregation processes for soil structural development and soil structural stability (Dexter, 1988; Baumgartl & Horn, 1993; Six *et al.*, 2001). In this context, “soil structural stability” describes the resistance of soil structures against external applied stress such as compaction, ploughing or heavy rainfall (Bronick & Lal, 2005). Soil structural stability directly has severe effects on various environmental levels, including soil biology (e. g. plant development and microbial activity), soil

physico-chemistry (e. g. hydrology and nutrient cycling) and soil workability for agricultural purposes (Dexter, 1988; Van Veen & Kuikman, 1990). For a fundamental understanding of soil structural stability, it is important to understand the nature of soil on the smallest scale: Soil as particulate system is predominantly defined by forces acting between primary soil particles, their contact behavior as function of particle size, shape and mineral composition and the presence of reactive soil constituents acting as binding agents (Ghezzehei & Or, 2001; Baumgarten *et al.*, 2012; Baumgarten & Horn, 2013). These include clay particles and various organic substances such as soil organic matter (SOM), root exudates and extracellular polymeric substances (EPS) with their possibility to take up water and swell (Lehrsch, 1998; Zhang *et al.*, 2005; Yazdandoust & Yasrobi, 2010). Here, “swelling” refers to both the sorption of water into clay structures and into the three-dimensional polymeric network of organic substances, typically referred to as “hydrogels” (Jaeger *et al.*, 2010; Shi *et al.*, 2016). In soil, hydrogel-forming polymers result from vegetal residues and mainly consist of biopolymers such as polysaccharides, lignin and proteins as part of the total SOM (Capitani *et al.*, 2001; Kögel-Knabner, 2002; Paul, 2014). In addition to soil-born biopolymers and various OM fractions such as mineral-associated organic matter (MAOM) or particulate organic matter (POM), manifold synthetic polymers have been intensively investigated in agricultural landscapes in order to sustain soil structural stability, soil health and thus agricultural efficiency (Graber *et al.*, 2006; Hussien *et al.*, 2012; Guilherme *et al.*, 2015).

Aside from the knowledge on fundamental processes governing soil structure formation, their description and quantification is important. Due to the variety of available testing methods, none of them is universally accepted (Diaz-Zorita *et al.*, 2002; Le Bissonnais, 2016). Thus, the choice of an appropriate testing method depends on 1) the type of stress applied and 2) the hierarchical level of the soil structure, in detail particle-particle associates, soil aggregates or the soil matrix (Dexter, 1988; Elimelech *et al.*, 1998; Horn & Fleige, 2003; Peth & Horn, 2006; Liu *et al.*, 2009). For aggregated soil with a defined hierarchy, sieving tests and aggregate stability tests are most commonly used due to the interrelated concept of soil fragment size and soil structural stability (Diaz-Zorita *et al.*, 2002). In the field of soil micromechanics, rheometry became an established testing method to investigate soil structural stability on the particle scale. Sonderegger (1985) was the first to perform rheological measurements in the context of soil sciences, dealing with the shear strength of pure clay pastes. From this time on, the application of rheometry to determine the mechanical behavior of soil has been intensively investigated (Chang *et al.*, 1993; Ghezzehei & Or, 2001; Horn & Baumgartl, 2002), further developed (Markgraf *et al.*, 2006; Vyalov, 2013) and finally well-established

(Baumgarten & Horn, 2013). As especially rheological measurements were performed in this thesis, the state-of-the-art knowledge on soil microstructural stability gained by rheometry was outlined in the following. For a detailed overview on the theoretical background of rheology in soil mechanics, see the review Baumgarten and Horn (2013) as well as the review of Brax *et al.* (2017) presented in Chapter 11.

Soil microstructural stability typically results from soil textural properties, organic binding agents and soil-water interactions as overall function of water content (Markgraf *et al.*, 2006; Holthusen *et al.*, 2011). Shear strength and angle of internal friction increase rapidly with sand content. However, clay swelling can negatively affect soil microstructural stability by decreasing solid-solid friction due to the weak cohesive forces between water molecules adsorbed onto clay surfaces (Baumgarten & Horn, 2013). Besides adsorbed water, soil pore water directly affects the rearrangement of soil particles and the force resistance during soil deformation: High water content typically reduces particle-particle friction and decreases soil microstructural stability (Holthusen *et al.*, 2012; Pértile *et al.*, 2016). The applied stress first overcomes the cohesion among water molecules, followed by the cohesion between soil particles (Ghezzehei & Or, 2001). A decrease in soil water content intensifies the interparticle bonds by increasing cohesive forces, particle-particle friction and capillary forces (adhesion). When soil dries, water recedes in small capillaries between soil particles with increased capillary forces, surface tension and the number and curvature of water menisci (Kemper & Rosenau, 1986; Lourenço *et al.*, 2012). Here again, soil texture predominantly affects the existing capillary forces in soil: In clay soil, adhesion and capillary forces are higher due to small pore sizes, whereas capillary forces in sand soil sharply decline at low water content due to big pore sizes (Holthusen *et al.*, 2012; Hartge & Horn, 2014).

Not only the soil water content but also its composition affects soil microstructural stability: Although the contribution of single ions to soil microstructural stability remains largely unclear, several authors have investigated the impact of ionic strength on the microstructural stability of soil- and clay suspensions (Chang *et al.*, 1993; Torrance, 1999; Abend & Lagaly, 2000; Sakairi *et al.*, 2005). For example, Torrance (1999) has shown that sodium (Na^+) reduces the microstructural stability of clay suspensions whereas calcium (Ca^{2+}) increases it, respectively. The results gained from clay suspensions can be taken as an indicator for the rheological behavior of clay-rich soils, although the transferability to naturally-structured soils is limited (Holthusen *et al.*, 2011). First rheological investigations dealing with the effect of soil solution composition on soil microstructural stability have been done by Markgraf *et al.* (2006) and Markgraf and Horn (2006). The authors have shown that Na^+ enhances the

dispersion and slaking of soil particles and thus decreases soil microstructural stability. Contrary to that, Markgraf and Horn (2007) and Holthusen *et al.* (2011) have shown that potassium (K^+) promotes soil microstructural stability by building up a sustainable contact between soil particles. However, the underlying mechanisms have not been fully identified until now. Polyvalent cations such as Ca^{2+} and magnesium (Mg^{2+}) contribute to soil aggregation and soil microstructural stability by bridging soil particles directly or via organic substances (Bronick & Lal, 2005; Markgraf *et al.*, 2012). Similar effects have been shown for Fe (hydr)oxides in the presence of organic substances (Markgraf & Horn, 2007).

Besides soil textural properties and soil water content, organic binding agents significantly contribute to soil microstructural stability. Rheological investigations of wet soils showed that soil roots and fungal exudates increase soil microstructural stability up to 10 times (Barré & Hallett, 2009). Markgraf and Horn (2007) and Markgraf *et al.* (2012) observed similar effects for SOM. Recently, Ajayi *et al.* (2016) have shown that biochar treatment significantly increased soil microstructural stability. However, the underlying processes are not yet fully identified. It is recently discussed that the swelling of organic substances and their presence as interparticulate hydrogel might contribute to soil structural stability by affecting particle-particle interactions and water binding properties (Ghezzehei & Or, 2001; Bronick & Lal, 2005; Barré & Hallett, 2009; Paluszek, 2011; Blume *et al.*, 2015). This current lack of knowledge results from the restricted adaptability of suitable testing methods to study in-situ hydration and swelling of interparticulate hydrogels in soil. Consequently, fundamental relationships between hydrogel swelling, soil-water interactions and soil structural stability are only scarcely known and need to be further investigated.

For the sake of completeness, it should be mentioned that imaging techniques such as Environmental Scanning Electron Microscopy (ESEM), resin impregnation, X-ray tomography and three-dimensional (3D) analysis are performed to image soil structural properties such as shapes, sizes and distributions of voids, aggregates and soil constituents within soil samples (Schon *et al.*, 2012; Albalasmeh & Ghezzehei, 2014; Pagenkemper *et al.*, 2015).

1.2 SOIL-WATER INTERACTIONS REVEALED BY 1H -NMR RELAXOMETRY

Water in soil is either retained in soil pores or transported through the soil matrix in direct relation to the pore size (Schaumann & Bertmer, 2014). However, various aspects of soil-water interactions such as water redistribution and swelling processes as well as their implications on soil quality and soil functioning remain unclear. In this context, 1H proton nuclear

magnetic resonance ($^1\text{H-NMR}$) relaxometry has the potential to close this research gap and overcome the current lack of knowledge.

$^1\text{H-NMR}$ relaxometry has been widely used to describe the water mobility in porous media such as boreholes and rock cores (As & Lens, 2001; Vogt *et al.*, 2002). In soil science, the application of $^1\text{H-NMR}$ relaxometry includes one-dimensional, two-dimensional as well as pulsed field gradient (PFG) measurements which allows the assessment of wetting kinetics, pore size distributions, influences of microbial activity and soil solution constituents and SOM swelling on soil-water interactions (Todoruk *et al.*, 2003; Schaumann *et al.*, 2005; Jaeger *et al.*, 2008; Jaeger *et al.*, 2009, Jaeger *et al.*, 2010). In the following the current state-of-the-art knowledge on soil-water interactions gained by $^1\text{H-NMR}$ relaxometry is summarized. For a more detailed overview on the theoretical background see the reviews of Bayer *et al.* (2010) and Schaumann and Bertmer (2014) as well as the review of Brax *et al.* (2017) presented in Chapter 11.

First studies on soil hydration and soil water redistribution using $^1\text{H-NMR}$ relaxometry have shown that relaxation time distributions significantly change in the course of water uptake (Manalo *et al.*, 2003; Todoruk *et al.*, 2003). In all studies, $^1\text{H-NMR}$ relaxometry was suitable to characterize soil-water interactions in more detail, especially due to the direct relationship between relaxation time distributions and water binding in the porous soil system: Water confined in small soil pores relaxes faster than water in larger pores or free bulk water as a result of an increased accessibility of the solid pore wall surface (Schaumann & Bertmer, 2014; Shi *et al.*, 2016). Hence, temporal shifts of the transverse relaxation time (T_2) towards short time ranges indicate the water movement from big into small soil pores as a result of increased pore wall hydrophilicity over time (Schaumann *et al.*, 2005; Hurrass & Schaumann, 2007).

