# Soil organic matter aging processes and their contribution to the sequestration of organic chemicals in soil

by

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# Declaration

I hereby declare that I autonomously conducted the work shown in this PhD thesis entitled: "Soil organic matter aging processes and their contribution to the sequestration of organic chemicals in soil". All used assistances and involved contributors are clearly declared.

This thesis has never been published elsewhere for an exam, as thesis or for evaluation in a similar context; to any department of this university or any scientific institution.

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The following parts of this thesis are published:

**Chapter 2:** All authors were involved in designing the experiments. The DSC measurements were performed by the first author. The NMR measurements were conducted by the second and fourth author. All authors contributed to writing the article. The contribution of the first author to the article was approximately 60 %.

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**Chapter 3:** The first, second and fourth author were involved in designing the experiments. The included experiments were performed by the first author. All authors contributed to writing of the article. The statistical analysis was performed by the third author. The contribution of the first author to the article was approximately 65 %.

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**Chapter 4:** The experiments were designed by the first and the sixth author. The experiments and the data analysis were conducted by the first author. To the experimental data analysis significantly contributed the first, second and sixth author. The computer modeling was performed by the third, fourth and fifth author. The contribution of the first author to the article is approximately 60 %.

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**To our families, friends and colleagues**

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# Abstract

Soil organic matter (SOM) is a key component responsible for sequestration of organic molecules in soil and regulation of their mobility in the environment. The basic structure of SOM is a supramolecular assembly responding dynamically to the environmental factors and the presence of interacting molecules. Despite of the advances in the understanding of sorption processes, the relation between sorbate molecules, SOM supramolecular structure and its dynamics is limited. An example of a dynamic nature of SOM is a physicochemical matrix aging that is responsible for SOM structural arrangement. The underlying process of the physicochemical aging is the formation of water molecule bridges (WaMB) between functional groups of molecular segments. Since WaMB influence the stiffness of SOM structure, it was hypothesized that formation of WaMB contributes to the sequestration of organic molecules. However, this hypothesis has not been tested experimentally until now. Furthermore, the knowledge about the influence of organic molecules on WAMB is based solely on computer modeling studies. In addition, the influence of organic molecules on some physical phases forming SOM is not well understood. Especially, the interactions between organic molecules and crystalline phases represented by aliphatic crystallites, are only presumed. Thus, the investigation of those interactions in unfractioned SOM is of high importance.

In order to evaluate the involvement of WaMB in the sequestration of organic molecules and to increase our understanding about interactions of organic chemicals with WaMB or aliphatic crystallites, the following hypotheses were tested experimentally. 1) Similarly to crystalline phases in synthetic polymers, aliphatic crystallites, as a part of SOM, cannot be penetrated by organic molecules. 2) The stability of WaMB is determined by the ability of surrounding molecules to interact with water forming WaMB. 3) WaMB prevent organic molecules to leave the SOM matrix and contribute thus to their immobilization. In order to test the hypotheses 1 and 2, a set of experiments including treatment of soils with chosen chemicals was prepared. Interaction abilities of these chemicals were characterized using interaction parameters from the Linear Solvation Energy Relationship theory. WaMB characteristics were monitored using Differential Scanning Calorimetry (DSC) allowing to measure the WaMB thermal stability and the rigidity of SOM matrix; which in turn was determined by the heat capacity change. In addition, DSC and $^{13}$C NMR spectroscopy assessed thermal properties and the structure of aliphatic crystallites. The spiking of samples with a model compound, phenol, and measurements of its desorption allowed to link parameters of the desorption kinetics with WaMB characteristics.

The investigation showed that the WaMB stability is significantly reduced by the presence of molecules with H-donor/acceptor interaction abilities. The matrix rigidity associated with WaMB was mainly influenced by the McGowan's volume of surrounding molecules, suggesting the importance of dispersion forces. The desorption kinetics of phenol followed a first order model with two time constants. Both of them showed a relation with WaMB stability, which supports the hypothesis that WaMB contribute to the physical immobilization of organic molecules. The experiments targeted to the crystallites revealed their structural change from the ordered to the disordered state, when in contact with organic chemicals. This manifested in their melting point depression and the decrease of overall crystallinity. Described structural changes were caused by molecules interacting with specific as well as non-specific forces, which suggests that aliphatic crystallites can be penetrated and modified by molecules with a broad range of interaction abilities.

This work shows that chosen organic molecules interact with constituents of SOM as exemplified on WaMB and aliphatic crystallites, and cause measurable changes of their structure and properties. These findings show that the relevance of aliphatic crystallites for sorption in soil may have been underestimated. The results support the hypothesis that physicochemical matrix aging significantly contributes to the immobilization of organic chemicals in SOM.

# Zusammenfassung

Die Organische Bodensubstanz (OBS) nimmt eine Schlüsselrolle in der Sequestrierung organischer Moleküle und damit in der Regulierung ihrer Mobilität in Böden ein. Sie besteht aus Molekülen, die durch supramolekulare Wechselwirkungen strukturiert sind und dynamisch auf Umweltfaktoren und andere Moleküle reagieren können. Der Einfluss von Sorbateigenschaften und supramolekularer Struktur der OBS und deren Dynamik auf Sorptionsprozesse an der OBS ist bisher nur begrenzt verstanden. Ein Beispiel für das dynamische Verhalten der OBS ist deren physikochemische Alterung, die zu Umstrukturierungen in der OBS-Matrix führt. Dieser liegt die Bildung von Wassermolekülbrücken (WaMB) zwischen funktionellen Gruppen einzelner Molekülsegmente zugrunde. Da die WaMB die Struktur der OBS und ihre Stabilität wesentlich beeinflussen, wird davon ausgegangen, dass diese zur Sequestrierung von organischen Molekülen in der OBS beitragen. Diese Hypothese wurde jedoch noch nicht experimentell überprüft. Bisheriges Wissen darüber, wie organische Moleküle die Eigenschaften von WaMB beeinflussen, basiert weitestgehend auf Computermodellierungen. Da unbekannt ist, wie Moleküle, die in die OBS eindringen, deren physikalische Phasen beeinflussen, bedürfen insbesondere die vermuteten Wechselwirkungen zwischen organischen Molekülen und aliphatischen kristallinen Phasen unbedingt einer experimentellen Überprüfung.

Dazu wurden in dieser Arbeit die folgenden Hypothesen experimentell getestet. 1) Analog zu kristallinen Phasen in synthetischen Polymeren können aliphatische Kristallite in der OBS nicht von organischen Molekülen durchdrungen werden. 2) Die Stabilität von WaMB wird durch die Fähigkeit, der sie umgebenden Moleküle mit Wassermolekülen zu interagieren, bestimmt. 3) WaMB können verhindern, dass organische Moleküle die OBS-Matrix verlassen und tragen dadurch zu ihrer physikalischen Immobilisierung bei. Um die Hypothesen 1 und 2 zu überprüfen, wurden Böden mit ausgewählten Chemikalien behandelt, deren Wechselwirkungspotenzial mit Parametern der Theorie der Linearen Solvatationsenergiebeziehung charakterisiert wurde. Die Eigenschaften der WaMB, wie thermische Stabilität und Mobilität der verknüpften OBS-Molekülsegmente, wurden mit der Dynamischen Differenzkalorimetrie (DDK) charakterisiert. Struktur und thermische Eigenschaften von aliphatischen Kristalliten wurden mithilfe von 13C-NMR-Spektroskopie und DDK untersucht. Die Dotierung von Bodenproben mit dem Modellschadstoff Phenol und Messungen zur Phenoldesorption ermöglichten es, die Parameter der Desorptionskinetik mit WaMB-Eigenschaften zu verknüpfen.

Die Ergebnisse zeigen, dass die WaMB-Stabilität wesentlich durch Moleküle mit H-Donor- und -Akzeptoreigenschaften gesenkt wird. Die mit den WaMB einhergehende Starrheit der OBS-Matrix wurde hauptsächlich durch das McGowan-Volumen der interagierenden Moleküle beeinflusst, was auf einen großen Einfluss der Dispersionskräfte hindeutet. Die Desorption von Phenol folgte einer Kinetik erster Ordnung mit zwei Zeitkonstanten, die beide mit der WaMB-Stabilität korrelierten, was die Hypothese stützt, dass WaMB zur physikalischen Immobilisierung von Phenol beiträgt. Die aliphatischen Kristalliten unterlagen nach Kontakt mit ausgewählten Chemikalien strukturellen Änderungen, die zu einem amorpheren Zustand und zu einer Senkung des Schmelzpunkts und einer signifikanten Abnahme der Kristallinität in der OBS führten. Diese strukturellen Änderungen konnten sowohl von Molekülen mit spezifischen, als auch von solchen mit unspezifischen Wechselwirkungen verursacht werden. Dies zeigt, dass Moleküle mit einem breiten Spektrum an Wechselwirkungspotenzialen in aliphatische Kristallite eindringen und deren Struktur verändern können.

Am Beispiel von WaMB und aliphatischen Kristalliten wurde aus dieser Arbeit ersichtlich, dass organische Moleküle mit Bestandteilen der OBS interagieren und messbare Änderungen in deren Struktur und Eigenschaften verursachen können. Neben der Relevanz von aliphatischen Kristalliten für

Sorptionsprozesse im Boden wurde gezeigt, dass die physikochemische Matrixalterung signifikant zur Immobilisierung von Schadstoffen in der OBS beiträgt.

# List of abbreviations

$A_{FAST}$: relative amount of phenol in the fast fraction
$A_{SLOW}$: relative amount of phenol in the slow fraction
$^{13}C$ CPMAS NMR: carbon-13 cross-polarization magic angle spinning nuclear magnetic resonance
C*: 50% of the heat capacity change during WaMB transition
COSMO: Conductor like Screening Model
$C_P$: heat capacity (at isobaric conditions)
$\Delta C_P$: change of heat capacity (at isobaric conditions)
DFT: density functional theory
DSC: differential scanning calorimetry
$E_{rel}$: relative stability energy
FID: flame ionization detector
GC-MS: gas chromatography mass spectrometry
$G_{sol}$: solvent energy
$G_{sol\_rel}$: solvent energy with respect to geometry in the gas phase
$^{1}H$ NMR: proton nuclear magnetic resonance
$^{2}H$ NMR: deuterium nuclear magnetic resonance
HS-GC-MS: headspace gas chromatography coupled with mass spectrometry
LSER: Linear solvation energy relationship
MDSC: modulated differential scanning calorimetry
Ph: phenol
RH: relative humidity
RTD: resistance temperature detector
SOM: soil organic matter
T*: temperature of water molecule bridges transition
Tg: temperature of glass transition
WaMB: water molecule bridges

# Chapter 1

## Introduction and Objectives

# 1. Introduction and objectives

## 1.1 Soil and its importance

Representing an upper layer of the earth's crust, soil is possessing a thickness of a few centimeters up to several tens of meters (Blume et al., 2010; Miller, 1953). Soil can be seen as an interface between lithosphere, hydrosphere, atmosphere and biosphere (Blume et al., 2010). As a consequence of mixing and soil forming processes, soil consists of minerals, organic matter, liquids, gases and organisms (Blume et al., 2010). The solid phase forms approximately 50% of soil’s volume and the remaining part is formed by pores filled with gases and liquids (Foth, 1991). Soil is a result of soil formation, pedogenesis, that includes a plethora of physical, chemical, biological and anthropogenic processes, which are in addition functions of the climate, relief, activity of organisms, parent materials and time (Blume et al., 2010).

Soil is the most important natural resource on the planet Earth (Young and Crawford, 2004), providing a number of ecosystem services, which can be classified as provisioning, regulating, cultural and supporting services (Adhikari and Hartemink, 2016). The provisioning services represent physical products supplied by the ecosystem such as food, fodder, wood and freshwater (Smith et al., 2015). The regulating services represent the benefits obtained from the regulation of ecosystem processes (Smith et al., 2015). Regulating services include regulations of water flow, soil erosion, atmospheric composition, waste decomposition and pollutant immobilization (Celentano et al., 2017). The cultural services provide non-material benefits, such as providing environment for science, education and tourism. The supporting services are involved in maintaining all other services. They include for instance soil formation, nutrient and water cycling (Baveye et al., 2016; Schmidt et al., 2011). The presented overview of ecosystem services clearly shows the importance of soil for the nature functioning as well as its immense contribution to human well-being.

## 1.2 Soil organic matter

SOM consists of organic compounds originating from diverse sources such as plant and animal tissues, manure, microorganisms and their products (Lehmann and Kleber, 2015; Schaumann, 2006a; Wershaw, 2004). Due to the different ages and stabilities, the compounds occur in various stages of biotic and abiotic decomposition (Foth, 1991; Lehmann and Kleber, 2015; Schaumann, 2006a, 2006b; Simpson and Simpson, 2012). From the chemical point of view, SOM is formed mainly from molecules derived from lignins, proteins, lipids, waxes, sterols, pectins, polysaccharides, polyesters and plethora of other biopolymers (Foth, 1991; Pascaud et al., 2017; Pignatello, 2012). SOM contains highly oxidized, functionalized fragments as well as micro-domains of preserved plant and animal tissues (Lehmann and Kleber, 2015; Schaumann, 2006a, 2006b). Accordingly, SOM is a highly heterogeneous and polydisperse mixture of compounds interacting via intermolecular forces and forming supramolecular assemblies (Lehmann et al., 2008; Lehmann and Kleber, 2015; Masoom et al., 2016; Piccolo, 2001; Schaumann, 2006a, 2006b; Wershaw, 2004).

