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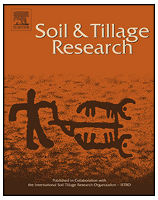

Intrinsic and model polymer hydrogel-induced soil structural stability of a silty sand soil as affected by soil moisture dynamics

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ABSTRACT

Moisture dynamics can favour 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 ^{1}H nuclear magnetic resonance relaxometry (^{1}H 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 ^{1}H 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 ^{1}H 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.

1. Introduction

Soil structure can be defined as the spatial arrangement of soil particles and its resulting pore system (Papadopoulos et al., 2006; Wagner et al., 2007). The stability of soil structure is an important soil property influencing biogeochemical processes in soil (Gerhardt, 1997). Especially soils with low soil organic matter (SOM) content and high sand content are typically poorly structured and unstable as their structural stabilization is particularly a function of water menisci and intrinsic soil properties, e.g. friction between soil particles (Kemper and Rosenau, 1984; Lourenço et al., 2012; Hartge and Horn, 2014). Under natural conditions, environmental processes such as wetting and drying can favour the formation of a stable soil structure due to a reorientation of soil particles and their subsequent cementation by organic substances as they are ad-/absorbed onto mineral surfaces (Le Bissonnais, 2005; Orts et al., 2000; Paluszek, 2011). Although soil is continuously exposed to subsequent wetting and drying events in nature, the resulting formation of a stable soil structure will be rather low if the SOM or clay content is not sufficient to permanently bind the primary soil particles together (Le Bissonnais, 1996; Orts et al., 1999). This low soil structural stability provides problems for both agricultural and natural systems due to an increased potential of surface runoff, soil compaction and crusting events (Al-Darby, 1996; Andry et al., 2009; Fuentes et al., 2013). Thus, continuous efforts have been

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Abbreviations: CEC, cation exchange capacity ($\mathrm{cmol_c\,Kg^{-1}}$); const, constant moisture conditions; cycle, drying/remoistening cycle; γ, deformation (%); G^*, complex shear modulus (Pa); G', storage modulus (Pa); G'', loss modulus (Pa); M_v, viscosity average molar mass; ^{1}H NMR, ^{1}H nuclear magnetic resonance; ρ, surface relaxivity ($\mu\mathrm{m\,s^{-1}}$); PAA, polyacrylic acid; r, pore radius (μm); S, untreated silty sand soil; SOM, soil organic matter; T, 1% PAA-treated silty sand soil; tan δ, loss factor; τ, shear stress (Pa); τ_{max}, maximum shear stress (Pa); T_1, longitudinal relaxation time (s); T_2, transverse relaxation time (s); $\mathrm{WHC_{max}}$, maximum water-holding capacity ($\mathrm{g\,Kg^{-1}}$ dry soil); δ, phase shift angle (°).

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done to increase the soil structural stability in agricultural landscapes, e.g. by appropriate agricultural management, organic matter amendments such as swellable synthetic- or biopolymers with a three-dimensional network structure (named synonymously 'hydrogel') and soil conditioners (Bai et al., 2010; Papadopoulos et al., 2006; Tisdall and Oades, 1982).

The stability of soil structure can be characterized by several approaches, e.g. the ability of the soil matrix to retain soil particle rearrangement after the application of disruptive forces such as mechanic compaction or hydraulic stress (Dıaz-Zorita et al., 2002). Up to now, water immersion tests and wet/dry sieving procedures of isolated soil aggregates (especially after polymer treatment) are the most commonly used test methods, based on the positive relationship between soil structural stability and soil aggregate size (Asghari et al., 2009; Dıaz-Zorita et al., 2002; Hillel, 2003; Liu et al., 2009). Although those test methods deliver reproducible results, the typical investigations of only certain sieve-size fractions cannot assess dynamic processes between organic structures (e.g. incorporated hydrogels), the soil matrix itself and associated changes in its stability (Loch, 1994; Posudin, 2014). Fuentes et al. (2013) and Hallett et al. (2000) showed higher stabilities for soil aggregates than for soil matrices as a result of differences in pore interconnectivity, particle arrangement and surface roughness. Especially water immersion tests of soil aggregates showed that their stabilization by organic substances was partly attributed to an increased hydrophobicity and thus a reduced wettability (Hallett et al., 2000; Zaher and Caron, 2008). Nevertheless, immersion of soil aggregates has the disadvantages of missing the assessment of soil structural dynamics in situ with an additional, superimposing impact of soil structural hydrophobicity at the same time.

In the context of soil structural stabilization by hydrogels, the dynamics between pore water, hydrogel swelling state and soil structural stability are still not yet fully known. Those dynamic processes, especially under changing moisture conditions, are essential to understand soil structural stabilization in the context of structural development and agricultural efficiency. Thus, despite currently applied methods to characterize soil structural stability (e.g. rheology, load frames or aggregate stability tests) and soil water dynamics (e.g. ^{1}H nuclear magnetic resonance relaxometry or water retention curves), none of those methods has been combined until now to assess the implications of soil moisture dynamics on the swelling processes of organic structures and soil structural properties linked with it.