Water redistribution processes identified by $^1\text{H-NMR}$ relaxometry indicate the possibility to assess porosity and pore size distributions from relaxation time distributions. For geological samples, $^1\text{H-NMR}$ relaxometry is well-established and typically used for the assessment of stone porosity and its pore-size distribution since years (Kleinberg *et al.*, 1994). First attempts to apply this approaches to soil samples was done by Hinedi *et al.* (1993), followed by Stoffregen *et al.* (1999) and Bird *et al.* (2005). Despite differences among publications, a rough classification of certain pore size regimes from relaxation time ranges is possible: Micropores (or tightly bound water) at $T_2 < 60$ ms, mesopores (or loosely bound water) at $T_2: 60 - 300$ ms and macropores (or bulk water) at $T_2 > 300$ ms (McBrierty *et al.*, 1996; Todoruk *et al.*, 2003; Bird *et al.*, 2005). However, the high uncertainty of the relaxation time ranges is rather unfavorable for the assessment of quantitative pore-size distributions in soils.

Furthermore, the conducted studies did not quantitatively assess the pore-size distributions due to the unknown and pore-size specific surface relaxivity of soil (Bayer *et al.*, 2010). Consequently, the specific surface relaxivity for each soil and pore size must be known and, if necessary, determined by additional methods such as microscopy, porosimetry or nitrogen adsorption measurements (Hinedi *et al.*, 1993; Kleinberg, 1999; Jaeger *et al.*, 2009).

In recent years, it has been shown that not only pore sizes affect the water mobility in soil but also the soil solution composition, soil microbial activity and the presence of reactive soil constituents (Bayer *et al.*, 2010). Concerning the soil solution composition, it has already been shown for geological samples that the bulk relaxation further accelerates and thus shortens the measured relaxation times by dissolved soil solution constituents (Dunn *et al.*, 2002). In soil, dissolved soil solution constituents include paramagnetic substances such as Fe^{2+} and Mn^{2+} , organic colloids and organo-mineral complexes (Jaeger *et al.*, 2008). Hence, their effects on the measured proton relaxation time should be taken into account when assessing soil-water interactions and quantitative pore sizes in soil (Jaeger *et al.*, 2006; Jaeger *et al.*, 2009).

Soil microbial activity typically results in the release of extracellular polymeric substances (EPS) and the formation of biofilms on soil mineral surfaces (Redmile-Gordon *et al.*, 2014; Schaumann & Bertmer, 2014). Biofilms bind pore water within their three-dimensional polymeric network, relieving drought stress, enhancing nutrient availability and consequently optimizing microorganisms' living conditions (Flemming & Wingender, 2000). Water confined in biofilm hydrogels can significantly differ in its mobility compared to bulk water: $^1\text{H-NMR}$ measurements of biofilm-containing solutions and soil showed significantly reduced T_2 with changes of the relaxation time distribution from monomodal (bulk water) to bimodal and trimodal shape in the course of water absorption into the hydrogel network (Radosta *et al.*, 1989; Hoskins *et al.*, 1999; Jaeger *et al.*, 2006; Jaeger *et al.*, 2010).

Comparable to microbial activity, reactive soil constituents directly affect water binding and soil-water interactions by their swelling (Schaumann *et al.*, 2005; Jaeger *et al.*, 2009; Shi *et al.*, 2016). Those swelling processes in soil are typically associated to organic and inorganic substances such as SOM and clay particles (Rycroft & Amer, 1995; Young, 2012). Although clay- and hydrogel swelling results in the formation of structured water phases in soil, the underlying swelling mechanisms are different and should be considered separately: Clay swelling results from clay interlayer penetration by water molecules with its volumetric expansion (Norrish, 1954). Besides the clay content, the swelling of clay particles results from the clay mineralogy, soil solution pH and soil solution composition (Rao & Mathew, 1995;

Chesworth, 2008). Contrary to clay swelling, hydrogel swelling results from the formation of a large, three-dimensional network of cross-linked macromolecules (polymer chains), which can take up water several times of his own weight (Ganji *et al.*, 2010; Cihlar *et al.*, 2014). In recent studies, the presence of organic substances resulted in intensity shifts towards longer relaxation times with changes of the relaxation time distributions to bimodal and trimodal shape. Schaumann *et al.* (2005) have demonstrated significant effects of SOM on the water distribution in high-OM soil, however, the authors could not decide if hydrogel swelling was the driving mechanisms for the observed intensity shifts in the relaxation time distributions. Studies combining ^1H -NMR relaxometry, thermoanalytical methods and thermogravimetric analyses showed that water redistributes during SOM swelling in soil with the additional formation of various water phases (McBrierty *et al.*, 1999; Todoruk *et al.*, 2003; Jaeger *et al.*, 2010), pore sizes (Schaumann *et al.*, 2005) and gel phases in SOM (McBrierty *et al.*, 1996; Schaumann *et al.*, 2004; Schaumann, 2005). For a more detailed overview on fundamental processes governing swelling processes in soil and their impact on soil physico-chemistry, see the review of Guilherme *et al.* (2015), respectively.

Although ^1H -NMR relaxometry enables to assess manifold soil-water interactions, the identification of swollen hydrogel and clay structures and therewith associated soil-water interactions are only scarcely investigated. Furthermore, the concrete differentiation between various water populations such as clay-associated water, hydrogel-associated water and mineral soil pore water remains partly unsolved and requires an appropriate combination and adaption of suitable testing methods and experimental approaches (Jaeger *et al.*, 2010; Baiamonte *et al.*, 2015; Shi *et al.*, 2016). Their identification could help to identify the still largely unknown contribution of hydrogel swelling and therewith associated soil-water interactions to soil structural stability.

2 OBJECTIVES AND HYPOTHESES

The main objective of this PhD thesis is to understand the largely unknown role of swollen interparticulate hydrogel structures on soil structural stability. In order to achieve this objective, it was necessary to develop, optimize and establish suitable testing methods and experimental designs. Under these conditions, it is possible to understand 1) how mutual interactions of reactive soil constituents, in particular swellable organic substances and clay particles, affect the water distribution in the porous soil system and 2) how interparticulate hydrogel and associated soil-water interactions contribute to soil structural stability.

Within the framework of the PhD thesis, different experiments were conducted as subsequently divided into several chapters: In the first step (Chapter 3) we investigated the potential and limitations of $^1\text{H-NMR}$ relaxometry for the identification of soil structural stabilization mechanisms during soil structural breakdown. We hypothesized that $^1\text{H-NMR}$ relaxometry enhances conventional stability testing methods by identifying clay swelling-induced soil structural breakdown in various soils samples. We expected that $^1\text{H-NMR}$ relaxometry enables to identify clay-associated water which will help to move one step closer to the differentiation of various water populations. To test this hypothesis, an innovative experimental approach has been developed in which conventional aggregate stability tests were combined with $^1\text{H-NMR}$ relaxometry measurements.

Based on the knowledge gained from the first experiment, the swelling of a model polymer in an unsaturated and unstable sandy soil under different moisture dynamics was investigated (Chapter 4). We assumed that swollen interparticulate hydrogel acts as viscous and elastic layer between mineral soil particles. Hence, the presence of hydrogel-associated water as identified by $^1\text{H-NMR}$ relaxometry will increase particle-particle friction and thus soil structural stability as function of moisture dynamics. The absence of swellable clay particles and SOM in the investigated soil should simplify the identification of hydrogel-associated water and its contribution to soil structural stability.

In the next step, the gained knowledge on clay- and hydrogel-associated water from the first two experiments was transferred to water-saturated artificial soils containing swellable clay particles and model polymer hydrogel (Chapter 5). We assumed that mutually restricted hydrogel and clay swelling will significantly increase hydrogel viscosity between mineral soil particles as function of polymer and clay content. This, in turn, should increase particle-particle friction and consequently soil structural stability. The identification of additional polymer-clay interactions and related soil-water interactions in the investigated artificial soils

will help to simplify the interpretation of natural humous soil containing soil-born complex organic substances and swellable clay particles, respectively.

In the last part of the thesis, all experiences gained from the previous experiments were transferred to a water-saturated natural soil containing various OM fractions such as particulate organic matter (POM) and mineral-associated matter (MAOM), respectively (Chapter 6). It was hypothesized that POM as additional granular material acts as physical separator between clay particles which consequently reduces clay swelling. In contrast, MAOM as viscous hydrogel-forming interparticulate OM glues soil particles, coats the mineral surfaces and restricts the swelling and volumetric expansion of clay particles in the soil matrix. In order to examine these hypotheses, we investigated the water binding and rheological stability of an agriculturally cultivated silty loam soil and its OM and mineral fractions by soil density fractionation and subsequent $^1\text{H-NMR}$ relaxometry and rheological measurements. The last experiment, together with the identification of fundamental mechanisms in more simplified systems, enabled to develop a schematic model for soil structural stability induced by various soil-water interactions.

Finally, the state-of-the-art knowledge on interparticulate hydrogel swelling in soil and its contribution to soil-water interactions were reviewed (Chapter 7). The evaluation of the conducted experiments (Chapters 3-5) as well as an extensive literature research on relevant process and suitable techniques to assess hydrogel swelling in soil formed the basis for the review, respectively. In this context, the term “gel effect” was introduced by Brax et al. to summarize hydrogel-swelling induced changes of soil properties.

3 CHARACTERIZATION OF WET-AGGREGATE STABILITY OF SOILS BY ¹H-NMR RELAXOMETRY

Buchmann, C.; Meyer, M.; Schaumann, G.E. (2015): *Characterization of wet aggregate stability of soils by ¹H-NMR relaxometry*. *Magnetic Resonance in Chemistry*, 53(9), pp.694-703. doi: 10.1002/mrc.4147



ABSTRACT

For the assessment of soil structural stability against hydraulic stress, wet sieving or constant head permeability tests are typically used but rather limited in their intrinsic information value. The multiple applications of several tests is the only possibility to assess important processes and mechanisms during soil aggregate breakdown, e.g. the influences of soil fragment release or differential swelling on the porous systems of soils or soil aggregate columns. Consequently, the development of new techniques for a faster and more detailed wet aggregate stability assessment is required. ¹H nuclear magnetic resonance relaxometry (¹H-NMR relaxometry) might provide these requirements because it has already been successfully applied on soils. We evaluated the potential of ¹H-NMR relaxometry for the assessment of wet aggregate stability of soils, with more detailed information on occurring mechanisms at the same time. Therefore, we conducted single wet sieving and constant head permeability tests on untreated and 1% polyacrylic acid-treated soil aggregates of different textures and organic matter contents, subsequently measured by ¹H-NMR relaxometry after percolation. The stability of the soil aggregates were mainly depending on their organic matter contents and the type of aggregate stabilization, whereby additional effects of clay swelling on the measured wet aggregate stability were identified by the transverse relaxation time (T_2) distributions. Regression analyses showed that only the percentage of water stable aggregates could be determined accurately from percolated soil aggregate columns by ¹H-NMR relaxometry measurements. ¹H-NMR relaxometry seems a promising technique for wet aggregate stability measurements but should be further developed for non-percolated aggregate columns and real soil samples.

