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The relation of structural mobility and water sorption of soil organic matter studied by ^{1}H and ^{13}C solid-state NMR

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ABSTRACT

The impact of low water contents on the molecular mobility of soil organic matter (SOM) and its most frequent components was investigated. Combined ^{1}H, ^{2}H, and ^{13}C solid-state nuclear magnetic resonance (NMR) techniques allow for an advanced insight into mechanisms of water uptake under defined atmospheres and its effect on SOM segment mobility. The major individual organic components of two peats, a gleyic podsol and a number of model substances (cutin, suberin, wood and cellulose) were distinguished with respect to their contribution to the ^{1}H and ^{13}C NMR spectra. Water molecules and mobile polymer constituents of SOM contribute to the mobile fraction in ^{1}H NMR wide line spectra. Poly(methylene), being most probably part of amphiphilic molecules, have been identified as SOM components that are mobilized in the presence of water. Even though being of hydrophobic nature, water acts as a plasticizer on such long chain aliphatic soil components. Differential scanning calorimetry measurements of SOM samples support this insight in terms of a thermal step transition. Based on our findings, comparison of experimental results from different soils with varying water contents and soil composition should consider mobility effects of both, aliphatic moieties as well as polar moieties of SOM.

1. Introduction

Water is an essential actor in biologic and geologic systems. It influences the physical and biogeochemical properties of soil organic matter in many different ways. Ions are dissolved in it and transported along preferential flows and diffusion pathways through the soil material. It is a habitat for microorganisms and an essential actor to form organo-mineral complexes (Totsche et al., 2010). In food science, the concept of water activity is known, giving a measure of water molecules available to biological or physicochemical processes (Barbosa-Cánovas et al., 2007). A minimum threshold of water content is required to allow bacteria, fungi and mold to colonize and grow. This threshold is not only determined by the capability to transport nutrients, but also by its property to be a medium for molecular mobility, ranging from rotational motion of molecule segments and translational and rotational motion of whole molecules to large constituents and organisms.

Adapted to soil properties, water activity is a measure of enabling growth of microbial communities and plant roots. On a molecular level, water is known to act as a plasticizer accelerating molecular motion of polymers at higher water contents (Levine and Slade, 1998; Roos and Karel, 1991). Both magnitudes, the macroscopic biologic system and the microscopic interaction of molecules, share the feature of a certain structural mobility. Water is essential to make soil organic matter and its molecular components accessible to processes such as formation, degradation and transformation under natural conditions. The understanding of the underlying processes of water activity on a molecular level is therefore of high interest.

Solid-state NMR is a powerful tool to study and visualize the mobility of the mostly insoluble soil organic matter substances and their physicochemical properties. A wide range of sophisticated solid-state NMR methods have been applied to unravel composition and molecular dynamics of SOM and its major constituents (Nelson and Baldock, 2005; Mao and Schmidt-Rohr, 2004; Kögel-Knabner and Hatcher, 1989; Simpson et al., 2001). Further, the macromolecular organic matter network in soil is significantly influenced by water molecules changing the soil matrix stability in terms of phase transitions and sorption properties as shown for example with calorimetric methods (Schaumann, 2005; Hurrass and Schaumann, 2007). NMR opens a view on the physicochemical matrix aging of SOM under the influence of water on a molecular level via ^{1}H wide line spectroscopy. Though rarely used for chemical characterization because of the low resolution it is possible to distinguish protons of different mobility in complex systems like SOM, by respective decomposition methods (Jäger et al., 2011).

The effect of thermal treatment on the proton mobility in SOM can be followed time dependently, using a simple high mobility/low mobility decomposition (Schaumann and Bertmer, 2008). Analytic methods have been systematically enhanced, leading to a first insight into long term ^{1}H dynamics after triggered thermal events in different types of soil that contain organic matter (Jäger et al., 2016).