Ecosystem services provided by soil, as listed in the chapter 1.1, are closely related to the content and quality of soil organic matter (SOM) (Lal, 2009; Piccolo, 1996), because SOM has a significant influence on the physical, chemical and biological properties of soil (Blume et al., 2010; Senesi and Loffredo, 1999; Senesi and Plaza, 2007). This can be demonstrated by the following examples. Higher quality and content of SOM is known to improve the soil’s structure, water infiltration to the soil and its water holding capacity (Blume et al., 2010). In addition, the content of functional groups in SOM contributes to the soil cation-binding capacity (mostly expressed as CEC) and thus increases soil fertility (Ankenbauer and Loheide, 2017; Beldin et al., 2007; Lal, 2009).

## 1.3 Sorption of organic chemicals in soils

SOM as well as mineral phase surfaces contribute to the sequestration of organic chemicals in soils (Kowalska et al., 1994). Mineral surfaces strongly interact with water molecules and ionic compounds via coulombic forces (Kowalska et al., 1994), which lead to an effective sorption of organic or biological cations (Kowalska et al., 1994; Petruzzelli and Helfferich, 1992). However, the sorption of hydrophobic organic molecules is limited (Chefetz and Xing, 2009; Churchman et al., 2006). As a result, hydrophobic compounds are predominantly sequestered in SOM (e.g., (Chefetz and Xing, 2009)), particularly in air-dried soils (Bronner and Goss, 2011) and in soils, in which the content of SOM forms more than 1 % (Chefetz and Xing, 2009; Chiou et al., 1979; Pignatello, 2012; Reid et al., 2000; Schwarzenbach and Westall, 1981; Xing, 2001).

Sorption processes in SOM are widely recognized to be the dominant factor that controls the mobility of organic molecules in the environment (Pignatello, 2012; Ran et al., 2013; Reid et al., 2000). More specifically, sorption is the main process governing concentration of organic chemicals in soil solution and subsequently impacting their biotic and abiotic degradation processes, their volatilization or their leaching to subsoils and groundwater (Mitchell and Simpson, 2013; Müller et al., 2007; Pignatello, 1989). Sorption processes reflect the extreme heterogeneity of SOM and diverse interaction abilities of sorbate molecules. Organic chemicals can be present in soils in their parent form or in form of their transformation and degradation products, since they can undergo biological, chemical and photochemical degradation (Petruzzelli and Helfferich, 1992). All these compounds can be classified into two groups according to their prevalent type of interactions with SOM (Senesi, 1993). The first group of compounds interacts predominantly via specific forces and have hydrophilic, ionic, ionizable, acidic or basic properties. The second group of compounds interacts mainly via non-specific forces and exhibits hydrophobic, nonionic and mostly non-polar features (Senesi, 1993). Accordingly, sorption mechanisms can be based on many types of interactions such as ion exchange, ion-dipole interactions, charge transfer, hydrogen bonding and van der Waals' forces (Bailey, George W., 1970; Gunther, 1970; Müller et al., 2007). A combination of these intermolecular forces leads to the sorption in complex systems. (Petruzzelli and Helfferich, 1992).

Understanding of the sorption processes underwent significant progress in the recent decades. The following chosen models show the gradual development of the sorption models and the increasing understanding of mutual interactions between SOM and pollutants. One of the first models, the solid-phase dissolution model, operated with linear isotherms, homogeneous binding-site energy distributions and noncompetitive sorption processes (Chiou et al., 1979). However, the increasing evidence for sorption-desorption hysteresis, the observed nonlinear sorption isotherms, the evidence for heterogeneous site energy distribution in SOM and the competitive sorption of sorbates (Pignatello and Xing, 1996) resulted in the development of new models derived from polymer science theory in SOM. The models include I) The Dual Mode Sorption Model (DMSM) (Xing and Pignatello, 1997) that is based on acting dissolution mechanisms in rubbery phases and concurrently acting dissolutions and hole filling mechanisms in glassy phases. II) The Distributed Reactivity Model for sorption (DRM) (e.g., (Weber et al., 1992)) that considers microscopic scale heterogeneity of natural soils as well as sediments and assumes both, near-linear absorption reaction and nonlinear adsorption reactions. After the discovery of a glass transition in humic acids (LeBoeuf and Weber, 1997), this model further developed in III) the Distributed Reactivity Domain Model (DRDM) (Leboeuf and Weber, 1997) that explains sorption behavior as composed in each case by a linear partitioning component and a Langmuir-like nonlinear adsorption component. The DRDM model was further used by (LeBoeuf et al., 2000; Weber et al., 2000), who suggested that the extension of isotherm nonlinearity is related to increasing glass transition temperature (Tg). IV) The Extended Dual-mode Model developed in high-pressure sorption of gasses in polymers (Kamiya et al., 1986), takes into account sorbate caused plasticization of sorbent matrix. This model was later adopted for sorption in soil SOM (Xia and Pignatello, 2001). The Link Solvation Model (LSM) explaining the solvent-assisted sorption of organic compounds in NOM was introduced by Borisover and Grabber (Borisover and Graber, 2002). This model assumes the creation of new sorption sites caused by the solvent penetration into sorbent structure, disruption of sorbent internal polar connections and their solvation (Borisover and Graber, 2002).

The complexity of sorption mechanisms linked with SOM heterogeneity is reflected in the large number of proposed sorption models. However, our understanding of sorption processes is still limited (Ondruch et al., 2017a; Pignatello, 2012; Ran et al., 2013), since most sorption studies correlate sorption parameters with soil properties (Ashour et al., 2015) and the assessment of processes acting on a molecular scale is extremely difficult in heterogeneous SOM matrix (Pignatello, 2012). Furthermore, SOM consists of various physical phases, which influence the sorption and sequestration mechanisms of organic molecules in soil. Therefore, the physical phases are described in the following chapter in detail.

## 1.5 Phases in soil organic matter and their dynamics

### 1.5.1 Overview

In the further text the term “phase” is used. A phase can be broadly defined as a system or region of matter, where relevant intensive properties are uniform (Brown, 2008). In polymer chemistry, distinct phases are considered domains that differ in chemical composition or physical states (Wunderlich, 2005). In this sense, basic constituents of each phase are atoms and molecules (Stanley and Wong, 1972; Wunderlich, 2005). Phases can be classified according to their dimensions into macroscopic phases which are bigger than 1000 nanometers (nm), micro- and nanophases which has less than 1000 nm and several nanometers, respectively (Wunderlich, 2005). In addition, properties of micro- and nanophases are greatly influenced by their surfaces via surface free energies and surface potentials (Wunderlich, 2005). As a result, properties of microscopic phases often significantly differ from the same phase with macroscopic dimensions (Wunderlich, 2005).

A homogeneous region of matter forming a phase can be transformed into another phase via a process called phase transition. As it results from a definition of a phase, during the phase transition relevant properties (e.g., heat capacity, density or degree of internal organization) change. Phase transition often occurs as a result of external conditions such as temperature or pressure. According to the original theory proposed by Paul Ehrenfest in 1933 (Ehrenfest, 1933), phase transitions are distinguished into first- and second-order phase transitions. Accordingly, first-order phase transitions are those, which have discontinuity in the first derivative of Gibbs energy with regard to thermodynamic variables, e.g. pressure and temperature, as shows the equations 1 and 2 (Brown, 2008; Holba, 2012; Hołyst and Poniewierski, 2012; Jaeger, 1998).

$$\text{molar entropy: } -S = \left(\frac{\partial G}{\partial T}\right)_p \neq 0 \tag{1}$$

$$\text{molar volume: } V = \left(\frac{\partial G}{\partial p}\right)_T \neq 0 \tag{2}$$

In contrast, the first derivative of Gibbs energy in case of second-order phase transitions is continuous, but shows discontinuity in its second derivatives, see the equations 3, 4, and 5 (Brown, 2008; Holba 2012; Hołyst and Poniewierski, 2012; Jaeger, 1998).

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = \frac{-c_p}{T} \neq 0 \qquad (3)$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = -V\kappa_T \neq 0 \qquad (4)$$

$$\left(\frac{\partial^2 G}{\partial T \partial p}\right) = V\alpha \neq 0 \qquad (5)$$

$G$ represents the Gibbs free energy, $T$ is temperature, $c_p$ is the heat capacity at constant pressure. $p$, $V$, $\kappa_T$ and $\alpha$ represent pressure, volume, isothermal compressibility and coefficient of thermal expansion, respectively. The definition of both transition types underwent some evolution, although the original Ehrenfest's classification is still used (Jaeger, 1998). New approaches distinguish phase transitions with respect to exchanged latent heat (Hołyst and Poniewierski, 2012; Jaeger, 1998; Tisza, 1961). Accordingly, transitions, where molar entropy as well as molar enthalpy changes, are called first-order transitions. These can be assessed via exchanged latent heat of transition by means of thermoanalytical techniques e.g., DSC (Brown, 2008). In contrast, during the second-order transitions (also generally called phase transitions of higher order), the latent heat of transition does not change. These transitions reveal changes of the heat capacity, the thermal expansion and the compressibility (Brown, 2008).

### 1.5.2 Crystalline phases

Crystalline phase is a homogeneous region of matter with ordered microstructure represented by crystals. Individual crystals consist of an arrangement of particles (atoms, ions, molecules or groups of molecules) into unit cell that via repetition forms a bigger three-dimensional structure of a crystal lattice (Wunderlich, 2005). The driving force for particles to form crystals is energy release and reaching the state with a minimum of potential energy. Crystals are formed via crystallization, during which latent heat of fusion is released (Wunderlich, 2005). Crystalline phases are interconvertable to melted phases via melting that is classified as a first order transitions process. Another basic feature of crystalline phase is its ability to diffract X-rays that is used to study its internal arrangement (Sperling, 2005; Wunderlich, 2005).

Although ideal crystalline phase consists of perfect crystals, which are in thermodynamic equilibrium, real crystalline phases in polymers contain crystals with amorphous defects that points to their non-equilibrium state (Wunderlich, 2005). These regions in semi-crystalline state are also categorized as mesophases. These are defined as phases of intermediate order occurring between liquid phase (mobile melt) and fully ordered crystalline phase (Wunderlich, 2005).

Significant portion of soil organic matter can be formed by crystalline phases (also known as crystalline domains) (Ondruch et al., 2017a). It is hypothesized (e.g., (Deshmukh, 2003; Hu et al., 2000)) that these phases originate from residues of semi-crystalline biopolymers (e.g., cellulose (Statton, 1956), kerogen (Weber et al., 2001), cutan and suberan (Hu et al., 2000)) or microbial activity (Ondruch et al., 2017a; Vissep and Mendel, 1971). Although, crystalline phases in SOM can be generally formed by diverse compounds, this work is focused on crystalline phases formed by aliphatic compounds due to their notable presence in various soils (sandy and peat soils) and lately observed dynamic behavior (Kučerík et al., 2014).

The aliphatic crystallites have been thoroughly described by Hu et al. in humins, humic acids extracted from peat soils and in bulk Pahokee peat (Hu et al., 2000). The authors applied $^{13}$C CPMAS NMR that on the bases of a chemical shift is able to assess chemical composition as well as conformational characteristics in heterogeneous matrixes (e.g., Tonelli and Schilling, 1981). The authors observed a sharp peak at $^{13}$C chemical shift of 32.9 ppm, typical for all-trans $(CH2)_n$ segments, which are much less mobile than the respective gauche conformation showing 30.0 ppm chemical shift. Using wide-angle X-ray diffraction, orthorhombic crystal modification was detected in these samples (Hu et al., 2000). In general, crystalline aliphatics can form different types of crystals. Odd paraffins tend to form an orthorhombic, rectangular layer structure, while the even paraffins up to $C_{24}H_{50}$ are triclinic with oblique layers (Wunderlich, 2005). In addition, the triclinic crystals are characterized by higher heat of fusion than orthorhombic crystals (Wunderlich, 2005). The minimal length of poly(methylene) chains, which allows to span a crystal, is discussed. Hu et al. proposed 25 $CH_2$ units as a minimum necessary to be exceeded for crystal formation (Hu et al., 2000). However, other crystalline forms accommodating even shorter carbon chains are not excluded (Wunderlich, 2005). The limiting factor for crystal formation is probably ambient temperature. The minimal number of $CH_2$ units may be 18, where alkane chains melts around 28 °C (Messerly et al., 1967). A further factor determining the melting temperature is the presence of functional groups in aliphatic chains, which in general, lower melting temperatures (Wunderlich, 2005).

Crystalline phases occurring in SOM are usually not considered in SOM sorption models, since they are compared with crystalline domains in polymers, which are non-penetrable for sorbates and thus excluded for sorption processes (Harland and Peppas, 1989; Lützow et al., 1999). Sorption studies performed on SOM precursors, semicrystalline biopolymers (e.g., cutans, suberans), suggested an influence of crystalline domains on sorption processes, since those domains contain polar sites and possess rigid structure (Deshmukh et al., 2005; Shechter and Chefetz, 2008). In particular, it is suggested that the sorption of polar organic compounds, e.g. exemplified with 1-naphtol, (Shechter et al., 2010), to crystalline domains may cause irreversible sorption and nonlinearity of sorption isotherms (Shechter et al., 2010). The mutual interactions between aliphatic crystallites presented in bulk soil samples and chosen organic molecules (phenol, naphthalene) were investigated in the chapter 2 and are published as following: “Influence of organic chemicals on aliphatic crystallites analyzed in whole soils”.

### 1.5.3 Amorphous phases

All amorphous phases represents a region of matter without long-range structural order (Roudaut et al., 2004; van Krevelen, 1997; Wunderlich, 2005) and include, besides others, liquids (melts), rubbery and glassy phases, which are particularly relevant in polymer and SOM matrixes (Cao et al., 2016; Pignatello, 2012; Wunderlich, 2005). These phases reveal short-time order, but differ in their short- and long-time stiffens (van Krevelen, 1997). For instance, liquid phases do not show long- and short-time stiffness. The rubbery phases differ from liquid phases via their short-time stiffness (van Krevelen, 1997). In contrast, the glass phases show both, short- and long-time stiffness (van Krevelen, 1997).