4 INTRINSIC AND MODEL POLYMER HYDROGEL-INDUCED SOIL STRUCTURAL STABILITY OF A SILTY SAND SOIL AS AFFECTED BY SOIL MOISTURE DYNAMICS

Buchmann, C.; Bentz, J.; Schaumann, G.E. (2015): *Intrinsic and model polymer hydrogel-induced soil structural stability of a silty sand soil as affected by soil moisture dynamics*. Soil and Tillage Research, 154, pp.22-33. doi: 10.1016/j.still.2015.06.014



ABSTRACT

Moisture dynamics can favor the formation of stable soil structure by reorientation of soil particles and their gluing by organic structures. While soils are naturally exposed to moisture dynamics, structural stabilization is rather low if the soil organic matter (SOM) or clay content is insufficient. Although it is accepted that hydrogel-forming, swellable organic substances can enhance structural stabilization, the underlying mechanisms are not yet fully understood due to the lack of appropriate testing methods. The objective of our study was to understand the impact of soil moisture dynamics on the swelling properties of an incorporated hydrogel and their implications for soil structural properties. A physically unstable, silty sand soil was treated with polyacrylic acid (PAA) as highly swellable model polymer and subjected either to drying/remoistening cycles or to constant moisture. At certain measurement points, we investigated swelling processes and water binding using ^1H nuclear magnetic resonance relaxometry (^1H NMR relaxometry) in order to characterize the state of water entrapped in the hydrogel and soil pores and combined this information with rheological characteristics of the soil sample. Contrary to the untreated soil, the polymer-treated soil revealed both higher deformation (γ) at the yield point and higher maximum shear stress (τ_{max}), which reacted dynamically, but not reversibly on moisture dynamics and water redistribution. Structural stability clearly increased with the proportion of PAA-associated water assessed by ^1H NMR relaxometry. This relation suggests that swelling–shrinking processes in the hydrogel could explain the hysteretic and time-dependent nature of hydrogel-induced soil structural stabilization. All in all, the combination of ^1H NMR relaxometry and rheology will help to investigate mechanisms governing the development of soil structural stability and SOM-associated water in dependence of environmental dynamics.

5 EFFECT OF WATER ENTRAPMENT BY A HYDROGEL ON THE MICROSTRUCTURAL STABILITY OF ARTIFICIAL SOILS WITH VARIOUS CLAY CONTENT

Buchmann, C.; Schaumann, G.E. (2017): *Effect of water entrapment by a hydrogel on the microstructural stability of artificial soils with various clay content*. Plant and soil, 414(1-2), pp.181-198. doi: 10.1007/s11104-016-3110-z



ABSTRACT

Background and aims: Interactions between soil constituents define soil microstructural stability and are enhanced by swellable organic substances (hydrogels) such as extracellular polymeric substances (EPS), root mucilage or synthetic polymers. This study aims to identify the still largely unknown mechanisms behind hydrogel-induced soil microstructural stability. We hypothesized that soil microstructural stability increased with increasing limitation of hydrogel swelling between soil particles. **Methods:** One- and two-dimensional ^1H proton nuclear magnetic resonance relaxometry (^1H -NMR relaxometry) measurements were performed with untreated and polyacrylic-acid (PAA) treated artificial soils at various clay content and PAA concentrations. The results on the water distribution and water mobility in the artificial soils were related to their microstructural stability as measured by rheology. **Results:** PAA treatment significantly increased soil microstructural stability up to five times, especially at high clay content. Soil microstructural stability increased with decreasing rotational mobility of water in the PAA-treated artificial. At the two highest PAA concentrations, the microstructural stability was the highest, although the mobility of water molecules was not further restricted. **Conclusion:** In artificial soils, the viscosity of hydrogel structures between mineral particles and the additional formation of an external network by polymer-clay interactions such as polyvalent cation bridging seem to promote microstructural stability.

6 THE CONTRIBUTION OF VARIOUS ORGANIC MATTER FRACTIONS TO SOIL-WATER INTERACTIONS AND STRUCTURAL STABILITY OF AN AGRICULTURALLY CULTIVATED SOIL

Buchmann, C.; Schaumann, G.E. (2018): *The contribution of various organic matter fractions to soil-water interactions and structural stability of an agriculturally cultivated soil* J. Plant Nutr. Soil Sci., online early. doi: 10.1002/jpln.201700437



ABSTRACT

The presence and mutual interactions of soil organic matter (SOM) and clay particles are major factors determining soil structural stability. In the scope of agricultural management and environmental sustainability, it remains unclear how various mineral and organic matter (OM) fractions, OM–clay interactions and swelling processes in the interparticle space determine soil–water interactions and thus soil structural stability. To investigate this issue, we isolated the mineral and OM fractions of an agriculturally cultivated silty loam soil by soil density fractionation and assessed their hydration characteristics and effects on soil structural stability combining $^1\text{H-NMR}$ relaxometry, soil rheology and single wet-sieving of soil aggregates. The results showed that agricultural management practices, in particular compost and ploughing, as well as various OM–clay interactions significantly affected soil–water interactions and soil structural stability. On the one hand, ploughing reduced soil structural stability by promoting clay swelling as a result of disrupted soil structures and reduced SOM content. On the other hand, compost treatment and reduced tillage increased soil structural stability. In all cases, soil density fractionation showed that compost-derived particulate organic matter (POM) and mineral-associated organic matter (MAOM) restricted clay swelling and resulted in a highly porous and mechanically stable soil matrix. In particular, POM increased soil structural stability by acting as nucleus for soil aggregation and by restricting clay swelling *via* its presence as solid, granular interparticulate material. In contrast, MAOM seemed to restrict clay swelling *via* clay surface covering and the formation of viscous interparticulate hydrogel structures.

7 BIOHYDROGEL INDUCED SOIL-WATER INTERACTIONS: HOW TO UNTANGLE THE GEL EFFECT? - A REVIEW

Brax, M.; Buchmann, C.; Schaumann, G.E. (2017): *Biohydrogel induced soil–water interactions: how to untangle the gel effect? A review*. J. Plant Nutr. Soil Sci., 180, pp. 121–141. doi:10.1002/jpln.201600453



ABSTRACT

Biohydrogels such as microbial exudates and root-derived mucilage are soil-born cross-linked polymers, able to form porous three-dimensional networks during water uptake. The gel effect is the variation of soil properties, such as soil hydrology and soil structural stability, resulting from biohydrogel swelling in soil. Conventionally, soil–water–hydrogel interactions are investigated by measuring soil bulk properties such as water retention curves and porosity, without further analyzing the effect of biohydrogel phases in soil on a quantitative basis. Therefore, the evaluation of advanced and novel methods for the characterization of biohydrogel phases in soil and soil–water–hydrogel interactions is necessary. This review evaluates currently available methods for their potential to analyze processes associated to the gel effect.

A promising approach to investigate the spatio-temporal distribution of biohydrogel phases in porous media is based on Nuclear Magnetic Resonance (NMR) such as ^1H -NMR relaxometry, as well as on imaging techniques such as Environmental Scanning Electron Microscopy (ESEM). Especially NMR techniques enable the identification of different water populations based on their differences in the relaxation, and thus the mobility of water molecules in biohydrogels and non-gel water in soil pores.

Rheology measures the flow behavior of biohydrogels, providing information on the structural behavior of the hydrogel network and its gelling mechanism. Soil rheology further quantifies the effect of the biohydrogel phases on the interactions between soil particles, and thus the impact on soil microstructural stability. However, rheology does not elucidate the spatio-temporal distribution and structural state of biohydrogel phases in soil.

All in all, a systematic combination of rheology, NMR and suitable imaging methods seems promising and necessary in order to elucidate the still widely unknown gel effect in soil.

8 SYNTHESIS AND GENERAL CONCLUSIONS

8.1 SCHEMATIC MODEL OF SOIL STRUCTURAL STABILITY AND SOIL-WATER INTERACTIONS INDUCED BY HYDROGEL SWELLING AND PARTICLE-PARTICLE INTERACTIONS

The combination of soil mechanical behavior and soil-water interactions by various stability testing methods and $^1\text{H-NMR}$ relaxometry enabled to identify fundamental mechanisms behind hydrogel swelling-induced soil structural stability in water-saturated and unsaturated soil. The mechanistic model derived from the conducted experiments includes the various contributions of the involved organic and mineral soil constituents to the strength and degree of both soil-water interactions and soil structural stability (Figure 2).