In this study, we aimed to obtain first insights into hydrogel-induced stabilization mechanism of the soil structure in dependency of moisture dynamics (constant water content vs. induced drying/remoistening cycles). For this, we assessed the water distribution and structural stability of an untreated and a 1% polyacrylic acid (PAA) treated silty sand soil by two techniques, ^{1}H NMR relaxometry and rheology. ^{1}H NMR relaxometry enables a differentiation between different water types within a hydrated porous medium (e.g. bound to clay particle surfaces or water within different pore sizes) and in swollen hydrogels (Bird et al., 2005; Jaeger et al., 2010; Todoruk et al., 2003). Furthermore, the relaxation times of water in swollen, organic structures such as hydrogels depend on both its swelling state and polymer concentration (Askin et al., 1993; Paradossi et al., 1997; Penke et al., 1998). This allows assessing information on soil–water–hydrogel dynamics in soil as function of incubation time and moisture dynamics. A differentiation between hydrogel-associated water and soil pore-associated water is possible under the simplified assumption that the relaxation time distributions of the swollen or partly dehydrating PAA hydrogel are different to that of the untreated soil body. In order to evaluate the potential of the PAA hydrogel to swell and release water in the presence of soil solution constituents, we also conducted a dehydration experiment with swollen PAA hydrogel.

From the rheological measurements, we expected to observe a higher soil structural stability after polymer treatment, likewise as function of incubation time and moisture dynamics, respectively. Assuming that the rheological stability of the untreated silty sand soil is mainly due to water menisci and intrinsic soil structural properties, the hydrogel-associated water in the polymer-treated soil should lead to a higher rheological stability and stronger changes in the water distribution determined by ^{1}H NMR relaxometry. Additionally, the rheological stability of the polymer-treated soil should show a dependency on subsequent drying/remoistening as a result of (a) water redistribution in different soil pores over time and (b) hydrogel dehydration (cementation effect) during drying, followed by subsequent water redistribution into the dehydrated PAA-hydrogel structures after remoistening.

2. Theoretical background

2.1. ^{1}H NMR relaxometry in soil

The principle of ^{1}H NMR relaxometry is based on the excitation of hydrogen spins by radio frequency pulses within a static magnetic field, causing a detectable net magnetization (Dunn et al., 2002). The required time to re-reach the equilibrium is the relaxation time (Meiboom and Gill, 1958; Schaumann and Bertmer, 2014). Relaxation times occur as spin–spin (transverse) and spin–lattice (longitudinal) relaxation as a result of interactions between the spin system and the surrounding environment. Since longitudinal relaxation time (T_1) measurements can be very time-consuming, transverse relaxation times (T_2) are most commonly used in soil science application (Dunn et al., 2002; Kleinberg, 1999). Relaxation times of protons in bulk water typically range between 1 and 3 s, but in porous systems such as boreholes, rock cores and soil samples, both T_1 and T_2 depends on the pore size and can therefore be used to estimate and characterize a porous system such as soils (Hinedi et al., 1993; Jaeger et al., 2009; Straley et al., 1997). This is possible since the relaxation time is determined by solid–fluid-interactions at the surfaces of the soil pore walls and can be related to the internal pore surface area S, its pore volume V and the respective surface relativity ρ as described in Eq. (1),

$$\frac{1}{T} = \rho \times \frac{S}{V} \approx \frac{\rho \times 2}{r} \tag{1}$$

which can be directly connected to the pore radius r for cylindrical pores for both T_1 and T_2 (Kenyon, 1992; Kleinberg, 1996). Eq. (1) is valid under the assumption of a fast-diffusion regime with a surface-limited relaxation process and a negligible water diffusion towards the surface (Brownstein and Tarr, 1979; Jaeger et al., 2010).

As pore sizes in heterogeneous porous systems are widely distributed, ^{1}H NMR relaxometry measurements typically result in a distribution of relaxation times. Thus, each amplitude of the relaxation time distribution at a given relaxation time indicates a certain pore size (Schaumann et al., 2005). In the course of water uptake and water movement in soil systems, especially changes in T_2, the relaxation time distributions and the resulting peak positions within the relaxation time distributions allow determining wetting and swelling kinetics in soil (Todoruk et al., 2003; Schaumann et al., 2005), soil pore size distributions (Jaeger et al., 2009) and hydraulic stability estimations of soil aggregates (Buchmann et al., 2014).

2.2. Soil rheology

Rheological methods have been recently applied to assess soil structural stability and soil particle interactions under mechanical