Furthermore, the amorphous phases differ in the intensity of intermolecular forces acting between their constituent particles (e.g., chains) (Treloar, 1974) that is the reason for differences in the mobility of their constituent particles (Schaumann, 2006b; Wunderlich, 2005). Relatively weak intermolecular forces act between chains in melts and rubbery phases. This allows, apart from vibration, large amplitude motion such as rotational and conformational changes (Treloar, 1974; Wunderlich, 2005). As a result, rubbery phases and melts in SOM or polymers are formed with flexible chains and have viscous, liquid-like properties (Pignatello, 2012).

In general, the forces between units building glassy phases allow only restricted motion (typically greater than 100 s) and with decreasing temperatures, only vibration of atoms and bonds is allowed (Roudaut et al., 2004; Wunderlich, 2005). Hence, the mobility of constituents forming glassy phases is similar to those forming crystalline phases (Schaumann, 2006b). Glassy phases consist of stiff chains forming a hard, brittle structure and reveal high viscosities (typically more than 1012 Pa s) (Hancock and Zografi, 1997; Pignatello, 2012; Roudaut et al., 2004; Sperling, 2005).

The transition between the rubbery and glassy phase is called glass to rubbery transition or simply glass transition. The transition from rubbery to glassy phase occurs when a temperature of matrix decreases below certain point (glass transition temperature – Tg) and crystallization is hindered (Haward, 1997;

Schaumann and LeBoeuf, 2005). This can be caused by the high cooling rate and structural complexity of the matrix, which both restrict crystallization (Haward, 1997; Schaumann and LeBoeuf, 2005). During the glass-rubbery transition, physical properties of the matrix changes dramatically. For instance, entropy, heat capacity and volume increases, rigidity and viscosity show a rapid decrease (Haward, 1997; Roudaut et al., 2004; Struik, 1978; Wunderlich, 2005). Glass-rubbery transition is classified as a second-order transition, however, its fundamentals are subject of a discussion (e.g., Queiroz and Šesták, 2010). The glass transition occurs in pure compounds in relatively narrow range of temperature, but with increasing matrix heterogeneity increases also this temperature range (Roudaut et al., 2004).

Both, glassy and rubbery phases are presented in SOM. The sorption to glassy phases is accompanied by non-Fickian diffusion and is expected to cause sorption non-linearity, slow desorption and sorption/desorption hysteresis (Cao et al., 2016; Pignatello, 2012; Schaumann and LeBoeuf, 2005). In contrast, the sorption to rubbery phases is expected to be relatively fast partitioning-like process with linear sorption behavior (Schaumann and LeBoeuf, 2005).

## 1.6 Aging processes in soil organic matter

### 1.6.1 Physical aging and glass transition

SOM is formed from a large part by amorphous phase that shows dynamic nature (Kučerík et al., 2014; Pignatello, 2012; Schaumann and Bertmer, 2008). In general, amorphous phases in polymers are far from thermodynamic equilibrium at temperatures below their glass transition (Struik, 1978). In this physical state, often compared to super-cooled liquids, the matrix has higher values of thermodynamic properties (e.g., specific volume, enthalpy, entropy) than in the state of internal thermodynamic equilibrium (Struik, 1978). Physical aging is the evolution of the matrix towards the thermodynamic equilibrium, at constant temperature and without the influence of external factors (e.g., stress) (Hutchinson, 1995). Physical aging manifests as a change in macro- and micro-structural properties and differ from other processes such as chemical aging (e.g., photo-oxidation or thermal degradation) or biological aging, which are both mostly of irreversible nature (Hutchinson, 1995; Struik, 1978).

Meta-stable glassy phases manifesting in form of classical glass transition were detected using DSC in biopolymers (e.g., lignin (Laborie et al., 2004; LeBoeuf et al., 2000), cellulose (Szcześniak et al., 2008) starch or DNA (Grunina et al., 2006)), as well as in humic acids (LeBoeuf and Weber, 1997; Young and LeBoeuf, 2000) and various soils such as forest soil (Schaumann and Antelmann, 2000), Rhinluch peat (Schaumann and LeBoeuf, 2005), Pahokee peat and Leonardite (DeLapp and LeBoeuf, 2004). Glass transition in soils showed reversible character and was thus presented in repeated heating and cooling DSC runs. However, in case of whole soils, glass transition was detected between 17 – 37 °C in thermally pretreated soils only, with very low water content (Schaumann and LeBoeuf, 2005). It was speculated that the glass transition observed in soils can be a result of a continuum of glass transitions in a broad temperature range (Schaumann and LeBoeuf, 2005). According to LeBoeuf and Weber, physical aging is at least partly involved in aging of organic molecules in SOM (LeBoeuf and Weber, 1997).

### 1.6.2 Plasticization

Penetration of solutes into glassy phases of various materials weakens non-covalent interactions between individual side-chains that results in an increase of mobility of individual segments (Cao et al., 2016; van Krevelen, 1997). This process is called plasticization and leads to a decrease of the glass transition temperature (Tg) (Cao et al., 2016; Roudaut et al., 2004; Wunderlich, 2005) This can significantly accelerate physical aging processes, when Tg decreases near to the ambient temperature (Roudaut et al., 2004). Further uptake of solutes into the matrix would lead to matrix swelling. The solute plasticizing the polymer is usually good solvent. Matveev et al., described good solvent as the following: “Thermodynamically, a good solvent shields inter- and intra-molecular interactions and can dissolve some macromolecular associations and crystalline regions” (Matveev et al., 2000).

### 1.6.3 Water in SOM matrix and water molecule bridges formation

Water is a known plasticizer for synthetic polymers (e.g., polymethylmethacrylate (Wypych, 2004)), biopolymers (e.g., starch (Hulleman et al., 1998)) and SOM (Jaeger et al., 2015; Schaumann, 2005; Schaumann and LeBoeuf, 2005). The molecules able to plasticize polymers can also have an opposite, an anti-plasticizing effect, when the formation of non-covalent bonds reduces chain mobility (Coyle and Martin, 1996; Schaumann, 2005; Schaumann and LeBoeuf, 2005). In order to cause an anti-plasticizing effect, the molecule has to be compatible with the polymer, has to be polar and to pose two bridging sites (Schaumann, 2005). In addition, the anti-plasticization effect is dependent on temperature and the concentration of the penetrant molecules (Coyle and Martin, 1996). Water molecules are a good example of this dual effect on the host matrix (Coyle and Martin, 1996; Schaumann, 2005). Crosslinking of polymer via hydrogen bonds connecting hydrophilic and charged groups (e.g., $-COOH$, $-COO^-$, $-NH_2$, $=NH$, $-OH$, -O-alkyl), reduces chain mobility (Coyle and Martin, 1996; Hurrass and Schaumann, 2005; Matveev et al., 2000; Schaumann, 2005). In contrast, with increasing water content, the water-based crosslinks are more hydrated, the number of water-water interactions increases and the plasticizing effect of water starts to dominate (Schaumann and LeBoeuf, 2005).

Water molecules contribute significantly to SOM structural organization (Kleber and Johnson, 2010; Masoom et al., 2016; Schaumann and Bertmer, 2008), cause conformational changes of SOM compartments (Coyle and Martin, 1996; Schulten and Violante, 2002) and change position of individual molecules (Schulten and Violante, 2002). Water clusters, or more specifically water molecule bridges – WaMB, connect individual SOM segments and form a supramolecular matrix (Aquino et al., 2011a, 2011b, 2009). Indeed, water is an important component of SOM matrix responsible for its formation and stiffening (Jaeger et al., 2015; Ondruch et al., 2017b; Schaumann and LeBoeuf, 2005). As a result, supramolecular structure of SOM stabilized with water-water interactions is a dynamic system responding flexibly to the changes of environmental conditions, such as temperature, moisture, pH, and presence of extraneous compounds (e.g., solvents or pollutants) (Ondruch et al., 2017a, 2017b, Schaumann et al., 2006a, 2006b; Schulten and Leinweber, 2000). In addition, it was hypothesized that WaMB can significantly contribute to physical immobilization of organic molecules in SOM since WaMB connect individual SOM segments and may prevent organic chemicals to enter or leave specific SOM regions (Aquino et al., 2011a; Jaeger et al., 2015; Ondruch et al., 2017b; Schaumann and Bertmer, 2008).

WaMB stabilize supramolecular structure of SOM, their disruption leads to the increase of molecular mobility of SOM constituents as determined by $^1H$ NMR (Jaeger et al., 2015; Schaumann et al., 2013) and to the increase the heat capacity of the SOM matrix as determined by DSC (Kučerík et al., 2014; Schaumann et al., 2005; Schaumann and LeBoeuf, 2005). The process of WaMB disruption is called WaMB transition and manifests as a step during a heating in measured heat flow or heat capacity curves (Hurrass and Schaumann, 2005). WaMB transition usually occurs in soils with certain water content between 40 and 75 °C in SOM, however, measured in hermetically closed sample pans. The temperature of the culmination of this process, labeled as T*, indicates WaMB thermal stability (Ondruch et al., 2017b). T* is a function of SOM properties, environmental conditions (e.g. temperature and humidity) as well as sample history (Hurrass and Schaumann, 2007; Kučerík et al., 2014; Ondruch et al., 2017b). The change of the heat capacity ($\Delta C$) during the WaMB transition, similarly to classical glass transition, shows the increase of SOM segment mobility during the process of WaMB disruption (Ondruch et al., 2017b). As an extensive investigation of a broad range of different soils reveled, $\Delta C$ reflect content and quality of SOM (Hurrass and Schaumann, 2005). The stability of WaMB, as measured via T*, can be significantly decreased by an increase of relative humidity (Schaumann, 2005; Schaumann and

LeBoeuf, 2005) or by molecules, which are able to interact with water via hydrogen bonds (Ondruch et al., 2017b).

Disruption of WaMB is followed by physicochemical aging leading to a gradual stabilization of SOM matrix and an increase of matrix stiffness (Jaeger et al., 2015). This can be observed by an increase of T*. Continual increase of the transition temperature (T*) revealed physicochemical aging processes that are independent of the classical physical aging that is typically observed in amorphous polymer matrixes (Schaumann, 2006b). In addition, experiments on soil samples, e.g. haplic podzol (G. E. Schaumann et al., 2013) and sapric histosol (Kučerík et al., 2014), showed that physicochemical matrix aging is predominant in SOM matrixes and contribute much more to the SOM rigidity than physical aging (Schaumann, 2006b). Physicochemical aging was proposed to cause an increase of SOM rigidity and subsequently an aging of organic chemicals in SOM matrix (Schaumann, 2006b; Schaumann and Bertmer, 2008).

## 1.7 Sorption processes

Sorption of organic chemicals in SOM in soils and sediments is considered to be the key process governing the mobility, availability and risk of organic chemicals in the environment (Chefetz and Xing, 2009; Pignatello, 2012; Pignatello and Xing, 1996; Ran et al., 2013). From the theoretical point of view, sorption includes two basic processes, adsorption and absorption (Petruzzelli and Helfferich, 1992). Adsorption is the bonding or the attraction of particles (atoms, ions or molecules) via physical forces onto the surface of another substance such as sorbent (Crini and Badot, 2010; Petruzzelli and Helfferich, 1992). In contrast, absorption is defined by Crini and Badot as “the incorporation of a substance in one state into another of a different state” (Crini and Badot, 2010). Typically, a substance in a mobile state is incorporated into a three-dimensional matrix. Since organic chemicals are commonly occurring in a mobile, gas or liquid state and SOM sorption domains are presented in a three-dimensional matrix, the undergoing sorption processes in SOM are ascribed to absorption (Pignatello, 2012). According to the specificity and strength of involved forces, chemisorption and physical sorption are to be distinguished (Malijevsky et al., 2005). The interactions between sorbent and sorbate based on weak van der Waals forces, having adsorption heat 5-50 kJ mol$^{-1}$ is referred to as physical sorption (Malijevsky et al., 2005). In contrast, as a chemisorption are defined very strong interactions, similar to the chemical bonds, having adsorption heat between 50 and 800 kJ mol$^{-1}$ (Malijevsky et al., 2005).

Apart from sorption processes, also processes connected with SOM dynamics (e.g., conformational changes of molecules forming SOM (Schlebaum et al., 1998), entrapment of molecules in SOM micro-pores (Reid et al., 2000)) were suggested to limit the mobility of organic chemicals in soils. Furthermore, it was assumed that environmental conditions can significantly influence the mobility of organic chemicals presented in SOM, because SOM responds dynamically to the changes of environmental conditions, such as changes of temperature, moisture and physicochemical environment (Schaumann, 2006b; Schaumann and Bertmer, 2008). These questions are discussed in detail in chapter 1.9.

Differential Scanning Calorimetry (DSC) was proved to be a versatile tool for characterizing physical phases in SOM, their dynamic response to the change of external conditions or their evolvement at relatively constant conditions linked with physical and physicochemical matrix aging. Therefore, DSC is introduced in the following chapter.

## 1.8 Introduction of techniques used in this study

### 1.8.1 Differential Scanning Calorimetry

As a part of calorimetry techniques, DSC measures the amount of exchanged heat. The quantity of exchanged heat is assessed via measurement of a temperature change in a known system. The key component and the real measurement device in each DSC are the temperature sensors, which are usually represented by thermocouples or resistant thermometers. The measurement principal is based on the Seebeck effect, allowing to determine temperature via measurement of electrical voltage (Brown, 2008; Höhne et al., 2003).