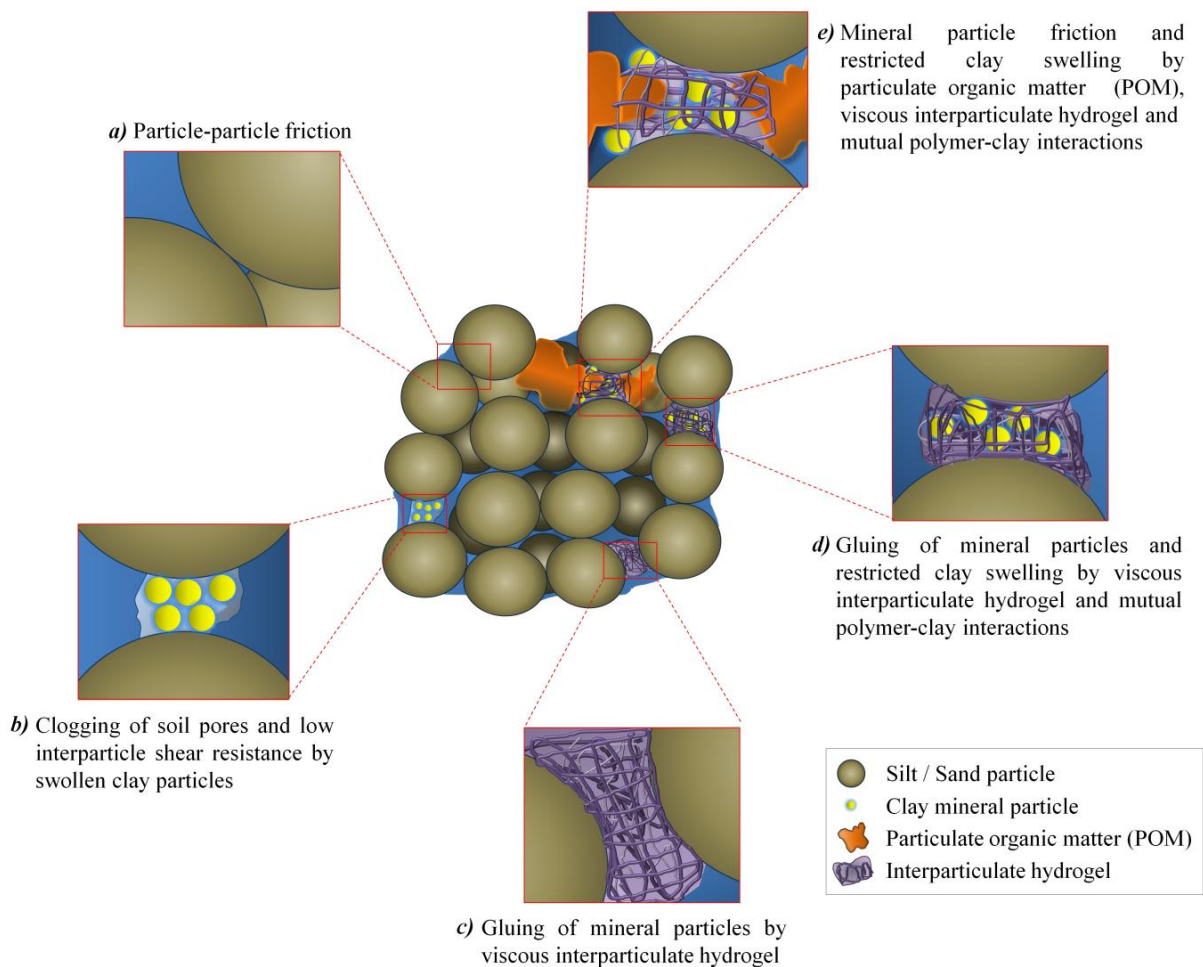


Figure 2: Schematic model for soil structural stability induced by interparticulate hydrogel swelling, clay swelling and various polymer-clay interactions in soil (own figure).

8.1.1 Soil containing negligible amounts of reactive soil constituents

In the simplest case, the investigated soils had high content and negligible amounts of reactive soil constituents such as swellable clay or hydrogel-forming organic substances. Here, the high sand content and the absence of swelling processes predominantly resulted in long relaxation times (T_{2WL}) in the relaxation time distributions of water-saturated (Chapter 5 and 6) and unsaturated soil (Chapter 4). Furthermore, water mobility in terms of translational (D/D_0) and rotational (T_1/T_2) mobility was not significantly restricted and comparable to pure inert sand (Chapter 6). Under water-saturated conditions, the long relaxation times and high water mobility mainly result from the coarse and highly porous soil pore system in which water molecules can freely move (Jaeger *et al.*, 2009; Meyer *et al.*, 2018). Hence, the pore-size distribution in dependence on soil texture mainly caused the long relaxation times and high water mobility in water-saturated soil with high sand content and negligible amounts of reactive soil constituents. In contrast, unsaturated conditions resulted in temporal shifts of the relaxation times towards shorter time ranges (Chapter 4). This typically results from the redistribution of water from initially large pores directly after wetting into smaller pores over time as a result of increasing pore wall hydrophilicity, higher capillarity and stronger intergranular adhesive forces (Todoruk *et al.*, 2003; Jaeger *et al.*, 2010; Lourenço *et al.*, 2012; Fuentes *et al.*, 2013).

The high water mobility and long relaxation times came along with low structural stability, independent of incubation time or moisture dynamics (Chapters 4 and 6). This indicates an insufficient physical stabilization in both water-saturated and unsaturated soils in the absence of appropriate binding agent such as soil organic matter (SOM). In this case, soil structural stability only results from particle-particle interactions in terms of friction under water-saturated conditions and additional capillary forces under unsaturated conditions in soil, respectively (Oades, 1993; Barzegar *et al.*, 1995; Orts *et al.*, 1999; Asghari *et al.*, 2009). According to the concept of force-chain development (Tembe *et al.*, 2010), an applied mechanical stress is typically transmitted through the soil skeleton via interconnected sand particles as function of grain size and water content (Baumgarten & Horn, 2013; Hartge & Horn, 2014; Le Bissonnais, 2016). The fact that neither moisture dynamics nor incubation times significantly affected the structural stability of the investigated unsaturated soil indicates that particle-particle friction and capillary forces do not necessarily increase soil microstructural stability (Chapter 4). All in all, soil-water interactions and soil structural stability in water-saturated and unsatu-

rated soil mainly result from intrinsic soil textural properties when no appropriate amounts of binding agents are present (*Mechanism a*) in Figure 2).

8.1.2 Soil containing swellable clay particles

In the presence of swellable clay particles, relaxation times and water mobility decreased together with soil structural stability (Chapters 3, 5 and 6). $^1\text{H-NMR}$ relaxometry measurements showed that the presence of swollen clay particles in both water-saturated and unsaturated soil typically results in peaks at $T_2 > 10$ ms in the relaxation time distribution (Chapters 3 and 6). Simultaneously, translational (D/D_0) and rotational (T_1/T_2) mobility of clay-associated water was significantly restricted and comparable to freely swollen clay particles in an excess of water (Chapters 5 and 6). These observations result from the high collision frequency of water molecules in the densely packed and swollen clay structures as well as from the subsequently reduced interparticle space after the swelling and volumetric expansion of clay particles in soil (Nakashima, 2000; Ameta & Wayal, 2008; Gueddouda *et al.*, 2008; Guichet *et al.*, 2008; Bahia & Ramdane, 2012).

Clay swelling and the formation of clay-associated water in water-saturated soil not only reduced water mobility and peak positions but also soil structural stability (Chapter 3, 5 and 6). This is attributed to the adsorption of water molecules onto mineral clay surfaces which provides only weak cohesive forces due to the relatively high spacing between the clay domains. Furthermore, the accumulation of swollen clay particles in the interparticle space typically results in the formation of a compacted clay matrix with low viscosity and low interparticle shear resistance (Ghezzehei & Or, 2001). The resulting insufficient transmission of applied mechanical stresses through the soil skeleton is well-known for soils containing swellable clay particles and only with low amounts of organic binding agents (Bronick & Lal, 2005; Baiamonte *et al.*, 2015; Shi *et al.*, 2016). Hence, clay-associated water with low mobility occupies the interparticle space and acts as lubricant between soil particles by consequently reducing solid-solid friction as shown by *Mechanism b*) in Figure 2.

8.1.3 Soil containing interparticulate hydrogel

In contrast to clay swelling, interparticulate hydrogel swelling increased water mobility together with soil structural stability for water-saturated (Chapters 5 and 6) as well as unsaturated soils (Chapters 3 and 4). In all conducted experiments, hydrogel-associated

water was more mobile than clay-associated water which results from the highly porous and flexible three-dimensional hydrogel network in the interparticle space in which water is less strongly bound than on mineral clay surfaces (Cihlar *et al.*, 2014; Brax *et al.*, 2017a; b). Outside the soil matrix, hydrogel formation can occur under defined and unrestricted conditions, e. g. in an excess of water and until reaching maximum swelling conditions (Ganji *et al.*, 2010). However, this is not the case in water-saturated soil as soil textural properties, soil solution composition and polymer-clay interactions restrict interparticulate hydrogel swelling accompanied by reduced water mobility and shifts of the relaxation time distribution towards shorter time range (Chapter 5-7). In general, the mobility of water molecules in three-dimensional hydrogel networks result from the distance of polymer chain segments, their interactions with each other and the additional interactions with absorbed water molecules (Kerr and Wicker 2000; Baumgartner *et al.* 2002; Shapiro 2011). In soil, interparticulate hydrogel swelling is typically restricted or reduced via the release of water or via the high crosslinkage of its polymer chains in the presence of dissolved polyvalent cations (Chapter 5). Both processes increase the structuring of hydrogel-associated water in the condensed three-dimensional hydrogel network which, in turn, increase hydrogel viscosity and water binding in the interparticle space (Knauss *et al.*, 1996; Carenza *et al.*, 1999; Hills *et al.*, 2000; Nakashima, 2000; Bai *et al.*, 2013).

Concerning the effect of interparticulate hydrogel on soil structural stability, our experiments showed significant relationships between hydrogel swelling-induced soil-water interactions and soil structural stability (Chapters 3, 5 and 6). In contrast to swollen clay particles, interparticulate hydrogel glues and interconnects soil particles forming a strong and elastic matrix with the ability to withstand externally applied mechanical and hydraulic stress. The high soil microstructural stability in the presence of interparticulate hydrogel indicates the contribution of hydrogel-associated water to elastic behavior of soil. Hence, water confined in the interparticulate hydrogel network provides a higher elasticity than capillary water (Chapter 4) or clay-associated water (Chapters 5 and 6) and consequently reduces the relative proportion of viscous deformation behavior of soil under cyclic or transient loads. Since the contribution of capillary forces to the microstructural stability of water-saturated soil is negligible (Blume *et al.*, 2015), the structural stability of the investigated water-saturated soils predominantly results from the hydrogel viscosity in the interparticle space as function of soil solution composition, degree of cross-linkage between the polymer chains and soil texture.

Under unsaturated conditions in soil, interparticulate hydrogel swelling showed comparable effects to water-saturated soil in terms of increased water mobility and soil microstructural stability (Chapters 3 and 4). However, it became evident that hydrogel swelling-induced soil microstructural stability strongly depends on environmental dynamics in terms of incubation time and moisture and not only on hydrogel viscosity and soil texture. Under unsaturated conditions, hysteresis effects are likely: During drying events, interparticulate hydrogel can easily release water over time into the surrounding soil matrix as result of water redistribution processes in soil via capillary forces (Todoruk *et al.*, 2003). This increases interparticulate hydrogel viscosity and thus enhances soil particle cementation and particle-particle friction (Chang *et al.*, 2015; Levy & Warrington, 2015). Additionally, dehydrated interparticulate hydrogel re-swells during rewetting of soil and the relative amount of stabilizing viscous hydrogel in the interparticle space re-increases which, in turn, reduces the relative amount of capillary or clay-associated water (Chapter 4). However, increasing number of drying/rewetting events reduces the potential of interparticulate hydrogel to re-swell as a result of closer soil particles attachment and restricted accessibility of water molecules to dehydrated interparticulate hydrogel structures in the strongly cemented interparticle space (Liu *et al.*, 2009; Yazdandoust & Yasrobi, 2010). All in all, the higher the hydrogel viscosity between the soil particles the more stable becomes the soil microstructure compared to soil structures solely stabilized by particle-particle friction under water-saturated and by additional capillary forces under unsaturated conditions, respectively (*Mechanism d*) in Figure 2).

