



Influence of organic chemicals on aliphatic crystallites analyzed in whole soils



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ABSTRACT

Crystalline aliphatic moieties in soil organic matter (SOM) have been under intensive investigation, but it is still unknown how they interact with organic chemicals in the unfractionated SOM. Our objective was to understand the changes in properties of soil aliphatic crystallites when being in contact with organic chemicals. For this, we treated an organic (sapric histosol) and a mineral soil (gleyic podzol) with phenol and naphthalene dissolved in different solvents. The crystallites were characterized in the unfractionated soil by their melting temperatures determined by differential scanning calorimetry (DSC) and by ¹³C CPMAS NMR spectra from the *trans* (33.0 ppm) and *gauche* (30.0 ppm) signals.

DSC identified two distinct types of crystalline domains differing in melting temperatures. Their reaction on solvent treatment and spiking allowed for the first time new insights into the nature of these domains in the unfractionated soil samples. Melting temperature and relative crystallinity were generally reduced by the presence of organic chemicals and solvent treatment, but in different way for each domain type. Thus, the domain types differ from each other in chemical nature. The domains melting at 68–75 °C (sapric histosol) responded similar to biopolymer residues and may originate from higher plants, while those melting at 82–93 °C (sapric histosol) and at 76–80 °C (gleyic podzol) responded similarly to lipids and are speculated to be of microbiological origin.

These findings open new perspectives for the mechanistic analysis of sorption processes in soil. Aliphatic crystalline domains may have been underestimated with respect to their qualitative relevance for sorption processes in soil.

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1. Introduction

Although our knowledge on interactions between SOM and organic molecules has significantly improved with respect to amorphous domains (e.g., LeBoeuf and Weber, 2000), the interactions of organic molecules with aliphatic crystallites (e.g., Hu et al., 2000) still require further attention. Aliphatic crystallites may originate from semi-crystalline residues of plant biopolymers like cutan, suberan or suberin (e.g., Turner et al., 2013) or from extractable lipids (waxes) of higher plants containing linear alkanes, fatty acids, and fatty alcohols (Chilom and Rice, 2005; Grasset et al., 2009). In addition, lipids of microbial origin containing even and odd numbered C₁₅–C₃₂ linear alkanes or fatty acids (Grasset et al., 2009) contribute to the aliphatic pools, and due

to their long chains they could occur presumably both in amorphous and crystalline forms.

Generally, the crystalline aliphatic domains are assumed to be less penetrable for organic molecules than amorphous domains (Hu et al., 2000) and investigations on synthetic semicrystalline polymers suggest that sorption and diffusion of organic molecules occur exclusively in the amorphous region (Harland and Peppas, 1989; Lützow et al., 1999). However, the non-linear sorption of some polycyclic aromatic hydrocarbons to cutan and suberan suggest their involvement in sorption of hydrophobic compounds (Deshmukh and Ashish, 2003; Hatcher and Deshmukh, 2006; Sachleben et al., 2004). The extent to which crystalline aliphatic fractions in SOM contribute to the sorption of organic chemicals is unknown. To our best knowledge, the experimental evidence of interactions of organic chemicals with aliphatic crystallites in unfractionated SOM is still missing. This issue is most probably due methodical challenges which can, however, be overcome by further exploitation of ¹³C NMR spectroscopy and differential scanning calorimetry (DSC).

¹³C CPMAS NMR spectra of humic substances often show two aliphatic carbon signals, representing chains in *trans* (33 ppm) and *gauche*

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(30 ppm) conformations, the former being attributed to crystalline domains (Hu et al., 2000; Mao et al., 2002). The ratio of intensities of these peaks suggested a content of 0.05–3% of aliphatic crystallites (Hu et al., 2000; Mao et al., 2002) in these materials. The decrease of the *all-trans* signal upon heating and its reappearance upon cooling indicated melting and recrystallization between 60 and 80 °C similar to crystallites in polyethylene (Hu et al., 2000). The melting temperature suggests ~3 nm large crystallites comprising 25–30 $-\text{CH}_2-$ units from the Gibbs-Thomson relationships (Hu et al., 2000).

Differential scanning calorimetry (DSC) can extend this knowledge by the melting temperature and the melting enthalpy of the crystallites. Crystallites in humic substances are reported to melt between 58 °C and 78 °C (Chilom and Rice, 2005). For some peats, DSC records of isolated solvent extracts showed two meltings, suggesting two families of aliphatic components (Chilom and Rice, 2005). The melting enthalpy suggests contents of 3.3% for leonardite (Chilom and Rice, 2005) and 2.8–7.6% for a sapric histosol (Kucerik et al., 2014). The melting point of aliphatic crystallites can be affected by the presence of diluents (Smith and Pennings, 1976; Smith et al., 1977), surface interactions with organic compounds (Dorset et al., 1989), crystal purity (DeAngelis and Papariello, 1968; Ke, 1961; Plato and Glasgow, 1969), polymorphism (David et al., 2011), or by changes in crystallite size (Jiang et al., 2003). Therefore, the reaction of the melting point on the treatment with solvents and chemicals of varying polarity will give direct information on the degree and type of interaction between these molecules and the crystallites. Despite this promising potential, this valuable parameter has not yet been investigated in the context with sorption processes.