DSC is a versatile method used for material characterization and identification of processes connected with thermal effects (Höhne et al., 2003). DSC is often applied for the analysis of heat quantities (e.g., heat of fusion, heat of reaction and heat capacity) or temperatures (e.g., temperature of crystallization or melting and boiling point). A great advantage of DSC is the possibility to analyze bulk materials without the necessity to perform their fractionation. This is beneficial for analysis of SOM, where fractionation and sample pretreatment would remove the key structural information connected with presented physical phases. DSC is commonly applied to study SOM structure and related thermal transitions, such as melting events (e.g., Chilom and Rice, 2005), glass (e.g., LeBoeuf and Weber, 1997) or WaMB transitions (e.g., Schaumann and LeBoeuf, 2005). Furthermore, DSC was used for identification and quantification of various SOM compartments, such as lipids (e.g., Chilom and Rice, 2005; Kucerik et al., 2014), biopolymers (e.g., Ondruch et al., 2017b) and different types of water in hydrated SOM samples (e.g., McBrierty et al., 1996). Taking together, DSC is a technique often used for characterization of matrixes with macromolecular and supramolecular structure such a SOM, biopolymers and synthetic polymers.

On the bases of technical design and measuring principles, Heat flux DSC and Power Compensation DSC, can be distinguished. The heat flux DSC was used in experimental part of this theses and its principal is further described. Heat flux DSC determines heat flow rate between the sample and the reference, which is represented by an inert material or, more frequently, empty aluminum pan. The differences in heat flow rate are measured as a function of time and temperature (Höhne et al., 2003). The measurement is performed in a chamber allowing gas flow. Purging gas, usually nitrogen, helium or dry air, removes moisture from the measuring chamber and provides defined thermal atmosphere eliminating artificial heat flows (Wunderlich, 2005). During the measurement, the furnace is heated and the heat flows through the aperture (consisting of constantan body, sample holders and sensors) to the sample and reference.

As mentioned above, the temperature of a sample sensor is assessed via potential difference and heat flow rate is calculated subsequently. The heat capacity at isobaric conditions, $C_P$, is obtained according to the Eq. 6,

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t) \qquad (6)$$

where $H$ represents the enthalpy, $T$ the temperature and $t$ the time. The following terms of the equation represent: the heat flow signal $dH/dt$, the heating rate $dT/dt$. and $f(T, t)$ represents a heat flow that is a function of time at an absolute temperature.

To the heat flux DSC belongs also a Turret-type heat flux DSC developed by TA Instruments. This DSC, TA Instruments type Q1000, was used for all thermoanalytical measurements given in this thesis and the technical setup is described in Fig. 1. In the furnace of Turret-Type DSC, the heat flows from the bottom of the furnace, through the walls of two hollow cylinders to the platform, where the sample and reference are placed (Fig. 1).

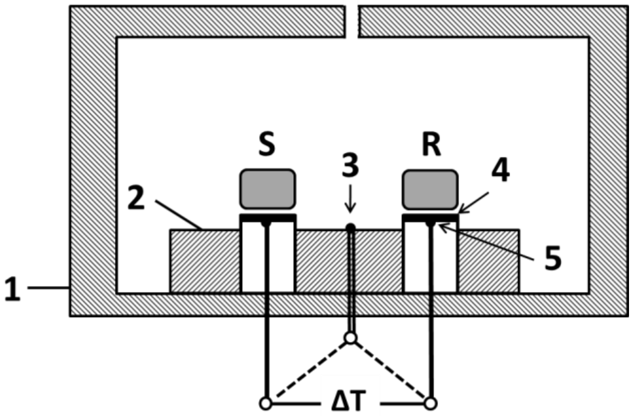

*Fig. 1. Simplified schema of a measuring chamber of heat flux DSC developed by TA Instruments. (1) silver furnace, (2) constantan body, (3) thermocouple consisting of chromel and constantan wire, (4) stage for reference or sample, (5) chromel area thermocouple (S) sample pan, (R) reference pan. ΔT represents temperature difference between both detectors. The figure was adapted from (Höhne et al., 2003).*

### 1.8.2 Solid-state nuclear magnetic resonance spectroscopy

The NMR spectroscopy is a technique based on a resonance of atomic nuclei in an external magnetic field. The specific frequencies at which the nuclei resonate are called chemical shifts and are distinctive for their chemical environment (Simpson and Simpson, 2012). The type of nuclei is thus determined by the chemical shift and their quantity is represented via peak intensity (e.g., Simpson and Simpson, 2012). Since $^{13}$C forms only approximately 1.1 % of the carbon in the environment, the sensitivity of the measurement is improved using proton-carbon cross polarization (CP) that compensate its low abundance. High spectra resolution is assured by the magic angle spinning (MAS) technique that removes the chemical shift anisotropy. $^{13}$C CPMAS NMR spectroscopy is effective technique allowing to assess the carbon distribution in highly heterogeneous samples. For detailed information about the physical and chemical principals of $^{13}$C CPMAS NMR, following literature is recommended (Simpson and Simpson, 2012; Wilson, 2013; Yannoni, 1982).

The $^{13}$C CPMAS NMR spectroscopy is widely used to study distribution of a carbon in SOM (Kögel-Knabner, 1997). This technique provides qualitative information about chemical composition (Simpson and Johnson, 2006), however, it is not fully quantitative, since the amount of carbons without direct contact with hydrogen atoms (e.g. in deprotonated carboxyl groups) are rather underestimated (Simpson et al., 2012). The quantification can be also limited via higher presence of paramagnetic compounds in soil samples, which can modify the signal intensity of carbon atoms in some functional groups. This is significant for soils with C:Fe ratio < 1 (Kögel-Knabner, 1997). However, the $^{13}$C CPMAS NMR spectroscopy is frequently used for semiquantitative purposes, in particular, for direct comparison of two soils with low abundance of paramagnetic elements.

The great advantage of the $^{13}$C CPMAS NMR spectroscopy is to perform in-situ measurements without the need for sample partitioning. This allow to study SOM in its naturals state. NMR is frequently used to analyze chemical composition (e.g., Kögel-Knabner, 1997) as well as physical phases, namely crystalline and amorphous phases, in SOM (Hu et al., 2000) and their biopolymeric precursors (Deshmukh, 2003; Deshmukh et al., 2005). $^{13}$C CPMAS NMR spectroscopy was also applied for identification of sorptive domains for immobilization of organic molecules in SOM (Simpson and Johnson, 2006) and its precursors (Sachleben et al., 2004). The interactions between organic molecules and SOM are often studied using solid-state $^{2}$H NMR and deuterium labeled compounds. This technique is based on the spectral density function, which connects the molecular motion with obtained spin relaxation parameters. The principles of $^2$H NMR can be found elsewhere (e.g., Lee et al., 1999). Resulting $^2$H wideline NMR spectra and their deconvolution for individual lineshapes provide the information about molecular motion.

## 1.9 Research needs and open questions

WaMB connects individual molecular segments of SOM and contributes to the rigidity of SOM (Schaumann, 2006b; Schaumann and Bertmer, 2008). A number of studies have proposed the physical immobilization of organic chemicals in SOM via WaMB formation (e.g., Schaumann, 2006b; Schaumann and Bertmer, 2008). However, this hypothesis has not been tested experimentally until recent time. In addition, the knowledge of how the presence of organic chemicals in SOM influences WaMB and their properties has not been available. These gaps in understanding were probably caused due to the technical and methodological difficulties in assessing processes occurring at a molecular scale in an enormously heterogeneous SOM matrix. The challenge in investigating the interactions between WaMB and molecules forming its direct SOM environment was partly overcome by computer modeling studies, working with simplified SOM models. In particular, the studies based on computer modeling performed by Aquino et al. (e.g., Aquino et al., 2011a) provided the basic knowledge of the relation between physicochemical properties of WaMB environment, characteristics of WaMB and SOM rigidity.

SOM can be formed by various physical phases, such as amorphous phases, including glassy and rubbery phases, and crystalline phases. The influence of organic molecules on structure and properties of physical phases in SOM was investigated with regard to glassy phases, their interactions with sorbate molecules and resulting plasticization of their matrixes (e.g., Cao et al., 2016; Pignatello, 2012). However, there was limited understanding about the influence of organic chemicals on crystalline phases, in particular, aliphatic crystallites. The interactions of aliphatic crystallites with organic molecules were investigated mainly on their precursors such as semi-crystalline biopolymers. Until about 2014, there were contradictory information including inert behavior (Hu et al., 2000), indirect (Deshmukh, 2003) and direct (Sachleben et al., 2004) involvement of aliphatic crystallites in sorption processes. Therefore, this work presents an experimental approach in order to determine the influence of organic chemicals on aliphatic crystallites.

As stated in this chapter, there are still open questions regarding the influence of organic molecules on individual compartments of SOM. In addition, the involvement of WaMB in the sequestration of organic molecules in SOM is only assumed. For this reason, following hypothesis were tested experimentally.

## 1.10 Research questions and hypotheses

The goal of this PhD thesis is to shed a light on characteristics of aliphatic crystallites, WaMB and its contribution to the sequestration of organic molecules in SOM. Special focus was put upon the understanding of changes in properties of aliphatic crystallites when being in contact with organic chemicals. To gain basic knowledge of the aliphatic crystallites, hypothesis H1 was formulated. Testing the hypothesis H1, one can conclude either on the inert character of aliphatic crystallites or their interaction abilities.

*H1) Organic chemicals do not penetrate into aliphatic crystalline domains in SOM.*

Another aim of this thesis is to assess the relation between WaMB stability and the physicochemical character of their direct environment. It is expected that testing the hypothesis H2 will help to answer the question: “Which interaction abilities of molecules in WaMB direct vicinity are relevant for WaMB thermal stability?”.

> *H2) The stability of WaMB increases with decreasing ability of surrounding molecules to interact with water molecules forming WaMB.*

The relation between WaMB stability and SOM segment mobility is of high interest. If hypothesis H3 is confirmed, it will allow to estimate to which extent WaMB stability determines the mobility of SOM molecular segments.

> *H3) The decrease in mobility of the molecular segments caused by WaMB is determined by WaMB stability (T*). In other words, WaMB control the rigidity of SOM matrix.*

The next objective of this thesis is to determine the involvement of WaMB in the sequestration of organic molecules in SOM. For this purpose, hypotheses H4 and H5 were tested experimentally. Testing the hypothesis H4 will help to estimate the portion of organic chemicals occurring in micro-pores closed by WaMB. Verifying the hypothesis H5 will allow to relate WaMB characteristics to the mobility of organic chemicals.

> *H4) A significant amount of organic chemicals is entrapped in micro-pores and closed by WaMB connecting individual SOM segments.*
>
> *H5) WaMB prevent organic molecules to enter and leave SOM matrix and contribute thus to their physical immobilization.*

## 1.11 Structure of the thesis

In order to evaluate the hypothesis H1) "Organic chemicals do not penetrate into aliphatic crystalline domains in SOM", aliphatic crystallites presented in soils were brought into contact with chosen organic chemicals. For this, two soils differing in their origin and composition were investigated in their natural state, i.e. conditioned in an atmosphere with a certain humidity degree. This allowed to investigate the unique structure of aliphatic crystallites presented in those soils. Soil samples were treated with a set of organic chemicals differing in polarity and functional groups, which helped to conclude on the interaction abilities of SOM crystallites. The quantity of applied organic chemicals incorporated in SOM was measured using HS-GC-MS. In order to investigate the response of aliphatic crystallites to the treatment, spectroscopic techniques, such as $^{13}$C CPMAS NMR, $^{2}$H NMR and thermoanalytical technique, represented by DSC, were applied. If aliphatic crystallites are penetrated with organic chemicals, the decrease of crystallinity assessed via $^{13}$C CPMAS NMR will be measured. This will also lead to a decrease of melting temperature, which will be assessed via DSC. The $^{2}$H NMR can assess the mobility of applied organic compounds and can provide a hint on their location in the SOM matrix.

Chapter 3 presents a study testing the hypothesis H2) "The stability of WaMB increases with decreasing ability of surrounding molecules to interact with water molecules forming WaMB". Testing the hypothesis H2 sheds a light on the relations between WaMB characteristics and physicochemical parameters of their environment. In the past, computer modeling studies predicted a direct influence of polarity of the environment on the stability of WaMB. This prediction was tested as follows. Soil samples in a natural state were treated with a large set of solvents and organic chemicals. Each compound used for treatment was characterized using interaction parameters provided by LSER theory. This allowed to quantitatively conclude on H-donor/acceptor interaction abilities, polarity and specific volume of each compound applied. The measurement of WaMB thermal stability (T*) using DSC in those samples allowed to verify the hypothesis H2. Furthermore, DSC provided the information about the change of heat capacity (C*) and thus a change of mobility of SOM segments during WaMB disruption. This allowed to verify the hypothesis H3) "A decrease in mobility of the molecular segments caused by WaMB is determined by WaMB stability (T*)". If this is the case, C* will be determined by the same interaction parameters as T*. Taking together, the identification of interaction parameters significantly influencing WaMB characteristics, represented by T* and C*, will contribute to the mechanical understanding of the relation between WaMB stability, their formation and physicochemical parameters of the environment.

Chapter 4 focuses on experimental testing the hypothesis H4) “A significant amount of organic chemicals is entrapped in micro-pores and closed by WaMB, connecting individual SOM segments”. Furthermore, the hypothesis H5) “WaMB prevent organic molecules to enter and leave SOM matrix and contribute thus to their physical immobilization” was tested. Both hypotheses were verified via measurements of desorption kinetics of phenol from soil samples with and without the presence of WaMB. If a large amount of phenol is entrapped in micro-voids closed by WaMB, then a lower amount of phenol will be desorbed during the time measured. If WaMB hinder organic molecules to leave certain regions of the SOM matrix, then a relation between WaMB stability and desorption characteristics (e.g., desorption time) will be observed. For this, thermal stability of WaMB was determined using DSC measurements. These measurements were accompanied by computer modeling using a simplified phenol-WaMB-SOM model. This provided information on stability and hydration energies of the phenol-WaMB-SOM model system, which indicated the preferential location of organic molecules in SOM of the prepared samples.