8.1.4 Soil containing swellable clay particles and interparticulate hydrogel

In all conducted experiments, the simultaneous presence of swellable clay particles and organic substances shifted the relaxation times and peak positions towards either shorter (clay swelling) or longer (hydrogel swelling) relaxation times with significantly increased soil structural stability (Chapters 3, 5 and 6). Although water mobility and signal intensity of both clay- and hydrogel-associated water decreased when they were simultaneously present, soil structural stability increased to greater extent than if they were present in isolation the interparticle space. These observations are attributed to various polymer-clay interactions in the interparticle space: On the one hand, interparticulate hydrogel partly absorbs clay particles into its three-dimensional hydrogel network which, in turn, results in the coverage of mineral clay surfaces by membra-

nous polymeric structures and thus the prevention of unrestricted clay swelling and volumetric expansion (Chapter 5). Similar membranous structures and effects on soil structural stability have been shown for natural soils and even model systems (Theng, 1982; Liu *et al.*, 2009; Maghchiche *et al.*, 2010; Markgraf *et al.*, 2012; Theng, 2012; Albalasmeh & Ghezzehei, 2014). This additional coating of clay particles by a hydrogel network increases soil microstructural stability by forming cation bridges with clay particles and thus increasing interparticle forces and soil particle interconnectivity (Barré & Hallett, 2009; Akimkhan, 2013). The longer the polymer chains and the higher the concentration of dissolved polyvalent cations, the more effective can polymer structures coat clay particle via cation bridges and consequently reduce their swelling and destabilizing effect between sand grains (Chapter 5 and 6). Since the investigated soils in this thesis showed high concentrations of dissolved polyvalent cations such as Fe^{3+} , Mg^{2+} and Ca^{2+} , the relevance of cation bridging between polymer structures and clay surfaces on the wettability of clay structures and thus on soil structural stability becomes evident (Liu *et al.*, 2009; Maghchiche *et al.*, 2010).

On the other hand, the simultaneous swelling of clay particles and hydrogel in the interparticle space counteracts each other via their competition for available water and pore space during their volumetric expansion (Chapter 5). Consequently, the resulting mutual swelling restriction reduces the relative proportion of both clay- and hydrogel-associated water together with their characteristic effects on water distribution and water mobility.

Interestingly, the various OM fractions in the water-saturated agriculturally cultivated soil showed comparable effects to the model polymer hydrogel investigated in this thesis (Chapter 6). Here too, both OM fractions (mineral-associated organic matter (MAOM) and particulate organic matter (POM)) counteracted interparticulate clay swelling with positive effects on soil-water interactions and soil structural stability. This already indicates the transferability of the mechanisms obtained from the experiments with artificial (Chapter 5) and artificially-treated soils (Chapter 4), respectively. However, the underlying mechanisms differ between the two OM fractions: MAOM presumably reduce the interconnectivity and wettability of clay particles via the coating of mineral clay surfaces and via the formation of hydrogel structures in the interparticle space. In contrast, POM rather acts as granular material in the interparticle space which spatially separated previously interconnected swollen clay particles from each other. Furthermore, the granular properties of POM and its mutual interactions with clay parti-

cles positively contribute to particle-particle friction and thus to the formation of stable, aggregated soil structures (*Mechanism e*) in Figure 2). The investigation of an agriculturally cultivated soil further reveals the importance of land use and the therewith associated OM dynamics on soil structural stability: On the one hand, additional OM input by compost treatment increases the amounts of POM and further promotes the formation of hydrogel-forming organic substances over time (Yamashita *et al.*, 2006). This, in turn, positively contributes to soil microstructural stability as extensively explained above for the developed mechanistic model. On the other hand, tillage in terms of ploughing disrupts intact soil structures and releases previously isolated, strongly bound OM and clay particles (Balesdent *et al.*, 2000). As a result, microorganisms can easily degrade the now readily available OM whereas clay particles can swell more easily in the interparticle space. Both processes negatively contribute to soil microstructural stability by reducing particle-particle gluing and internal cohesion as proposed in the developed mechanistic model and indicated by various other studies (Aoyama *et al.*, 1999; Chaplain *et al.*, 2011; Curaqueo *et al.*, 2011; Grosbellet *et al.*, 2011).

8.2 FINAL CONCLUSION AND OUTLOOK

¹H-NMR relaxometry was combined for the first time with soil structural stability testing methods in order to understand the contribution of interparticulate hydrogel to soil-water interactions and soil structural stability. The results showed that interparticulate hydrogel significantly contributes to soil structural stability and soil-water interactions by changing the water mobility in the soil matrix together with the strength of particle-particle interactions. In wet and water-saturated soils, this positive contribution predominantly depends on the viscosity of the interparticulate hydrogel and various polymer-clay interactions as function of soil solution composition, soil textural properties and external factors in terms of moisture dynamics and agricultural management practices. On the one hand, the higher the hydrogel viscosity between the soil particles the more stable becomes the soil structure in water-saturated and unsaturated soil. On the other hand, in the context of soil structural development and soil aggregation, the importance of mutual interactions between swollen hydrogel structures and clay particles becomes evident. Here, interparticulate hydrogel can reduce the dispersive and plastic shearing effects of swollen clay particles by restricting their swelling and by their additionally bridging via polyvalent cations over large scales. These findings are especially important for the understanding of soil structural development and for taking appropriate

and sustainable management measures to maintain the sustainability of natural and cultivated soil. The mechanistic model developed in this thesis depicts all essential processes affecting soil structural stability and shall serve as a basis for understanding the contribution of interparticulate hydrogel and OM to soil structural stability.

Despite the good explanation of hydrogel swelling-induced soil-water interactions and soil structural stability, several challenges remain and need further investigation in future work: Firstly, one-dimensional $^1\text{H-NMR}$ relaxometry could not clearly differentiate hydrogel-associated water from mineral-associated soil pore water. This was only possible when the relaxation times and peak positions of the two water populations completely differed and did not merged in the relaxation time distribution. Even two-dimensional T_1 - T_2 and PFG $^1\text{H-NMR}$ relaxometry measurements could not clearly differentiate certain water populations. Accordingly, two-dimensional T_2 -D measurements relating measured diffusion coefficients D to relaxation times T_2 might help to overcome this challenge by distinguishing between specific water populations based on their mobility e. g. moving and non-moving water (Bayer *et al.*, 2010; Jaeger *et al.*, 2010). Prospectively, the two-dimensional T_2 -D $^1\text{H-NMR}$ relaxometry technique should be established for the $^1\text{H-NMR}$ relaxometer used in the conducted studies.

Secondly, the effect of polymer-clay interactions in terms of sorption and flocculation on the $^1\text{H-NMR}$ relaxometry measurements are only scarcely known (Cooper *et al.*, 2013). For example, dissolved polyvalent (paramagnetic) cations could affect the sorption of polymeric organic substances on clay mineral surfaces and additionally accelerate proton relaxation in soil (Kleinberg *et al.*, 1994; Bryar *et al.*, 2000). Hence, it remains unclear to which extent proton relaxation is affected by polymer-clay interactions and how this affects, for example, the quantitative estimation of pore sizes and various water populations from relaxation times as done by Jaeger *et al.* (2009) and Meyer *et al.* (2018).

Thirdly, only PAA was used as hydrogel-forming model polymer in this thesis. Although PAA swelling has comparable effects on water mobility and soil structural stability to soil-born hydrogel-forming biopolymers, model polymers do not necessarily reflect the complexity and heterogeneity of soil-born hydrogel-forming biopolymer such as mucilage in terms of chemical composition and physico-chemical properties (Mayer *et al.*, 1999; Schaumann & Thiele-Bruhn, 2011). In this context, soil density fractionation has a great potential to identify the effects of various soil-born OM fractions on soil-water interactions and soil structural stability. However, the use of model polymer

hydrogels with comparable physico-chemical properties seems to be a more promising approach due to low costs and small efforts (Mimmo *et al.*, 2003; Barré & Hallett, 2009). In order to replace soil-born hydrogel-forming biopolymers by model polymers, the most important parameters describing the properties of soil-born hydrogel-forming biopolymers needs to be identified.

Fourthly, and lastly, most of the experiments were performed at high water content or even under water-saturated conditions. These hydration states have only minor relevance in the field where soil is rather dry or field-moist (Al-Shayea, 2001). However, the experimental approaches in this thesis enabled to investigate the role of interparticulate hydrogel and its viscosity on soil structural stability and soil-water interactions in an isolated manner. In the course of this, repeated loading at various frequencies, e.g. when tractors frequently passage fields during intensive farming, are well-known to affect stress-strain behavior of soil by continuous alternating pore water-pressure conditions and therewith associated shear resistance at particle contacts (Ghezzehei & Or, 2001; Horn & Smucker, 2005; Peth & Horn, 2006). In this context, it remains largely unclear to which extent interparticulate hydrogel contribute to soil microstructural stability at various loading frequencies and matric potentials. Here, further investigations should be carried out together with the evaluation of additional, eventually more suitable rheological parameters.

9 REFERENCES

- Abend, S. & Lagaly, G. 2000. Sol–gel transitions of sodium montmorillonite dispersions. *Applied Clay Science*, **16**, 201-227.
- Ajayi, A., Holthusen, D. & Horn, R. 2016. Changes in microstructural behaviour and hydraulic functions of biochar amended soils. *Soil and Tillage Research*, **155**, 166-175.
- Akimkhan, A. 2013. Adsorption of polyacrylic acid and polyacrylamide on montmorillonite. *Russian Journal of Physical Chemistry A*, **87**, 1875-1880.
- Al-Shayea, N.A. 2001. The combined effect of clay and moisture content on the behavior of remolded unsaturated soils. *Engineering Geology*, **62**, 319-342.
- Albalasmeh, A.A. & Ghezzehei, T.A. 2014. Interplay between soil drying and root exudation in rhizosheath development. *Plant and Soil*, **374**, 739-751.
- Ameta, N. & Wayal, A.S. 2008. Effect of bentonite on permeability of dune sand. *Electronic Journal of Geotechnical Engineering*, **13**, 1-7.
- Aoyama, M., Angers, D.A. & N'Dayegamiye, A. 1999. Particulate and mineral-associated organic matter in water-stable aggregates as affected by mineral fertilizer and manure applications. *Canadian Journal of Soil Science*, **79**, 295-302.
- As, H.V. & Lens, P. 2001. Use of ¹H NMR to study transport processes in porous biosystems. *Journal of Industrial Microbiology & Biotechnology*, **26**, 43-52.
- Asghari, S., Neyshabouri, M.R., Abbasi, F., Aliasgharzad, N. & Oustan, S. 2009. The effects of four organic soil conditioners on aggregate stability, pore size distribution, and respiration activity in a sandy loam soil. *Turkish Journal of Agriculture and Forestry*, **33**, 47-55.
- Bahia, L. & Ramdane, B. 2012. SAND: An Additive for Stabilization of Swelling Clay Soils. *International Journal of Geosciences*, **3**, 719-725.
- Bai, R., Basser, P.J., Briber, R.M. & Horkay, F. 2013. NMR water self-diffusion and relaxation studies on sodium polyacrylate solutions and gels in physiologic ionic solutions. *Journal of applied polymer science*, **131** (6), 1-7
- Baiamonte, G., De Pasquale, C., Marsala, V., Cimò, G., Alonzo, G., Crescimanno, G. & Conte, P. 2015. Structure alteration of a sandy-clay soil by biochar amendments. *Journal of Soils and Sediments*, **15**, 816-824.
- Balesdent, J., Chenu, C. & Balabane, M. 2000. Relationship of soil organic matter dynamics to physical protection and tillage. *Soil and Tillage Research*, **53**, 215-230.
- Barré, P. & Hallett, P. 2009. Rheological stabilization of wet soils by model root and fungal exudates depends on clay mineralogy. *European Journal of Soil Science*, **60**, 525-538.
- Barzegar, A.R., Rengasamy, P. & Oades, J.M. 1995. Effects of clay type and rate of wetting on the mellowing of compacted soils. *Geoderma*, **68**, 39-49.