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As an alternative pathway to understand the impact of water on the soil structure we studied the ability of SOM to sorb water and compared it to their ^{1}H NMR spectra. In other studies, out of the strength of water vapour adsorption, mobility states of water molecules have been derived in cellulose (Zografi et al., 1984). Alternatively, the physiological impact of biopolymers can be derived out of adsorption isotherms, as shown for the case of lignin in conifer cuticles (Reina et al., 2001). We claim that a comparable assignment can be adapted to SOM.

The water content has a major influence on the longitudinal relaxation time T_1 of protons and via proton spin relaxation editing (PSRE) the mobility of different carbon species can be distinguished (Smernik, 2006). Smernik (2006) studied two HF-treated Australian soils with different char content and observed that SOM was increasingly mobilized with increasing water content. Based on ^{13}C NMR spectra, the most affected component was a carbonyl-rich one. A three-component model was defined, with the hemicellulose being identified as the one to change its relaxation behavior between low and high water contents.

In this manuscript we followed a different approach focusing on the analysis of ^{1}H wide line NMR spectra of different soils and organic soil components directly with respect to mobile and immobile fractions under varying humidity. Together with their corresponding ^{13}C NMR spectra and in combination with a T_2 filter as well as H_2O/D_2O exchange experiments, we classified different contributors to the wide line spectra. Based on this we introduce a multi component model for the ^{1}H NMR spectra. DSC thermograms of the same samples were included in our analysis.

2. Materials and methods

To study the effects of water contents between 5% and 40% of mass (on dry matter basis) on proton mobility and adsorption properties in SOM, we chose two peats, a sapric histosol (SP) from Neustadt, Lower Saxony, Germany (54.3 wt-% C_{org}) as our major sample of interest and a sapric histosol (RH) from Rhinluch, Brandenburg, Germany (50 wt-% C_{org}). Further, a gleyic podsol (LW) from Fuhrberg, Lower Saxony, Germany (1.88 wt-% C_{org}), representing soils with a dominant sand and clay fraction, is included when analyzing structural effects. The properties of these samples have been described in detail elsewhere (Schaumann, 2005; Jäger et al., 2011; Jäger et al., 2016; Schaumann and LeBoeuf, 2005; Schaumann et al., 2013). We additionally focused our investigations on a couple of substances, chosen to represent selectively specific structural features of soil samples. Microcrystalline cellulose (MCC) and spruce wood (SPR) were included to represent polysaccharides and polysaccharides with lignin, respectively, which occur abundantly in organic soils. To represent the aliphatic H-alkyl carbon fraction we chose (solidified) cutin (CUT) and suberin (SUB). All samples were used in powder form or sieved to grain sizes below 2 mm. The spruce wood was taken directly from a forest site close to Jena, Germany, dried and ground. The cellulose was purchased from Euro OTC (Bönen, Germany). The cutin and suberin we received from Prof. P. E. Kolattukudy, Burnett School of Biomedical Sciences at the University of Central Florida who also characterized these substances (Kolattukudy, 1981).

All samples were stored in plastic desiccators (SICCO company, Grünsfeld, Germany) with atmospheres of 6 different relative humidities for at least six months for equilibration to establish defined water contents in the samples at a constant temperature of 20 °C. The atmospheres were obtained via saturated salt solutions (Greenspan, 1976). We used LiCl (11% rel. H.), $CaCl_2$ (31%), K_2CO_3 (43%), NaBr (58%), NaCl (75%), and $ZnSO_4$ (90%) to cover a large range of humidities. For the extreme cases of humidity (11% and 90%) the actual humidity in the desiccator differed from the theoretical values by up to 10% (LiCl equilibrated at about 21% and $ZnSO_4$ at about 99%), the others only varied in the order of 2–3%.

To determine the resulting water content in the samples, we heated them in an oven at 110 °C for 30 min and compared the sample mass before and after heating. The water content is presented on a dry matter basis. To make sure that only water is evaporated during heating, we checked the volatilization below 120 °C via combined thermal gravimetric and mass spectroscopy (TGMS, Netzsch STA 449 *F*1 Jupiter® and MQS 403 Aëolos®). The results are given in the Supplementary section, Fig. S1.