Chapter 5 includes a synthesis of information provided in this thesis and an outlook for further research. Supporting Information to the chapters 2, 3 and 4 are included in the annexes.

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# Chapter 2

# Influence of organic chemicals on aliphatic crystallites analyzed in whole soils

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# Chapter 3

# Influence of organic chemicals on water molecule bridges in soil organic matter of sapric histosol

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# Chapter 4

## Influence of water molecule bridges on sequestration of phenol in soil organic matter of sapric histosol

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# 4. Influence of Water Molecule Bridges on Sequestration of Phenol in Soil Organic Matter of Sapric Histosol

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## 4.1 Abstract:

Water molecule bridges (WaMB) can stabilize the supramolecular structure of soil organic matter (SOM) by connecting individual SOM compartments. WaMB are hypothesized to act as desorption barrier and thus to physically immobilize molecules in SOM. In order to test this hypothesis, we prepared two sets of soil samples - pre-aged samples with WaMB developed, and vacuumed samples, in which WaMB were disrupted. The samples were spiked with phenol and then stored under controlled humidity. The degree of phenol immobilization in SOM was assessed by desorption kinetics of phenol into a gas phase. It was compared with WaMB thermal stability (T*) obtained by modulated differential scanning calorimetry (MDSC) and results were related to computer modeling providing stability and solvation energies of phenol-WaMB-SOM models.

The desorption kinetics of phenol was best described by a first order model with two time constants ranging between one and ten hours. In pre-aged samples, the time constants correlated with T* showing that desorption time increases with increasing WaMB stability. Computer modeling proposed that phenol molecules are preferentially locked in nanovoids with polar OH groups pointed to WaMB in the most stable configurations. Both findings support the hypothesis that WaMB can act as a desorption barrier for phenol.

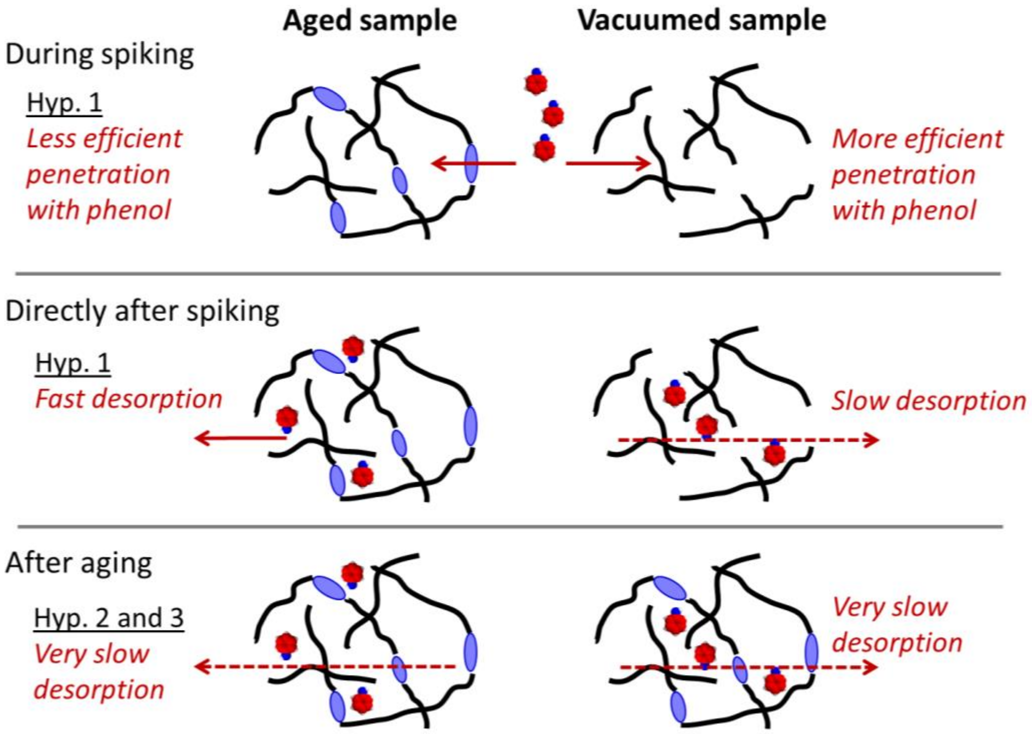
## 4.2 Introduction

Soil organic matter (SOM) is a key component of soil that is responsible for soil essential functions, such as sorption and immobilization of nutrients and contaminants (Scheffer et al., 2010). Sorption and desorption of organic molecules from SOM were intensively studied in regard to: (a) SOM chemical composition (e.g., presence of aromatic and aliphatic compounds (Chefetz and Xing, 2009)), (b) soil and SOM porosity (e.g., Ran et al., 2013; Werth and Reinhard, 1997) and (c) occurrence of physical domains (e.g., glassy and rubbery domains (Pignatello and Xing, 1999)). Physical domains are assumed to be decisive for selectivity, kinetics and reversibility of sorption (Pignatello, 2012). Broad evidence shows that the glassiness of SOM phases causes sorption hysteresis and is assumed to be involved in high desorption resistance (LeBoeuf, Weber, and Walter, 2000; Pignatello, 1999, 2012). Moreover, the glassy phases dynamically respond to changes of environmental conditions, such as temperature, moisture content and concentration of sorbing chemical that leads to a modification of its sorption and desorption properties (Pignatello, 2012). Nevertheless, the link between sorption and desorption processes and SOM supramolecular structures is still not yet completely understood on a mechanistic basis (Pignatello, 2012; Ran et al., 2013). For instance, it is still unclear to which extent determine microporosity of SOM sorption processes and sequestration of chemicals (Pignatello, 2012; Ran et al., 2013). SOM consists of a continuum of materials covering large, intact, plant, and microbial biopolymers and their highly transformed and functionalized fragments (Lehmann and Kleber 2015; Masoom et al., 2016). This extreme variety of compounds is a basis for formation of a supramolecular structure stabilized by intermolecular forces (Schaumann 2006a, 2006b). Water molecules can act as agents for structural organization of SOM (Kleber and Johnson, 2010; Masoom et al., 2016; Schaumann, et al., 2013b; Schaumann and Bertmer, 2008) forming clusters between hydrophilic functional groups known as water molecule bridges, WaMB (Aquino et al., 2011b). They are assumed to react dynamically on changes in temperature (Schaumann and LeBoeuf, 2005), relative humidity (Schaumann, 2005) and the presence of organic chemicals (Ondruch et al., 2017b). For example, WaMB can be disrupted by elevated temperature that causes a sudden increase in structural mobility as measured by $^1$H NMR (Jäger et al., 2016; Schaumann et al., 2013a) WaMB disruption can be detected as a thermal step transition showing abrupt increase of heat capacity using differential scanning calorimetry (DSC) (Schaumann and LeBoeuf, 2005) at the WaMB transition temperature, T*, which reflects the thermal stability of the WaMB (Ondruch et al., 2017b). T* can be reduced in fast manner by abrupt changes in relative humidity (Schaumann, 2005; Schaumann and LeBoeuf, 2005) and by the addition of molecules able to participate in H-donor and H-acceptor interactions that consequently reduce SOM matrix rigidity (Ondruch et al., 2017b). This fast process is followed by a slow physicochemical aging that leads to a successive WaMB reformation and matrix stiffening (Schaumann, 2005; Schaumann and LeBoeuf, 2005). Structured WaMB can be formed up to distances of ~1.3 nm (Aquino et al., 2009) or even longer (up to ~2 nm) if combined with cation linkages (Kunhi Mouvenchery et al., 2013). The presence of WaMB within soil has been hypothesized to prevent organic molecules to enter or leave specific regions of SOM and thus cause their physical immobilization in the SOM matrix (Aquino et al., 2011a; Jaeger et al., 2015; Schaumann and Bertmer, 2008). First indications for this hypothesis were found by Ondruch et. al. (Ondruch et al., 2017b). However, the link between the presence and stability of WaMB and the sorbate desorption has never been proven experimentally. To verify this hypothesis, it is necessary to determine the relationship between the parameters of desorption kinetics and characteristics of WaMB, such as its thermal stability and dynamics. In the present time, there is a lack of studies investigating the nature of WaMB in SOM. The central findings relevant for the current study were previously investigated in the group of researchers authoring this article. For this reason, references stated in this work are extensively based on studies of a group of prof. Schaumann.

The desorption of organic compounds from soils and sediments typically occurs in two stages (Li and Werth, 2004; Van Noort et al., 2003). Desorption has often been described as a first order two-compartment process (Cornelissen et al., 1997, 2000; Schrap et al., 1994a; S. M. Schrap et al., 1994b). The fast stage ranges from minutes to hours and the slow stage spans weeks to years (Li and Werth, 2004). Using silica gel, Norwood soil and other materials suggested that the fast stage can be a result of a diffusion limitation in mesopores (2 – 50 nm) filled with water due to capillary condensation (Farrell and Reinhard, 1994; Werth and Reinhard, 1997). In that study, the slow desorbable fraction was attributed to a retarded first-order desorption and diffusion in micropores (<2 nm) (Werth and Reinhard 1997).

In this study the hypothesis that the entrapment of an organic molecule in SOM is linked with the stability and age of WaMB was tested by means of sorption to and desorption of phenol from a histosol sample. The following specific hypotheses were evaluated: i) during spiking phenol penetrates into the SOM without WaMB more efficiently than into the SOM with WaMB, and this subsequently leads to slower desorption from the SOM samples without WaMB (Scheme 1, Hyp. 1); ii) the presence of WaMB in the SOM containing phenol, WaMB act as a desorption barrier hindering phenol desorption (Scheme

1, Hyp. 2). If this hypothesis holds, a direct relation between WaMB stability and desorption kinetics is expected; iii) the deceleration of desorption can be ascribed either to an entrapment of the chemical in voids confined by WaMB or WaMB-based diffusion limitation in the matrix (Scheme 1, Hyp. 3).



***Scheme 1*** *Hypothesized sorption and sequestration of phenol in SOM with and without presence of WaMB. WaMB are depicted as blue ellipses and SOM structure as black curved lines. Hypothesis1: Different efficiency of SOM penetration into the matrix with and without WaMB. This is expected to cause different rates of desorption. Hypothesis 2 and 3: Development of stable WaMB is expected to decelerate the rate of desorption.*

## 4.3. Materials and methods

### Materials

As a model soil, we used an organic, clay-free sample of the sapric histosol which was characterized and described in detail in our previous publications (Jäger et al., 2011; Ondruch et al., 2017a; Ondruch al., 2017b; Schaumann et al., 2013a). In brief, the sapric histosol has 52% content of organic carbon and ~6.8 % of ash that is predominantly formed from salts and ash. Clay minerals are presented only in a negligible amount (Jäger et al., 2011). Therefore, processes observed in the experimental part of this study occurred in SOM without contribution of SOM-clay interactions (Ondruch et al., 2017b).

Cation exchange capacity is 123 mmol$_c$ kg$^{-1}$ and pH ($CaCl_2$ 0.01 M) is 2.7 (Schaumann et al., 2013a). According to our previous study (Ondruch et al., 2017b), 63 % of functional groups in the SOM of sapric histosol (O-Alkyl, N-Alkyl; O-Aryl, N-Aryl and carbonyl and carboxylic moieties) have H-acceptor/donor interaction ability. 15 % of moieties (Aryl-H and aryl-C carbons, olefinic-C) can eventually undergo H-acceptor interactions. 22 % of the SOM is formed by alkyl-C and these moieties can interact only via weak dispersion forces. The content of functional groups important for the WaMB formation in sapric histosol is comparable with other peats and forest soils (Ondruch et al., 2017b).

The hexane used for treatment of SOM as well as the phenol used for spiking were of GC purity (≥99.5%) and were purchased from Merck (Germany) and Sigma-Aldrich (USA), respectively.

### Sample Preparation

Preparation of samples spiked with phenol

In this work, two types of samples were prepared.

I) The “pre-aged samples” were sapric histosol samples equilibrated at 76 % of RH in moisturizing chamber for 29 days prior to spiking with phenol. These samples contained 19.3 ± 0.4 wt.% of water.

II) The “vacuumed samples” were treated using vacuum 0.3 Pa for 3 days prior to spiking with phenol. The large part of water was removed during the process, and the rest water content decreased to 3- 8 %.

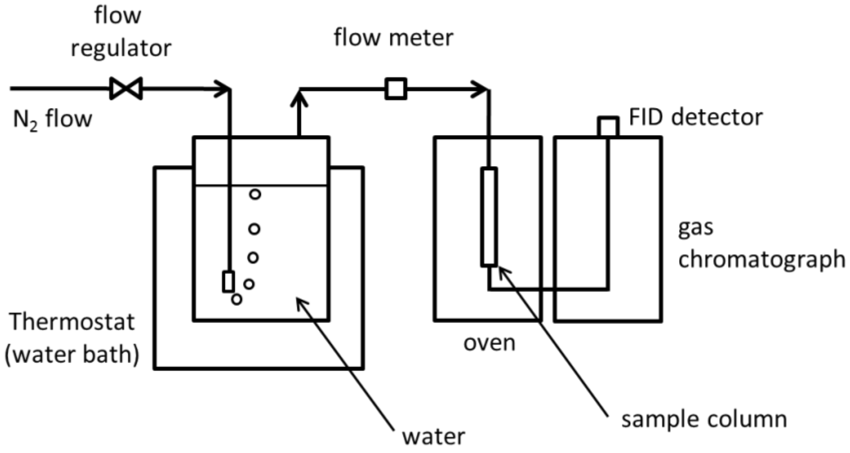
The pre-aged samples and the vacuumed samples were spiked with phenol using the same method as described in our previous study (Ondruch et al., 2017b). Briefly, 0.1 g of phenol was dissolved in 2 g of hexane. The solution was carefully mixed with 1.9 ± 0.01 g of the soil to assure the contact of the solution with the whole soil volume. The contact time was 24 hours during which the hexane evaporated (residual amount 0.8 ± 0.3 mg/g of soil), while most of the phenol (49 ± 3 mg/g) remained in the soil as analyzed in our previous study (Ondruch et al., 2017b). From each sample type, 2 – 3 independent replicates were prepared.