- Baumgarten, W. & Horn, R. 2013. Assessing soil degradation by using a scale-spanning soil mechanical approach: A review. In: *Advances in GeoEcology 42* (eds. Krümmelbein, J., Horn, R. & Pagliai, M.), pp. 1-61. Catena Verlag, Cremlingen.
- Baumgarten, W., Neugebauer, T., Fuchs, E. & Horn, R. 2012. Structural stability of Marshland soils of the riparian zone of the Tidal Elbe River. *Soil and Tillage Research*, **125**, 80-88.
- Baumgartl, T. & Horn, R. 1993. Die Bestimmung der Aggregatstabilität - ein Methodenvergleich. *Zeitschrift Fur Pflanzenernahrung und Bodenkunde*, **156**, 385-391.
- Bayer, J.V., Jaeger, F. & Schaumann, G.E. 2010. Proton Nuclear magnetic resonance (NMR) relaxometry in soil science applications. *The Open Magnetic Resonance Journal*, **3**, 15-26.
- Bird, N.R.A., Preston, A.R., Randall, E.W., Whalley, W.R. & Whitmore, A.P. 2005. Measurement of the size distribution of water-filled pores at different matric potentials by stray field nuclear magnetic resonance. *European Journal of Soil Science*, **56**, 135-143.
- Blume, H.-P., Brümmer, G.W., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K. & Wilke, B.-M. 2015. *Scheffer/Schachtschabel - Soil Science*. Springer, Heidelberg.
- Brax, M., Buchmann, C. & Schaumann, G.E. 2017a. Biohydrogel induced soil–water interactions: How to untangle the gel effect? A review. *Journal of Plant Nutrition and Soil Science*, **180**, 121-141.
- Brax, M., Buchmann, C. & Schaumann, G.E. 2017b. Effect of mucilage on water properties in the rhizosphere monitored by ¹H-NMR relaxometry. *Microporous and Mesoporous Materials*, **269**, 47-50.
- Bronick, C.J. & Lal, R. 2005. Soil structure and management: a review. *Geoderma*, **124**, 3-22.
- Bryar, T.R., Daughney, C.J. & Knight, R.J. 2000. Paramagnetic effects of iron(III) species on nuclear magnetic relaxation of fluid protons in porous media. *Journal of Magnetic Resonance*, **142**, 74-85.
- Capitani, D., Crescenzi, V., De Angelis, A.A. & Segre, A.L. 2001. Water in Hydrogels. An NMR Study of Water/Polymer Interactions in Weakly Cross-Linked Chitosan Networks. *Macromolecules*, **34**, 4136-4144.
- Carenza, M., Cojazzi, G., Bracci, B., Lendinara, L., Vitali, L., Zincani, M., Yoshida, M., Katakai, R., Takacs, E., Higa, O.Z. & Martellini, F. 1999. The state of water in thermoresponsive poly(acryloyl-L-proline methyl ester) hydrogels observed by DSC and ¹H-NMR relaxometry. *Radiation Physics and Chemistry*, **55**, 209-218.
- Chang, I., Im, J., Prasadhi, A.K. & Cho, G.-C. 2015. Effects of Xanthan gum biopolymer on soil strengthening. *Construction and Building Materials*, **74**, 65-72.

- Chang, S., Ryan, M. & Gupta, R. 1993. The effect of pH, ionic strength, and temperature on the rheology and stability of aqueous clay suspensions. *Rheologica Acta*, **32**, 263-269.
- Chaplain, V., Défossez, P., Richard, G., Tessier, D. & Roger-Estrade, J. 2011. Contrasted effects of no-till on bulk density of soil and mechanical resistance. *Soil and Tillage Research*, **111**, 105-114.
- Chesworth, W. 2008. *Encyclopedia of soil science*. Springer, New York.
- Cihlar, Z., Vojtova, L., Conte, P., Nasir, S. & Kucerik, J. 2014. Hydration and water holding properties of cross-linked lignite humic acids. *Geoderma*, **230-231**, 151-160.
- Cooper, C.L., Cosgrove, T., van Duijneveldt, J.S., Murray, M. & Prescott, S.W. 2013. The use of solvent relaxation NMR to study colloidal suspensions. *Soft Matter*, **9**, 7211-7228.
- Curaqueo, G., Barea, J.M., Acevedo, E., Rubio, R., Cornejo, P. & Borie, F. 2011. Effects of different tillage system on arbuscular mycorrhizal fungal propagules and physical properties in a Mediterranean agroecosystem in central Chile. *Soil and Tillage Research*, **113**, 11.
- Dexter, A.R. 1988. Advances in characterization of soil structure. *Soil and Tillage Research*, **11**, 199-238.
- Diaz-Zorita, M., Grove, J. & Perfect, E. 2002. Aggregation, fragmentation, and structural stability measurement. *Encyclopedia of Soil Science*, 37-40.
- Dunn, K.-J., Bergman, D.J. & Latorraca, G.A. 2002. *Handbook of Geographical Exploration-Seismic Exploration: Nuclear Magnetic Resonance-Petrophysical and Logging Applications*. Pergamon Press, Oxford.
- Elimelech, M., Jia, X., Gregory, J. & Williams, R. 1998. *Particle deposition & aggregation: measurement, modelling and simulation*. Butterworth-Heinemann, Oxford.
- Flemming, H.-C. & Wingender, J. 2000. Extracellular polymeric substances (EPS) - the construction material for biofilms. *Vom Wasser*, **94**, 245-266.
- Fuentes, I., Seguel, O. & Casanova, M. 2013. Shear strength of aggregates compared with bulk soil of two haploxerolls from Chile. *Journal of Soil Science and Plant Nutrition*, **13**, 819-831.
- Ganji, F., Vasheghani-Farahani, S. & Vasheghani-Farahani, E. 2010. Theoretical description of hydrogel swelling: a review. *Iranian Polymer Journal*, **19**, 375-398.
- Ghezzehei, T.A. & Or, D. 2001. Rheological properties of wet soils and clays under steady and oscillatory stresses. *Soil Science Society of America Journal*, **65**, 624-637.
- Graber, E.R., Fine, P. & Levy, G.J. 2006. Soil stabilization in semiarid and arid land agriculture. *Journal of Materials in Civil Engineering*, **18**, 190-205.

- Gregorich, E.G., Turchenek, L., Carter, M. & Angers, D.A. 2001. *Soil and environmental science dictionary*. CRC Press, Boca Raton.
- Grosbellet, C., Vidal-Beaudet, L., Caubel, V. & Charpentier, S. 2011. Improvement of soil structure formation by degradation of coarse organic matter. *Geoderma*, **162**, 27-38.
- Gueddouda, M., Lamara, M., Aboubaker, N. & Taibi, S. 2008. Hydraulic conductivity and shear strength of dune sand-bentonite mixtures. *Electronic Journal of Geotechnical Engineering*, **13**, 1-15.
- Guichet, X., Fleury, M. & Kohler, E. 2008. Effect of clay aggregation on water diffusivity using low field NMR. *Journal of Colloid and Interface Science*, **327**, 84-93.
- Guilherme, M.R., Aouada, F.A., Fajardo, A.R., Martins, A.F., Paulino, A.T., Davi, M.F., Rubira, A.F. & Muniz, E.C. 2015. Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: A review. *European Polymer Journal*.
- Hartge, K.H. & Horn, R. 2014. *Einführung in die Bodenphysik*. Schweizerbart, Stuttgart.
- Hillel, D. 2003. *Introduction to environmental soil physics*. Academic press, Massachusetts
- Hills, B., Godward, J., Debatty, M., Barras, L., Saturio, C. & Ouwerx, C. 2000. NMR studies of calcium induced alginate gelation. Part II. The internal bead structure. *Magnetic Resonance in Chemistry*, **38**, 719-728.
- Hinedi, Z.R., Kabala, Z.J., Skaggs, T.H., Borchardt, D.B., Lee, R.W.K. & Chang, A.C. 1993. Probing soil and aquifer material porosity with nuclear magnetic resonance. *Water Resources Research*, **29**, 3861–3866.
- Holthusen, D., Peth, S. & Horn, R. 2011. Impact of potassium concentration and matric potential on soil stability derived from rheological parameters. *Soil & Tillage Research*, **111**, 75-85.
- Holthusen, D., Reeb, D. & Horn, R. 2012. Influence of potassium fertilization, water and salt stress, and their interference on rheological soil parameters in planted containers. *Soil and Tillage Research*, **125**, 72-79.
- Horn, R. & Baumgartl, T. 2002. Dynamic properties of soils. *Soil physics companion*, **389**.
- Horn, R. & Fleige, H. 2003. A method for assessing the impact of load on mechanical stability and on physical properties of soils. *Soil & Tillage Research*, **73**, 89-99.
- Horn, R. & Smucker, A. 2005. Structure formation and its consequences for gas and water transport in unsaturated arable and forest soils. *Soil & Tillage Research*, **82**, 5-14.
- Hoskins, B.C., Fevang, L., Majors, P.D., Sharma, M.M. & Georgiou, G. 1999. Selective Imaging of Biofilms in Porous Media by NMR Relaxation. *Journal of Magnetic Resonance*, **139**, 67-73.