Following this idea, the aim of our work was to understand the effect of organic molecules on the properties of crystalline aliphatic domains, using the example of naphthalene, phenol and a set of solvents differing in polarity. Naphthalene is an apolar aromatic compound able to undergo van der Waals interactions. Phenol can additionally undergo H-donor and H-acceptor interactions. Crystallinity and melting temperature were assessed using DSC and ^{13}C CPMAS NMR spectroscopy. We hypothesized that, phenol and naphthalene do not penetrate into crystalline domains, similarly to synthetic polymers. If this hypothesis holds true, no changes will be observed by ^{13}C CPMAS NMR (relative crystallinity) and DSC (melting temperature). If this hypothesis does not hold true, i.e., if organic molecules do penetrate into crystalline aliphatic domains, this will reduce their crystallinity, thus resulting in reduced melting temperatures and a reduced crystalline signal in the ^{13}C CPMAS NMR spectrum.

2. Materials and methods

2.1. Materials

A sapric histosol (SH) from Totes Moor (Fuhrberg, Germany) and a gleyic podzol was obtained from “Fuhrberger Feld”, Lakwiese (GP), (Fuhrberg, Lower Saxony, Germany), which are described in detail elsewhere (Jäger et al., 2011; Schaumann et al., 2013), have been used. The sapric histosol consists of $93.2 \pm 0.2\%$ of organic matter and has an organic carbon content of 52%, a cation exchange capacity of $123 \text{ mmol}_c \text{ kg}^{-1}$ and a pH (0.01 M CaCl_2) of 2.7 (Schaumann et al., 2013). The content of paramagnetic elements in sapric histosol is as follows: iron $16.9 \pm 0.1 \text{ mmol}_c \text{ kg}^{-1}$, manganese $21.6 \pm 0.3 \text{ mmol}_c \text{ kg}^{-1}$. The gleyic podzol sample has an organic carbon content of 1.3%, a cation exchange capacity of $36 \text{ mmol}_c \text{ kg}^{-1}$ and a pH (CaCl_2 0.01 M) of 5.1 (Schaumann et al., 2013).

The solvents (methanol, acetone, hexane) used for treatment of soil samples, were of GC purity and purchased from Merck (Darmstadt, Germany). Phenol and naphthalene were of GC grade ($\geq 99.5\%$; Sigma-Aldrich (Saint Louis, Missouri, USA)). In selected experiments, where the mobility of the sorbed chemical was of interest, ^2H -labeled compounds, phenol-3,5- d_2 and naphthalene- d_8 , were used. The phenol-3,5- d_2 (containing 98.8% of D atoms) and naphthalene- d_8 (containing 99% of D

atoms) were purchased from Chiron (Trondheim, Norway) and Sigma-Aldrich (Saint Louis, Missouri, USA), respectively.

2.2. Spiking of soils with chemicals

The purpose of the spiking was to prepare a sample in which the organic matter can be characterized using ^{13}C CPMAS NMR and DSC, and the mobility of ^2H -labeled chemicals can be assessed using ^2H NMR. In order to obtain the required sensitivity towards the ^2H signal of the incorporated chemical, it was added in relatively high amount (5 wt.%). $0.100 \pm 0.001 \text{ g}$ of either phenol or naphthalene were dissolved in $2.00 \pm 0.01 \text{ g}$ of one of the following solvents: water, methanol, acetone or hexane. Due to the low solubility of naphthalene in water, spiking of naphthalene via water was not performed. In addition, the soils were treated also using pure solvents.

$2.1 \pm 0.01 \text{ g}$ of each solution were carefully mixed with $1.9 \pm 0.01 \text{ g}$ soil in order to assure contact of the solution with the complete soil volume. During the following 24 h, the solvent slowly evaporated. As an additional control, untreated soils were used. All samples were equilibrated in separate desiccators at 76% relative humidity and 19 °C for 30 days. Before sampling, each sample was gently homogenized using a spatula.

The amounts of residual solvents and spiked chemical were determined using headspace gas chromatography coupled with a mass spectrometer (HS-GC-MS). The water content in samples treated using water was determined gravimetrically. Exact amounts of analyzed chemicals normalized to the SOM content, as well as detailed information about both analyses are given in the supplementary material (SM) section 1.

2.3. Differential scanning calorimetry (DSC)

Each soil sample was measured in three replicates. 3–6 mg of sapric histosol or 7–9 mg of gleyic podzol sample were weighed into a Tzero pan (TA Instruments, New Delaware) and hermetically sealed. The following temperature protocol was applied: the pan was placed into the DSC cell at 20 °C, cooled at 10 °C/min to -50 °C and then heated to 110 °C (Hurrass and Schaumann, 2005). The upper temperature limit did not reach the degradation temperature of soil samples measured (Kucerik et al., 2014). Further details about DSC setup and calibration are described in the SM section 2.

The DSC record of gleyic podzol shows an endothermic peak on the heat flow curve, which represents a melting event (Fig. 1a). The melting temperature was extracted as a minimum in the second derivative. The DSC record of sapric histosol (Fig. 1b) shows three thermal events. As discussed in detail elsewhere (Kucerik et al., 2014), the record shows a disruption of water molecule bridges (WaMB) at 50 °C and two endothermic meltings of aliphatic crystallites, occurring between 65 and 85 °C (referred to as “melting A”) and in the range 85–100 °C (referred to as “melting B”), respectively. To separate melting from WaMB disruption, the second derivative of the DSC record was used (Fig. 1a, b), in which the melting temperature corresponds to the peak minimum. The evaluation method and identification of individual thermal events in sapric histosol is further discussed in the SM section 3. The data are reported as a mean of three replicate measurements. The degree of uncertainty was determined from the standard error and used as value for the uncertainty.

2.4. Solid-state NMR

^{13}C NMR measurements were performed according to the procedure described in detail in the SM section 4. The sapric histosol consists primarily of organic matter. Gleyic podzol is a sandy soil with low content of SOM and low CEC. In both soils, the content of paramagnetic elements (see chapter 2.1) is low enough to be assumed to have negligible impact on the NMR linewidth. More important, the amount of paramagnetic

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