### Modulated Differential Scanning Calorimetry (MDSC)

In comparison to a standard DSC, MDSC applies periodical temperature modulation that causes instantaneous high heating rates which improves the signal to noise ratio (sensitivity) (Jörimann, 1999; Simon, 2001). Furthermore, the low underlying heating rate significantly enhances resolution (Jörimann, 1999; Simon, 2001). These advantages allow to separate overlapping thermal events which commonly occur in classical DSC records of multicomponent materials such as soils (Kučerík et al., 2014; Simon, 2001; Verdonck et al., 1999). For each MDSC analysis 3–5 subsamples were prepared. Average and standard deviation was calculated from each T* dataset. This allowed elimination of possible artefacts caused by heterogeneity of SOM. All subsamples were exposed to the following thermal regime. The hermetically sealed pan with sample was placed into DSC oven at 20 °C, cooled at 10 °C/min to -60 °C, held 1 minute at this temperature and then heated to 110 °C. The heating rate applied was 2.5 °C/min with a modulation ±2 °C of the temperature amplitude (Kučerík et al., 2014). This comparably low heating rate allowed separation of WaMB transition from melting of aliphatic moieties (Kučerík et al., 2014). Further details about the MDSC setup and calibration can be found elsewhere (Ondruch et al., 2017a). The temperature of WaMB transition (T*) in all DSC records was evaluated in the same way as described in our previous study (Ondruch et al., 2017a).

### Desorption kinetics of phenol into the gas phases

The measurement of desorption kinetics of phenol was performed using apparatus allowing humidity control of carrier gas successfully used in sorption and desorption studies (Boutboul et al., 2000; Li and Werth, 2004). The measurements were performed as follows. 20 mg of the soil sample were inserted into a 10 mm long stainless steel column with 4.6 mm of inner diameter (Duratec, Germany). The column was equipped with two sieves (5 μm mesh) at the beginning and the end in order to prevent sample outlet and then placed into the oven Jetstream 2 (Knauer, Germany) that maintained temperature at 25.0 ± 0.1 °C. The sample column was connected with gas chromatograph HRGC 5160 (Carlo Erba, Italy) equipped with a flame ionization detector (FID) that was operating at 200 °C. The nitrogen carrier gas flow was regulated at 35.0±1.5 mL/min using precision regulator DRF.31 S (Knocks, Germany) and measured using mass flow meter EL-Flow (Bronkhors, Nederland). The humidity of the carrier gas was set at 76 % that was assured by a bottle filled with water through which the nitrogen was bubbled. The temperature of the bottle was maintained at 21.6 °C using thermostat Julabo F12-ED (Seelbach, Germany). Phenol content was quantified by means of a FID detector as function of time after starting the carrier gas flow. Each experiment was repeated 2-3 times. The experimental setting is depicted in Scheme 2.



***Scheme 2*** *Apparatus for desorption kinetics experiments.*

The desorption of phenol is reflected by the time-dependent FID signal (see results, Fig. 1). The FID signal is affected by phenol, but also by volatile organics from soil and residual hexane. Desorption of these compounds was tested on the blank sample and soil treated using pure hexane. Desorption of volatile organic compounds and hexane was observed only in first 20 minutes. For this reason, only the FID record in the range 1 – 40 hours was evaluated for all measured phenol-spiked samples.

A first order two-compartment model was fitted to the recorded FID data (Schrap et al., 1994, Cornelissen et al., 1997). Although several models including exponential and power functions were tested by means of OriginLab 7.5 software (OriginLab, USA), the best fit (typically, $R^2 > 0.998$; $\chi 2$/DoF (Chi-Square / degree of freedom) $< 1x10^{-6}$) was obtained when using the bi-exponential function (Eq. 1). This is in accordance with the expected kinetic mechanisms, which mathematical description comprises of two-first order rate processes (Schrap et al., 1994a, Schrap et al., 1994b, Cornelissen et al., 1997, Cornelissen et al., 2000).

$$y = y_0 + A_1 e^{\frac{-x}{t_1}} + A_2 e^{\frac{-x}{t_2}} \qquad \text{Eq. 1}$$

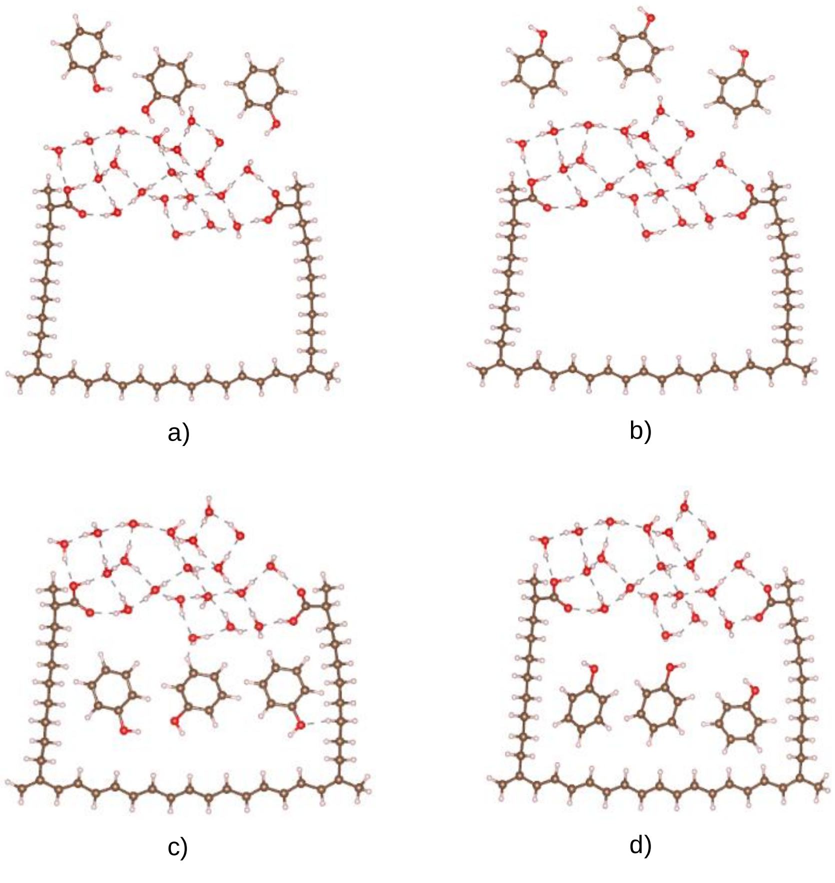
$y_0$ is the offset, $A_1$ and $A_2$ are the amplitudes, $t_1$ and $t_2$ represent the desorption time constants and $x$ is time.

As explained in the previous paragraph, the FID signal is proportional to the concentration of phenol in the gas phase. A higher signal at the beginning of the measurement would suggest a higher amount of phenol desorbable during the first hours in vacuumed samples than in pre-aged samples (see results, Fig. 1). However, our experimental setup does not allow exact baseline setting. This limits the direct comparison of signal intensities and prevents absolute quantification of desorbed phenol via integration of the fitting function. The relative amount of phenol in the fast fraction ($A_{FAST}$) can be assessed from the ratio of amplitudes $A_1$ and $A_2$ according to Eq. 2.

$$A_{FAST} = \frac{A_1}{A_1 + A_2} \times 100 \qquad \text{Eq. 2}$$

**Molecular modeling**

The WaMB stability in presence of phenol molecules was evaluated by means of computational molecular modeling. A nanospatial model of SOM representing a supramolecular connection of two polar SOM segments through WaMB was created (see Scheme 3). Similar to (Aquino et al., 2011b), this model consists of two parallel aliphatic chains, geometrically restricted on the one bottom. The bottom ends are connected through conjugated CH=CH chain. The top of both aliphatic chains is terminated with a methyl group bound to carbon, to which carboxyl group is attached. Both carboxyl groups are over bridged through twenty water molecules forming the WaMB. In this way a nanovoid hole was created inside of WaMB-SOM model. To model interactions of phenol (Ph) with the WaMB-SOM structure several scenarios for the localization of Ph molecules were suggested. In a first case, three phenol molecules (see Scheme 1) were placed outside the WaMB-SOM nanovoid with the orientation of the phenol OH group outwards (model_1) and inwards (model_2) the WaMB. In a second case, three Ph molecules were placed inside the WaMB-SOM nanovoid having again similar orientations as in the first case (model_3 and model_4 in Scheme 3). We decided to use three Ph molecules to enhance the differences in calculated energies among Ph-WaMB-SOM models. Since the environment in SOM plays an important role on the WaMB stability (Aquino et al., 2011a, Ondruch et al., 2017), the calculations were performed beyond to the isolated system (gas phase) also considering a polar (hydrophilic) and a non-polar (hydrophobic) environments. Dielectric constants (ε) for methanol (32.70) and n-hexane (1.88) were taken to represent the polar and non-polar domains in SOM, respectively. Geometry optimization, stability and the calculations were performed at the density functional theory (DFT) level using PBE functional (Perdew and Wang 1992, Perdew et al., 1996) and the basis set TZVP (Schäfer et al., 1992) approach. Most of the commonly used functionals in DFT lack dispersion interactions (they could play a role in the stabilization of Ph molecules in a proximity of nonpolar parts of the SOM structure) To overcome this problem the D3 dispersion correction of Grimme et al (Grimme et al., 2010) was included throughout all calculations. The calculations were performed by means of the Turbomole program suite (Ahlrichs et al., 1989). To model global environmental polar and nonpolar effects of SOM a COSMO (COnductor like Screening MOdel) approach implemented in the Turbolmole code was used (Klamt and Schüürmann 1993).



***Scheme 3*** *Supramolecular connection of two polar SOM segments. a) model_1 – the Ph molecules are placed outside of the WaMB with the OH groups pointing toward the WaMB b) model_2 – the Ph molecules are positioned outside of the WaMB with the opposite orientation of the OH groups with respect to the WaMB. c) model_3 – the Ph molecules are localized inside of the nanovoid of the WaMB-SOM frame and the OH groups pointing toward the nonpolar aliphatic chain, and the aromatic rings are close to the WaMB, d) the Ph molecules are placed inside of the nanovoid of the WaMB-SOM frame with OH groups pointing toward the WaMB. Colors are related to the atoms as follows: carbon – brown, oxygen – red, and hydrogen – white.*

## 4.4 Results

### Desorption kinetics of phenol into the gas phase

Individual measurements of phenol desorption differed in their baseline values. The baseline varied approximately in a range 0.000 to –0.085 V. Therefore, FID signals are given in Volts without any absolute quantification in this chapter. During the first minutes, the vacuum-treated samples provided a FID signal of 0.3 ± 0.1 V, whereas the samples containing WaMB produced an initial signal of 0.18 ± 0.01 V (Fig. 1). After one hour, the FID signal was comparable for both sample types, which suggests that the strongest difference in desorption kinetics should be observed in the fast regime.

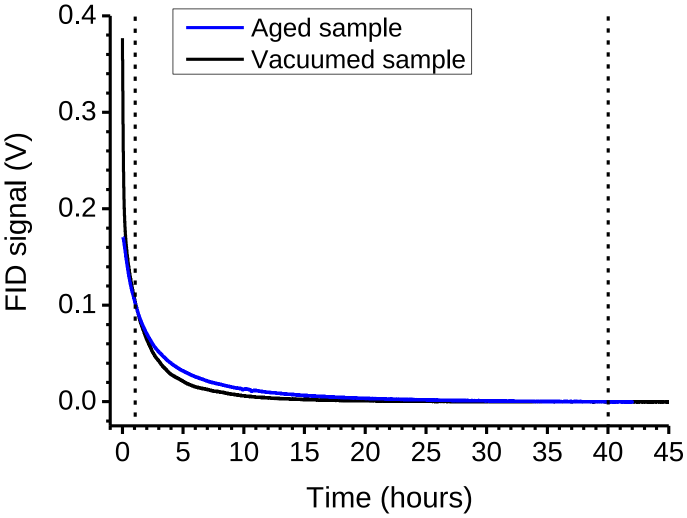


*Fig. 1 Examples of desorption profiles of phenol from pre-aged (blue curve) and vacuumed (black curve) samples. In order to compare the development of the FID records, both records were adjusted to zero volts at the time point 40 hours, where the curves reached a plateau. The dashed lines show the range used for evaluation of time constants.*

The time dependence of the FID signal was described by the use of the bi-exponential model (Eq. 1). The goodness of the fit can be further assessed via $\chi^2/DoF$ showing the quantitative difference between the predicted and the input values. Obtained $\chi^2/DoF$ was typically lower than $1x10^{-6}$ showing high suitability of the bi-exponential model. The time constants fell to a range 0.9 – 2.0 h ($t_1$) for the fast desorbing fraction and to a range 4.7 – 10.4 h ($t_2$) for the slowly desorbing fraction, respectively. The phenol fraction desorbing fast ($A_{FAST}$; Eq. 2) from the vacuumed sample accounted for 73 ± 2 % of the signal, without showing a significant development during the aging period of 29 days (Fig. 2). In the pre-aged samples, $A_{FAST}$ accounted for 76 ± 1 % of the signal for most of the time, except for the 10th day, when $A_{FAST}$ decreased to 62 ± 6 %. Large error bars of presented average values indicate that a sudden decrease of $A_{FAST}$ is a result of data scattering. The sudden decrease of fast desorbing fraction does not show a relation to the T* or to both desorption time constants. Taken together, the amount of

$A_{FAST}$ in the pre-aged and vacuumed samples did not differ significantly, expect for the day 10. Therefore, the initial signal difference between the vacuumed and the pre-aged sample (FID signal during first minutes in Fig. 1) is not reflected in $A_{FAST}$. Therefore, it could be attributed to a very fast desorbing fraction with a time constant clearly below 1 hour, which is not detected by the chosen approach due to the low amount of data points during the first hour of desorption. The conclusions for the $A_{FAST}$ fraction are also valid for the phenol fraction in the slowly desorbable state that forms the remaining percentage part of phenol as follow: $A_{SLOW}$ (%) = (100- $A_{FAST}$).