- Hurrass, J. & Schaumann, G.E. 2007. Hydration kinetics of wetttable and water repellent soil samples. *Soil Science Society of America Journal*, **71**, 280-288.
- Hussien, R.A., Donia, A.M., Atia, A.A., El-Sedfy, O.F., El-Hamid, A.R.A. & Rashad, R.T. 2012. Studying some hydro-physical properties of two soils amended with kaolinite-modified cross-linked poly-acrylamides. *CATENA*, **92**, 172-178.
- Jaeger, F., Bowe, S. & Schaumann, G.E. 2009. Evaluation of ^1H NMR relaxometry for the assessment of pore size distribution in soil samples. *European Journal of Soil Science*, **60**, 1052-1064.
- Jaeger, F., Grohmann, E. & Schaumann, G.E. 2006. ^1H NMR Relaxometry in natural humous soil samples: Insights in microbial effects on relaxation time distributions. *Plant and Soil*, **280**, 209-222.
- Jaeger, F., Rudolph, N., Lang, F. & Schaumann, G.E. 2008. Effects of soil solution's constituents on proton NMR relaxometry of soil samples. *Soil Science Society of America Journal*, **72**, 1694-1707.
- Jaeger, F., Shchegolikhina, A., van As, H. & Schaumann, G.E. 2010. Proton NMR Relaxometry as a Useful Tool to Evaluate Swelling Processes in Peat Soils. *The Open Magnetic Resonance Journal*, **3**, 27-45.
- Kemper, W. & Rosenau, R. 1986. Aggregate stability and size distribution. In: *Methods of Soil Analyses Part 1: Physical and Mineralogical Methods* (ed. Klute, A.), pp. 425-442. ASA-SSSA, Madison.
- Kleinberg, R.L. 1999. Nuclear Magnetic Resonance. In: *Methods in the Physics of Porous Media* (ed. Wong, P.-Z.), pp. 337-385. Academic Press, California.
- Kleinberg, R.L., Kenyon, W.E. & Mitra, P.P. 1994. Mechanism of NMR relaxation of fluids in rock. *Journal of Magnetic Resonance, Series A*, **108**, 206-214.
- Knauss, R., Fleischer, G., Gruender, W., Kaerger, J. & Werner, A. 1996. Pulsed field gradient NMR and nuclear magnetic relaxation studies of water mobility in hydrated collagen II. **36**, 241-248.
- Kögel-Knabner, I. 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology & Biochemistry*, **34**, 139-162.
- Le Bissonnais, Y. 2016. Aggregate stability and assessment of soil crustability and erodibility: I. Theory and methodology. *European Journal of Soil Science*, **67**, 11-21.
- Lehrsch, G.A. 1998. Freeze- Thaw Cycles Increase Near-Surface Aggregate Stability. *Soil Science*, **163**, 63-70.
- Levy, G.J. & Warrington, D.N. 2015. Polyacrylamide Addition to Soils: Impacts on Soil Structure and Stability. In: *Functional Polymers in Food Science: From Technology to Biology 2* (eds. Cirillo, G., Spizzirri, G.U. & Iemma, F.), pp. 9-32. Scrivener Publishing, Salem.

- Liu, J., Shi, B., Jiang, H., Bae, S. & Huang, H. 2009. Improvement of water-stability of clay aggregates admixed with aqueous polymer soil stabilizers. *CATENA*, **77**, 175-179.
- Lourenço, S., Gallipoli, D., Augarde, C., Toll, D., Fisher, P. & Congreve, A. 2012. Formation and evolution of water menisci in unsaturated granular media. *Géotechnique*, **62**, 193-199.
- Maghchiche, A., Haouam, A. & Immirzi, B. 2010. Use of polymers and biopolymers for water retaining and soil stabilization in arid and semiarid regions. *Journal of Taibah University for Science*, **4**, 9-16.
- Manalo, F.P., Kantzas, A. & Langford, C.H. 2003. Soil Wettability As Determined from Using Low-Field Nuclear Magnetic Resonance. *Environmental Science and Technology*, **37**, 2701-2706.
- Markgraf, W. & Horn, R. 2006. Rheological-stiffness analysis of K+-treated and CaCO₃-rich soils. *Journal of Plant Nutrition and Soil Science*, **169**, 411-419.
- Markgraf, W. & Horn, R. 2007. Scanning electron microscopy–energy dispersive scan analyses and rheological investigations of South-Brazilian soils. *Soil Science Society of America Journal*, **71**, 851-859.
- Markgraf, W., Horn, R. & Peth, S. 2006. An approach to rheometry in soil mechanics—Structural changes in bentonite, clayey and silty soils. *Soil and Tillage Research*, **91**, 1-14.
- Markgraf, W., Watts, C.W., Whalley, W.R., Hrkac, T. & Horn, R. 2012. Influence of organic matter on rheological properties of soil. *Applied Clay Science*, **64**, 25-33.
- Mayer, C., Moritza, R., Kirschner, C., Borchard, W., Wingender, R.M. & Flemming, H.-C. 1999. The role of intermolecular interactions: studies on model systems for bacterial biofilms. *International Journal of Biological Macromolecules*, **26**, 3-16.
- McBrierty, V.J., Martin, S.J. & Karasz, F.E. 1999. Understanding hydrated polymers: the perspective of NMR. *Journal of Molecular Liquids*, **80**, 179-205.
- McBrierty, V.J., Wardell, G.E., Keely, C.M., O'Neill, E.P. & Prasad, M. 1996. The characterization of water in peat. *Soil Science Society of America Journal*, **60**, 991-1000.
- Meyer, M., Buchmann, C. & Schaumann, G.E. 2018. Determination of quantitative pore size distribution of soils with ¹H-NMR Relaxometry. *European Journal of Soil Science*, **online early**.
- Mimmo, T., Marzadori, C., Francioso, O., Deiana, S. & Gessa, C.E. 2003. Effects of aluminum sorption on calcium-polygalacturonate network used as soil–root interface model. *Biopolymers*, **70**, 655-661.
- Nakashima, Y. 2000. Effects of clay fraction and temperature on the H₂O self-diffusivity in hectorite gel: A pulsed-field-gradient spin-echo nuclear magnetic resonance study. *Clays and clay minerals*, **48**, 603-609.

- Norrish, K. 1954. The swelling of montmorillonite. *Discussions of the Faraday society*, **18**, 120-134.
- Oades, J.M. 1993. The role of biology in the formation, stabilization and degradation of soil structure. *Geoderma*, **56**, 377-400.
- Orts, W.J., Sojka, R.E., Glenn, G.M. & Gross, R.A. 1999. Preventing soil erosion with polymer additives. *Polymer News*, **24**, 406-413.
- Pagenkemper, S.K., Athmann, M., Uteau, D., Kautz, T., Peth, S. & Horn, R. 2015. The effect of earthworm activity on soil bioporosity–Investigated with X-ray computed tomography and endoscopy. *Soil and Tillage Research*, **146**, 79-88.
- Paluszek, J. 2011. Physical quality of eroded soil amended with gel-forming polymer. *International Agrophysics*, **25**, 375-382.
- Paul, E.A. 2014. *Soil microbiology, ecology and biochemistry*. Academic press, London
- Peng, X., Horn, R. & Hallett, P. 2015. Soil structure and its functions in ecosystems: Phase matter & scale matter. *Soil & Tillage Research*, **146**, 1-3.
- Pértile, P., Reichert, J.M., Gubiani, P.I., Holthusen, D. & Costa, A.d. 2016. Rheological Parameters as Affected by Water Tension in Subtropical Soils. *Revista Brasileira De Ciencia Do Solo*, **40**.
- Peth, S. & Horn, R. 2006. The mechanical behavior of structured and homogenized soil under repeated loading. *Journal of Plant Nutrition and Soil Science*, **169**, 401-410.
- Radosta, S., Schierbaum, F. & Yuriev, W.P. 1989. Polymer-Water Interaction of Maltodextrins. Part II: NMR Study of Bound Water in Liquid Maltodextrin-Water Systems. *Starch - Stärke*, **41**, 428-430.
- Rao, S.N. & Mathew, P.K. 1995. Effects of exchangeable cations on hydraulic conductivity of a marine clay. *Clays and clay minerals*, **43**, 433-437.
- Redmile-Gordon, M.A., Brookes, P.C., Evershed, R.P., Goulding, K.W.T. & Hirsch, P.R. 2014. Measuring the soil-microbial interface: Extraction of extracellular polymeric substances (EPS) from soil biofilms. *Soil Biology & Biochemistry*, **72**, 163-171.
- Rycroft, D.W. & Amer, M.H. 1995. *Prospects for the drainage of clay soils*. Food & Agriculture Org., Rome.
- Sakairi, N., Kobayashi, M. & Adachi, Y. 2005. Effects of salt concentration on the yield stress of sodium montmorillonite suspension. *Journal of Colloid and Interface Science*, **283**, 245-250.
- Santamarina, J.C. 2003. Soil behavior at the microscale: particle forces. *Geotechnical Specific Publications*, 25-56.
- Schaumann, G.E. 2005. Matrix relaxation and change of water state during hydration of peat. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **265**, 163-170.

- Schaumann, G.E. & Bertmer, M. 2014. Soil-Water Interactions. In: *NMR Spectroscopy: A Versatile Tool for Environmental Research* (eds. Simpson, M.J. & Simpson, A.J.), 291-303. John Wiley & Sons, Ltd., Chichester.
- Schaumann, G.E., Hobley, E., Hurraß, J. & Rotard, W. 2005. H-NMR Relaxometry to monitor wetting and swelling kinetics in high organic matter soils. *Plant and Soil*, **275**, 1-20.
- Schaumann, G.E., Hurraß, J., Müller, M. & Rotard, W. 2004. Swelling of organic matter in soil and peat samples: insights from proton relaxation, water absorption and PAH extraction. In: *Humic Substances: Nature's Most Versatile Materials* (eds. Ghabbour, E.A. & Davies, G.), pp. 101-117. Taylor and Francis, Inc., New York.
- Schaumann, G.E. & Thiele-Bruhn, S. 2011. Molecular modelling of soil organic matter: Squaring the circle? *Geoderma*, **169**, 55-68.
- Schon, N., Gray, R. & Mackay, A. 2012. Quantification of soil macro pore size and shape using resin impregnation. *New Zealand Journal of Agricultural Research*, **55**, 309-315.
- Shi, F., Zhang, C., Zhang, J., Zhang, X. & Yao, J. 2016. The changing pore size distribution of swelling and shrinking soil revealed by nuclear magnetic resonance relaxometry. *Journal of Soils and Sediments*, **17** (1), 1-9.
- Six, J., Guggenberger, G., Paustian, K., Haumaier, L., Elliott, E.T. & Zech, W. 2001. Sources and composition of soil organic matter fractions between and within soil aggregates. *European Journal of Soil Science*, **52**, 607-618.
- Sonderegger, U. 1985. Interpretationsversuch des Scherverhaltens reiner Tone auf Basis von Texturuntersuchungen. *Eclogae Geologicae Helvetiae*, **78**, 137-149.
- Stoffregen, H., Debschütz, W., Wessolek, G. & Yaramanci, U. 1999. NMR-Messungen an Bodenmaterialien bei unterschiedlichen pF-Stufen. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft*, **91**, 266-269.
- Tembe, S., Lockner, D.A. & Wong, T.F. 2010. Effect of clay content and mineralogy on frictional sliding behavior of simulated gouges: Binary and ternary mixtures of quartz, illite, and montmorillonite. *Journal of Geophysical Research: Solid Earth (1978–2012)*, **115**.
- Theng, B.K.G. 1982. Clay-polymer interactions; summary and perspectives. *Clays and Clay Minerals* **30** (1): 1-10.
- Theng, B.K.G. 2012. *Formation and properties of clay-polymer complexes*. Elsevier Science, New York.
- Todoruk, T.R., Langford, C.H. & Kantzas, A. 2003. Pore-Scale Redistribution of Water during Wetting of Air-Dried Soils As Studied by Low-Field NMR Relaxometry. *Environmental Science and Technology*, **37**, 2707-2713.
- Torrance, J.K. 1999. Physical, chemical and mineralogical influences on the rheology of remoulded low-activity sensitive marine clay. *Applied Clay Science*, **14**, 199-223.