For ^{1}H wide line NMR measurements we used methods described in detail elsewhere (Jäger et al., 2011). A DEPTH sequence was used to suppress the probe background in the spectra (Bendall and Gordon, 1983). For easy sample management an MAS NMR probe was used to allow for fast sample change and reproducible position within the magnet. Samples were placed in 4 mm zirconia rotors and slightly compressed by hand. The rotors were then closed using either a temperature resistant TORLON cap for thermal treatment and subsequent ^{1}H static measurements or a Kel-F cap for ^{13}C CPMAS measurements.

All ^{1}H, ^{2}H and ^{13}C measurements were performed using an AVANCE 400 spectrometer (Bruker, Karlsruhe, Germany) at a field of 9.39 T (resonance frequencies 400.15 MHz for ^{1}H, 61.42 MHz for ^{2}H, and 100.62 MHz for ^{13}C, respectively). For the ^{1}H measurements the excitation pulse length was 2.7 μs and the recycle delay was 0.25 s, which is more than five times the longitudinal relaxation time T_1. To obtain a good signal to noise ratio and still being quick in measuring, 256 scans were performed, so a single experiment took about 1 min. The same parameters were chosen for all samples. We used a decomposition scheme, fitting a Lorentzian curve representing the mobile protons and a Gaussian curve representing the less mobile protons to the wide line spectra by using the dmfit program (Massiot et al., 2002). The 90°-pulse length for the ^{2}H NMR measurements was 6.5 μs. For the spectra we acquired 64 scans with a recycle delay of 0.25 s. The ^{13}C NMR measurements were performed via cross polarization (CP, Hartmann and Hahn, 1962) with a recycle delay of 2 s and a contact time for magnetization transfer of 2 ms. The cross polarization experiment with T_2-filter was performed with a delay of 20 μs between ^{1}H 90° and contact pulse and a contact time of 2 ms. The number of scans was adjusted to the amount of sample and until sufficient quality of the spectrum was obtained, which is usually taking at least 4 h. The MAS frequency was 10 kHz for all ^{13}C measurements.

For the H_2O/D_2O exchange experiments, D_2O of 99.9% purity (MERCK, Darmstadt, Germany) was used. The samples were dried as described above. The mass equivalent of the evaporated water was then replaced by deuterated water. Still the ratio of SOM and water may not be exactly as before and may differ by up to 1%. As a very small portion of water might withstand the drying, the exchange procedure was repeated a further two times. The SP showed strong water repellency after drying, so it was necessary to stir the sample for about 1 min intensely after the D_2O had been added.

Differential scanning calorimetry (DSC) experiments were performed in order to quantify thermally induced transitions (Schaumann, 2005; Schaumann and LeBoeuf, 2005) with a DSC Q1000 (TA Instruments, Eschborn, Germany) using a refrigerated cooling system (RCS) and nitrogen as purge gas. 1–3 mg of sample were placed into aluminium pans, which were hermetically sealed. Three to seven replicates per sample were measured depending on the thermogram quality. The temperature program involved abrupt cooling to -50 °C, heating at 10 K min^{-1} from -50 °C to 110 °C, followed by a second abrupt cooling and a second heating cycle. The baseline was corrected with TZero technology® by TA Instruments. Data were analyzed using Universal Analysis 4.1 (TA Instruments). DSC thermograms were analyzed for step transitions and for their re-occurrence in the second heating run. Transitions occurring only in the first heating have been subject to previous studies (Schaumann and LeBoeuf, 2005; Kucerik et al., 2014). A step transition temperature T^* is determined by the inflection point, which was indicated by application of three tangent lines. It can be interpreted as the temperature at which the supramolecular structure of soil organic matter stabilized by hydrogen bonds collapses. Therefore, T^* can be interpreted as a parameter for the rigidity of the soil