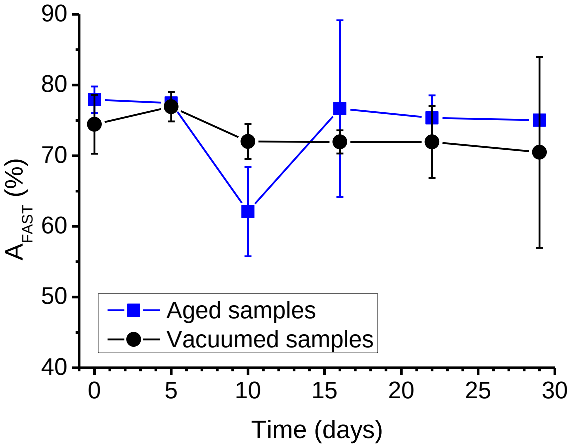


*Fig. 2 Development of the relative amount of phenol present in fast desorbable state ($A_{FAST}$) as function of the aging time.*

**Water content, desorption kinetics and WaMB thermal stability**

Water content. The water content increased slightly from 17.0 % to 18.2 % in the pre-aged samples during the first days of aging at 76 % of RH. Then it varied around 18.2 ± 0.6 % during the rest days (see SI Figure S1). The vacuumed samples sorbed water during the first 4 days of aging at 76 % of RH and reached a water content of 17.5 ± 0.3 %, similar to that in pre-aged samples (SI Figure S1).

Desorption kinetics of phenol. The time constant $t_1$ for phenol desorption from vacuumed samples increased from 1.2 ± 0.2 h to 1.9 ± 0.3 h in the first 5 days and then fluctuated between 1.5 and 2.0 h (Fig. 3a). $t_2$ first increased during 10 days and then fluctuated from 7.7 to 8.5 in a range 10 – 29 days (Fig. 3a). Thus, phenol desorption from the vacuumed sample was fast in the beginning and became slower during aging.

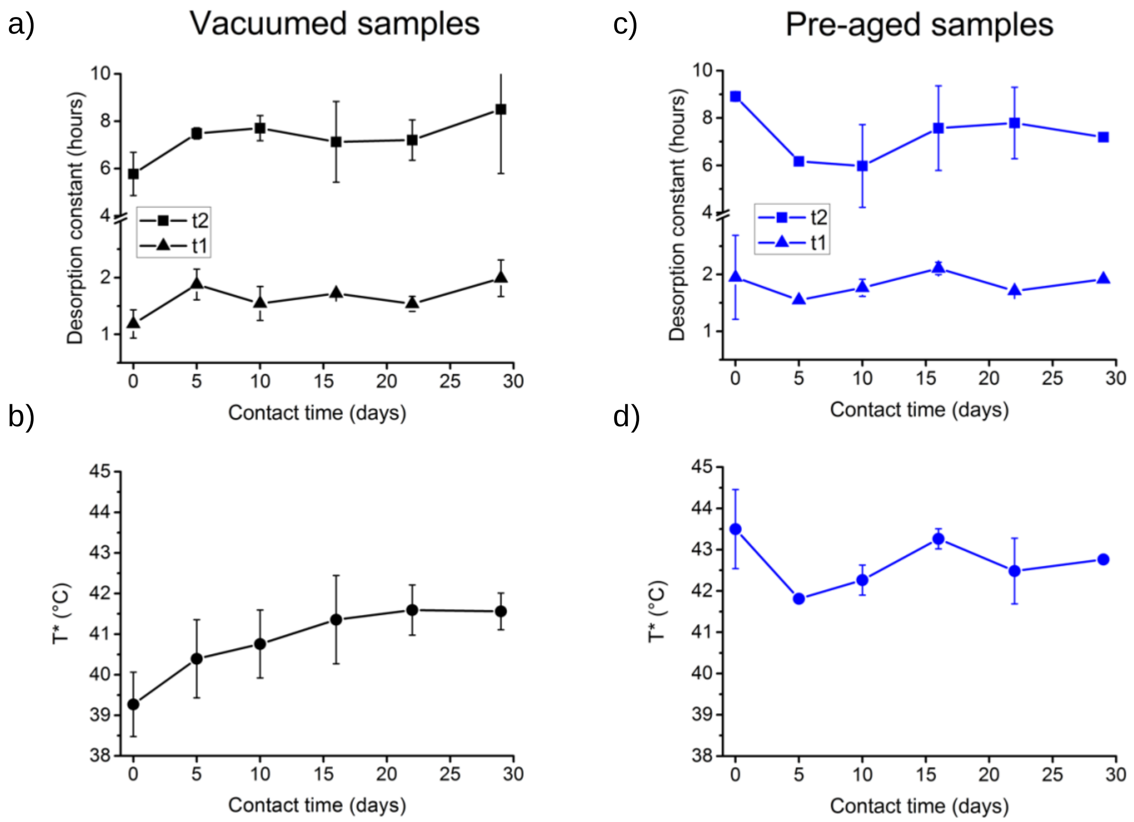


*Fig. 3 Time development of (a, c) desorption constants - $t_1$ and $t_2$ (a, c) and, WaMB thermal stability - T* in vacuumed (black) and pre-aged (blue) samples (b, d). Points and error bars represent average values and standard deviations, respectively.*

For the pre-aged samples, $t_1$ was 1.9 ± 0.7 h at day 0 and fluctuated between 1.5 and 2.1 h during following 29 days (Fig. 3c). Changes of $t_1$ and $t_2$ occurred in the range of their uncertainties, which reflects the sensitivity of the measurements to development of both time constants in selected time period. Thus, in contrast to the vacuumed sample, the desorption rate from pre-aged samples did not show any clear decrease with aging time.

WaMB transitions. All pre-aged samples showed WaMB transitions, but directly after treatment using vacuum, no WaMB transition was observed during the first 24 h of air drying after their spiking with phenol (see the materials and methods chapter). After this time WaMB transition showed T* of 39.3 ± 0.8 °C and T* increased to 41.6 ± 0.5 °C during the first 22 days. Later, T* remained constant until day 29 (Fig. 3b). In the pre-aged samples, T* showed values in a range of 41.8 – 43.5 °C throughout the experiment, with no clear trend with time (Fig. 3d).

For the pre-aged samples, T* was higher than 50 °C before spiking with phenol. 24 h after spiking with phenol, T* was 4.2 °C higher in the pre-aged sample than in the vacuumed sample. The difference between pre-aged and vacuumed sample decreased to ~1 °C during 29 days (Fig. 3b, d). Thus, thermal WaMB stability 24 h after spiking with phenol was lower in the vacuumed sample than in the pre-aged sample, but after one month, both samples revealed a comparable WaMB stability.

Although $t_1$ and $t_2$ fluctuated within the error bars for the pre-aged samples, the trends with aging time are comparable to those of T* in the whole range of 29 days (Fig. 3). The significant relation between $t_1$ and T* can be seen in the linear regression ($R_2 = 0.877$; $P < 0.01$) (Fig. 4). Similarly, $t_2$ in pre-aged samples also decrease in first days then followed by a fluctuation between 6.0 and 7.8 h (Fig. 3c). Strong similarity between T* and $t_2$ development (Fig. 3c, d) is reflected in their linear regression ($R_2 = 0.922$; $P < 0.005$) (Fig. 4) showing their mutual relationship. Including data from vacuumed samples, an overall trend can be observed. Independently of the sample preparation, the relation between both desorption time constants and T* is positive (Fig. 4).

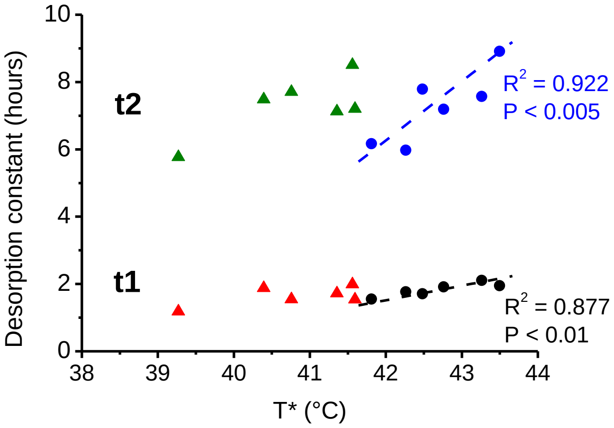
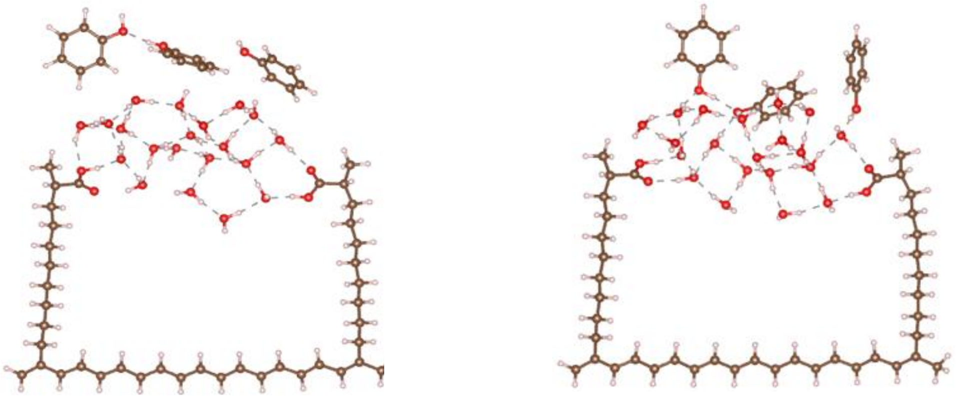


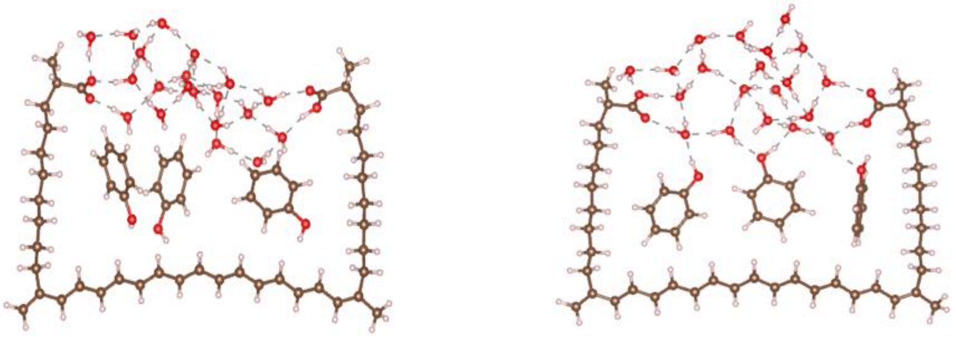
*Fig. 4 Relation between T* and desorption constants $t_1$ and $t_2$. The triangles and circles represent vacuumed and pre-aged samples, respectively. Individual symbols show an average of 2 – 3 t values and at least 10 T* values. The maximal uncertainties are T*= ±1 °C; $t_1$ = ±0.7 h; $t_2$ = ±2.7 h and are detailed in Fig. 3. The results of linear regression were calculated including uncertainties.*

### Computer modeling

The computer modeling was performed in order to determine stabile geometries of the Ph-WaMB-SOM model in environments differing in their polarities. This provides a clue on the preferential mechanism of WaMB-based physical sequestration of phenol. The optimized geometries of all four Ph-WaMB-SOM models (isolated, gas phase) are shown in Fig. 5 (the geometries of the models with the inclusion of environmental effects are collected in Supplementary material (SI Fig. 3). Table 1 collects relative stability energies ($\Delta E_{rel}$, related to that model, which was the most stable in the gas phase calculations, particularly model_4), solvation free energies ($\Delta G_{sol}$, as a difference between total electronic energies with and without solvent effect for the same geometry optimized in the COSMO calculation), and a difference between total electronic energies obtained for the models optimized in gas and in the COSMO calculations ($\Delta G_{sol\_rel}$). Thus, the later relative energy includes also conformational changes in the geometry of the models upon the environmental (solvation) effect.



a) model_1 b) model_2



c) model_3 d) model_4

**Figure 5.** Optimized geometries of the isolated structures (models 1-4)

The common feature for all four models is the water molecule bridge between the polar tails (carboxyl groups) of the aliphatic chains, in which a predominant interaction is hydrogen bonding within the bridge and/or WaMB and –COOH groups, respectively. $H_2O$ molecules and carboxyl groups form multiple hydrogen bonds (usually 2 or 3), in which they often act as proton donor and/or acceptor, respectively. These hydrogen bonds are usually of a strong-to-moderate strength (Steiner 2002, Aquino, et al., 2011a). The four models of Ph-WaMB-SOM system differ by a position and orientation of phenol molecules with respect to the water molecule bridge (Fig. 5 Phenol molecules can interact mainly in two ways: 1) via polar –OH groups that can form hydrogen bonding with polar species, and 2) via the nonpolar (but polarizable) aromatic ring that can be involved in dispersion interactions or weak hydrogen bonding with strong proton donors (Steiner 2002). In our four models both types of interactions are involved in the stabilization of the models but in a different portion. It is reflected in a relative stability ($\Delta E_{rel}$) as shown in Table 1. The model_4 is the most stable as in this model all interactions are effectively involved in the stabilization. Phenol molecules are trapped inside of the WaMB-SOM nanovoid and their polar –OH groups form hydrogen bonding with water molecules in the WaMB. Nonpolar aromatic rings interact with a) with neighboring aromatic rings and) with nonpolar aliphatic chains framing the WaMB-SOM nanovoid. In the model_3 the phenol molecules are also locked inside of the nanovoid but polar –OH groups do not interact with the water bridge. The stability of this configuration is mainly due to nonbonding dispersion interactions. Its stability is similar to the model_2, in which phenol molecules are out of the nanovoid and they point with the –OH groups towards the water bridge forming hydrogen bonds. Their mutual interactions are weak as they have more space around than in case of the molecules locked inside the nanovoid. Thus, the dominant force for their position is coming from hydrogen bonds. The model_1 is significantly less stable configuration than others. In this configuration phenol molecules interact with the water molecule bridge through the aromatic ring (weak –OH···$\pi$ interactions). Moreover, two phenol molecules are connected through hydrogen bonds between hydroxyl groups. Generally, the hydrogen bonds formed by phenol molecules are relatively strong ranging in an interval of 1.6-1.9 Å and they are the main reason for the forming of the stable complexes with the WaMB-SOM models.