- Van Veen, J. & Kuikman, P. 1990. Soil structural aspects of decomposition of organic matter by micro-organisms. *Biogeochemistry*, **11**, 213-233.
- Vogt, C., Galvosas, P., Klitzsch, N. & Stallmach, F. 2002. Self-diffusion studies of pore fluids in unconsolidated sediments by PFG NMR. *Journal of Applied Geophysics*, **50**, 455-467.
- Vyalov, S.S. 2013. *Rheological fundamentals of soil mechanics*. Elsevier Science, New York.
- Yamashita, T., Flessa, H., John, B., Helfrich, M. & Ludwig, B. 2006. Organic matter in density fractions of water-stable aggregates in silty soils: effect of land use. *Soil Biology and Biochemistry*, **38**, 3222-3234.
- Yazdandoust, F. & Yasrobi, S.S. 2010. Effect of cyclic wetting and drying on swelling behavior of polymer-stabilized expansive clays. *Applied Clay Science*, **50**, 461-468.
- Young, R. 2012. *Soil properties and behaviour*. Elsevier Science, New York.
- Zhang, B., Horn, R. & Hallett, P.D. 2005. Mechanical resilience of degraded soil amended with organic matter. *Soil Science Society of America Journal*, **69**, 864-871.

10 ANNEX

10.1 LIST OF ABBREVIATIONS

$^1\text{H NMR}$	^1H proton nuclear magnetic resonance relaxometry	
D/D_0	normalized self-diffusion coefficient of water	[-]
EPS	extracellular polymeric substances	
ESEM	environmental scanning electron microscopy	
MAOM	mineral-associated organic matter	
PAA	polyacrylic acid	
PAM	polyacryl amide	
PFG	pulsed field gradient	
POM	particulate organic matter	
SOM	soil organic matter	
T_1	longitudinal relaxation time	[s]
T_1/T_2	longitudinal to transverse relaxation time ratio	[-]
T_2	transverse relaxation time	[s]
$T_2\text{-D}$	diffusion-weighted transverse relaxation time	
$T_{2\text{WL}}$	longest relaxation time in the relaxation time distribution	[s]
WSA	water –stable aggregates	[%]
τ_{YP}	shear stress at the yield point	[Pa]

10.2 LIST OF TABLES

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10.3 LIST OF FIGURES

Figure 1: Classification of typical soil mineral particles with a vast scale of formed aggregates and pore types in terms of size and designation (redrawn after Peng *et al.*, 2015 and modified)..... 1

Figure 2: Schematic model for soil structural stability induced by interparticulate hydrogel swelling, clay swelling and various polymer-clay interactions in soil (own figure). 15

10.4 LIST OF ATTACHED FILES ON CD-ROM

- Dissertation thesis (PDF and Word format)
- Published articles (PDF format)
- Supporting information (PDF format)

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Applied ecology

1997 – 2006 **Higher education entrance qualification**
Gymnasium Max-Slevogt, Landau

Employment history:

Since 07.2013 *Scientific assistant*
University Koblenz-Landau, Campus Landau, Institute for
Environmental Sciences, Department of Environmental-
and Soil Chemistry

09.2012 – 06.2013 *Working student*
Ecotox consult Dr. Michael Meller, Ludwigshafen
Department of Regulatory Ecotoxicology

05.2012 – 08.2012 *Internship*
Ecotox consult Dr. Michael Meller, Ludwigshafen
Department of Regulatory Ecotoxicology

08.2011 – 09.2011 *Internship*
AgroScience IfA, Mußbach
Department of Ecochemistry

10.6 PUBLICATIONS

Peer-reviewed articles:

1. Buchmann, Christian; Schaumann, Gabriele Ellen (2018): *The contribution of various organic matter fractions to soil-water interactions and structural stability of an agriculturally cultivated soil*. Journal of Plant Nutrition and Soil Science, online early
2. Meyer, Maximilian; Buchmann, Christian; Schaumann, Gabriele Ellen (2018): *Determination of quantitative pore size distribution of soils with $^1\text{H-NMR}$ Relaxometry*. European Journal of Soil Science, 69 (3): 393-406
3. Brax, Mathilde; Buchmann, Christian; Schaumann, Gabriele Ellen (2018): *Effect of mucilage on water properties in the rhizosphere monitored by $^1\text{H-NMR}$ relaxometry*. Microporous and Mesoporous Materials, 269: 47-50
4. Brax, Mathilde; Buchmann, Christian; Schaumann, Gabriele Ellen (2017): *Biohydrogel induced soil-water interactions: how to untangle the gel effect? A review*. Journal of Plant Nutrition and Soil Science, 180 (2): 121-141
5. Muñoz, Katherine; Buchmann, Christian; Meyer, Maximilian; Schmidt-Heydt, Markus; Steinmetz, Zacharias; Diehl, Dörte; Thiele-Bruhn, Sören; Schaumann, Gabriele Ellen (2017): *Physicochemical and microbial soil quality indicators as affected by the agricultural management system in strawberry cultivation using straw or black polyethylene mulching*. Applied Soil Ecology, 113: 36-44
6. Steinmetz, Zacharias; Wollmann, Claudia; Schaefer, Miriam; Buchmann, Christian; David, Jan; Tröger, Josephine; Muñoz, Katherine; Frör, Oliver; Schaumann, Gabriele Ellen (2016): *Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation?*. Science of the Total Environment, 550: 690-705
7. Liu, Liu; Wilkinson, Jeremy; Koca, Kaan; Buchmann, Christian; Lorke, Andreas (2016): *The role of sediment structure in gas bubble storage and release*. Journal of Geophysical Research: Biogeosciences, 121 (7): 1992-2005.
8. Buchmann, Christian; Schaumann, Gabriele Ellen (2016): *Effect of water entrapment by a hydrogel on the microstructural stability of artificial soils with various clay content*. Plant and Soil, 414 (1-2): 181-198
9. Buchmann, Christian; Felten, Andreas; Peikert, Benjamin; Munoz, Katherine; Bandow, Nicole; Dag, Arnon; Schaumann, Gabriele Ellen (2015): *Development of phytotoxicity and composition of a soil treated with olive mill wastewater (OMW): An incubation study*. Plant and Soil, 386 (1): 99-112
10. Buchmann, Christian; Meyer, Maximilian; Schaumann, Gabriele Ellen (2015): *Characterization of wet aggregate stability of soils by $^1\text{H-NMR}$ relaxometry*. Magnetic Resonance in Chemistry, 53: 694-703
11. Buchmann, Christian; Bentz, Jonas; Schaumann, Gabriele Ellen (2015): *Intrinsic and model polymer hydrogel-induced soil structural stability of a silty sand soil as affected by soil moisture dynamics*. Soil and Tillage Research, 154: 22-33

Non-peer-reviewed articles:

1. Kurtz, Markus; Tamimi, Nisreen; Buchmann, Christian; Steinmetz, Zacharias; Keren, Yonatan; Peikert, Benjamin; Borisover, Mikhail; Diehl, Doerte; Marei, Amer Shoqeir; Hasan, Jawad; Zipori, Isaac; Dag, Arnon; Schaumann, Gabriele Ellen (2016): *Soil based wastewater treatment - Effective utilization of olive mill wastewater*. WaterSolutions (1): 82-86

Oral presentations:

1. Buchmann, Christian; Kamutzki, Silvana; Horvat, Malte; Peth, Stephan; Schaumann, Gabriele Ellen: *How do various organic matter fractions affect soil – water interactions and soil structural stability on different scales?* DBG Jahrestagung, Göttingen, September 2017
2. Buchmann, Christian; Schaumann, Gabriele Ellen: *Hydrogel swelling in soil and its contribution to soil microstructural stability*. Biohydrology, Almeria, September 2016
3. Buchmann, Christian; Bentz, Jonas; Schaumann, Gabriele Ellen: *Structural stability of a silty sand soil as affected by polymer hydrogel and moisture dynamics*. DBG Jahrestagung, München, September 2015
4. Buchmann, Christian; Meyer, Maximilian; Schaumann, Gabriele Ellen: *Characterization of wet aggregate stability of soils by ¹H-NMR relaxometry*. Biogeochemical Interfaces in Soil Symposium, Leipzig, October 2014
5. Buchmann, Christian; Felten, Andreas; Peikert, Benjamin; Munoz, Katherine; Bandow, Nicole; Dag, Arnon; Schaumann, Gabriele Ellen: *Short-term effects of Olive mill wastewater application on degradation of polyphenols, ecotoxicology and carbon isotope ratio of a Mediterranean soil*. Soil Waste Water Workshop, Landau i. d. Pfalz, March 2013

Poster presentations:

1. Buchmann, Christian; Schaumann, Gabriele Ellen: *Effect of water entrapment by a hydrogel on the structural stability of artificial soils*. Magnetic Resonance in Porous Media (MRPM13), Bologna, September 2016
2. Buchmann, Christian; Felten, Andreas; Peikert, Benjamin; Munoz, Katherine; Bandow, Nicole; Dag, Arnon; Schaumann, Gabriele Ellen: *Short-term effects of Olive mill wastewater application on phytotoxicity towards *Lepidium sativum*, microbial soil respiration and extractable total phenolic content*. Soil Waste Water Workshop, Landau i. d. Pfalz, March 2013