The COSMO calculations were performed in order to mimic nonpolar (low dielectric constant represented by hexane value of 1.88) and polar (higher dielectric constant represented by methanol value of 32.7) domains that can surround the WaMB connections in the different domains of the SOM. The relative stability energies with respect to the most stable model_4 are shown in Table 1. Evidently, both environments have impact on the stability and the more significant changes are observed for the stronger polar environment (methanol). Whereas the difference in the relative stability decreases with increasing polarity for the model_1 and model_2, the trend for the model_3 is opposite showing its slight increasing of instability with respect to the model_4. The increasing stability of the model_1 and model_2 can be attributed to the enhancing effect of the environment on the strength of the hydrogen bonds formed by phenol and water molecules. For example, the hydrogen bond between two phenol molecules in the model_1 (visible in Fig. 5) has a value of 1.83 Å decreases to the value of 1.77 Å in the polar (methanol) environment. This effect is less significant in the models with phenol molecules trapped in the nanovoid because the WaMB-SOM frame shields the environment effect.

Table 1) Solvation and stability energies calculated for the optimized geometries considering polar (methanol model) and nonpolar (hexane model) environments. All energies are in kcal/mol. $\Delta G_{sol}$ (solvent energy) – it is a difference in the energy with and without solvent model for the same geometry; $\Delta G_{sol\_rel}$ – solvent energy with respect to geometry in the gas phase –it includes also conformational changes upon solvation

| MODEL | gas | hexane | | | methanol | | |
|---|---|---|---|---|---|---|---|
| | $\Delta E_{rel}$ | $\Delta E_{rel}$ | $\Delta G_{sol}$ | $\Delta G_{sol\_rel}$ | $\Delta E_{rel}$ | $\Delta G_{sol}$ | $\Delta G_{sol\_rel}$ |
| model_1 | 19.1 | 17.1 | -19.7 | -18.7 | 14.7 | -63.4 | -53.0 |
| model_2 | 6.3 | 4.1 | -20.2 | -19.0 | 0.7 | -65.9 | -54.2 |
| model_3 | 5.9 | 6.8 | -17.0 | -15.9 | 7.8 | -59.6 | -46.6 |
| model_4 | 0 | 0 | -17.9 | -16.8 | 0 | -60.0 | -48.6 |

The solvation energies collected in Table 1 ($\Delta G_{sol}$) show a difference between the models with phenol molecules outside (model_1 and model_2) and inside (model_3 and model_4) the WaMB. The former models have a higher solvation energy because they occupy larger solvation cavity in the COSMO calculations than the later models. Table 1 also includes relative solvation energies ($\Delta G_{sol\_rel}$), which reflect also configurational changes in the nonpolar and polar environment with respect to the geometry in the gas phase. As expected, the difference between $\Delta G_{sol}$ and $\Delta G_{sol\_rel}$ is minimal (1-2 kcal/mol). On the other hand, the polar environment affects the geometry of the phenol-WaMB-SOM models more significantly than nonpolar environment with a configurational energy achieving ~10-13 kcal/mol.

In general, the calculations showed that the adsorption of phenol molecules in the heterogeneous and complex structures such as SOM can be of a different strength. The most stable sites seem to be polar fragments overbridged by the WaMB forming nanovoids inside of the SOM structures, in which phenol molecules can be trapped. The dominant force in the interaction of phenol molecules with the WaMB has origin in hydrogen bonding with the water molecules. Polar domains can also stabilize the adsorption of phenol in the SOM (see small difference in the relative stability between model_2 and model_4).

However, the trapping of the phenol molecules in the SOM cavities can be kinetically slow as it will require an energy for opening the WaMB.

## 4.5 Discussion

### Influence of WaMB Stability on Phenol Desorption

The evaluation of $A_{FAST}$ revealed that the phenol fraction desorbing very fast was only slightly, but not significantly larger in the pre-aged samples than in the vacuumed samples. Thus, on the basis of the obtained data, it can neither be confirmed nor excluded that the chosen sample preparation led to a shift in the distribution of phenol between the slowly and the fast desorbing fraction as suggested by hypothesis I. Thus, the results did not support that the presence or absence of WaMB directs phenol into different types of moieties. Thus, a direct entrapment of phenol in nanovoids closed by WaMB cannot be confirmed by our results, because such entrapment would reduce the amount of phenol in the fast desorbing fraction (see Fig. 1).

However, the initially longer time constants for phenol desorption from the pre-aged sample than from the vacuumed sample (Fig. 3a, c) imply that WaMB already present in SOM did decelerate phenol desorption from the SOM matrix. Furthermore, the positive trend between T* and the desorption time constants in the pre-aged and vacuumed samples suggests that the desorption rate decreases with increasing WaMB stability, which supports the hypothesis II. On the other hand, despite the similarity of the time constants between pre-aged and vacuumed samples, T* differed between both sample types. It cannot be excluded that the difference in time constants is hidden behind the relatively large variation of desorption constants $t_1$ and $t_2$. But this also may suggest that absolute values of T* in a sample may be of less importance than T* changes during aging.

The direct relation between T* and both desorption constants, $t_1$ and $t_2$ in pre-aged samples, strongly supports the hypothesis ii) assuming that WaMB are acting as a barrier hindering phenol desorption. As reported in the literature (Werth and Reinhard 1997, Farrell, Grassian et al., 1999, Li and Werth 2004) the existence of both fractions reflects sorbent – sorbate interactions determined by (a) matrix porosity and (b) matrix compositional heterogeneity (distribution of sorption sites and their varying affinity to the sorbate). Strong relation between T* and $t_1$ and $t_2$ shows the dominant influence of WaMB on both phenol fractions. In the range of 30 days, the $t_1$ and $t_2$ fluctuated and their values showed a change up to 25 % and 33 %, respectively (see Fig. 3c). It can be excluded that the compositional heterogeneity of investigated samples has changed in this scope during the time of 30 days. This suggests that both, the fast and the slow desorbable phenol fractions, are linked with dynamic behavior of WaMB that connect individual SOM segments and is thus associated with porosity of the structure. In addition, stronger relation between T* and $t_2$ ($R^2 = 0.922$, $p < 0.005$, slope = $1.8 \pm 0.3$) than T* and t1 ($R^2 = 0.877$, $p < 0.01$, slope = $0.43 \pm 0.08$), as can be seen in the Fig. 4, shows higher influence of WaMB on the slow desorbing fraction of phenol. Since WaMB can bridge distances lower than 2 nm (Aquino et al., 2009, Kunhi Mouvenchery et al., 2013) the main influence of WaMB is on the level of micropores.

The results provided by computer modeling help further to elucidate the mechanism of physical sequestration of phenol associated with WaMB in micropores. Higher stability of modelled geometries, where determined, when phenol molecules were oriented with its -OH groups to WaMB and were interacting with WaMB via H-bonds (model 2 and 4, Fig. 5) than in the case, where phenol molecules were interacting with WaMB only via dispersion forces (models 1 and 3, Fig. 5). This is further supported by the observation that phenol molecules interacting with WaMB via H-bonds form the most stable geometries despite of the different polarities of the environment (Tab. 1). This suggests that WaMB contribute to the sequestration of phenol in both cases, where the phenol molecules are inside as well as outside the cavity. This would explain the initially longer time constants of phenol desorption from the pre-aged sample than from the vacuumed sample (Fig. 3a, c), revealing that WaMB already present in SOM did decelerate phenol desorption from the SOM matrix.

The highest stability showed the geometry, where phenol was inside the cavity and interacting with WaMB via H-bonds. In this particular case, one can assume that WaMB stability has a decisive impact on the physical sequestration of phenol. However, the trapping of the phenol molecules in the SOM cavities can be kinetically slow as it will require an energy for opening the WaMB. The relation between the slow desorbing fraction and WaMB thermal stability in aged samples (Fig. 4) thus supports the hypothesis III ascribing the deceleration of phenol to the WaMB-based diffusion limitation in the matrix or optionally, to an entrapment of the chemical in voids confined by WaMB.

WaMB has lower but still significant influence on the fast desorbing fraction than on the slow desorbing fraction (Fig 4). The fast fraction should be associated with larger pores (mesopores) than the slow fraction. Mesopores represent pores having diameters in the range 2 – 50 nm. These distances are not expected to be directly connected by WaMB (Aquino et al., 2009, Kunhi Mouvenchery et al., 2013). However, the study (Schaumann et al., 2013) based on NMR wideline spectroscopy and $^1$H-NMR-relaxometry measurements suggests an existence of several types of water forming WaMB, differing in their degree of confinement. Water molecules with low degree of confinement, forming the outer WaMB region may reach distances belonging into the range of mesopores. In addition to this, previous studies have demonstrated that WaMB formation leads to an increase of SOM matrix rigidity (Schaumann and LeBoeuf 2005), (Schaumann et al., 2013, Jäger et al., 2016). Increase of matrix rigidity may consequently influence the diffusion of phenol in the matrix and cause deceleration of its fast desorbable fraction.

## 4.6 Conclusions

This study confirmed the assumption that WaMB are involved in the physical immobilization of organic molecules in SOM, which was up to now only predicted by theoretical considerations and model calculations. The results are in line with the hypothesis assuming that thermally stable WaMB in SOM containing phenol act as a physical barrier in the matrix for phenol desorption and that the diffusion barrier becomes more effective with increasing thermal stability of WaMB. Based on the model calculations, phenol should be preferentially trapped in microvoids enclosed by WaMB. Since WaMB stability is highly sensitive to changes in environmental conditions such as temperature or relative humidity, environmental changes can have significant influence on entrapment of organic chemicals in SOM.

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# Chapter 5

## Synthesis and Outlook

# 5. Synthesis and outlook

Previous chapters provided evidence that chosen organic molecules interact with constituents of SOM, as exemplified on WaMB and aliphatic crystallites, and cause measurable changes of their structure and properties. In addition, the assumption that WaMB are involved in the physical immobilization of organic molecules in SOM was confirmed. Mentioned results demonstrate a close relation between interacting molecules and supramolecular structure of SOM, its functions and properties. This relation is further analyzed in this synthesis.

As stated in chapter 2, the chosen spiking compounds, phenol and naphthalene, were able to penetrate aliphatic crystallites forming SOM in the investigated soil samples. In contrast, crystalline phases in synthetic polymers have relatively inert character that excludes penetration and/or diffusion of small molecules through crystalline phases (Harland and Peppas, 1989, Lützow et al., 1999). In order to explain this peculiar difference in properties of aliphatic crystallites contributing to SOM and crystalline phases of synthetic polymers, three explanations are proposed in the following lines. I) Aliphatic crystallites present in SOM are classified as micro-phases. These are significantly influenced by their surfaces that often leads to differences from properties of the same phase of higher dimensions (Wunderlich, 2005). In general, synthetic semi-crystalline polymers crystallizing from melts and solutions possess lamellar sizes of 10–30 nm (Hu et al., 2000; Jiang et al., 2003; Prime and Wunderlich, 1969), although at appropriate conditions, lamellar sizes of higher orders of magnitude can be obtained (Prime and Wunderlich, 1969). In comparison to this, properties of the 3 nm large aliphatic crystals observed in soils (Hu et al., 2000) can significantly differ from those in synthetic polymers. II) Crystalline phases present in SOM can occur in a metastable state and thus differ from those present in synthetic polymers. Although aliphatic crystallites in soils reveal a first order transition, these crystalline phases can occur in a metastable state that could be the reason for their sensitivity to changes of environmental conditions. An example of those crystals in metastable state can be mixed crystals having structural defects and consisting of carbon chains of different lengths (Kučerík et al., 2014). Metastable state of analyzed crystallites suggest also their behavior and recrystallization at the presence of small molecules, e.g. water as described in chapter 2. According to the phase classification provided by Wunderlich, metastable crystalline phases may be classified as mesophases (Wunderlich, 2005). III) It was shown that different types of aliphatic crystallites can occur in SOM. These types differ in their origin, properties and presence of functional groups. More specifically, the presence of functional groups can increase interaction abilities of aliphatic crystallites in comparison with the chains forming crystals of synthetic polymers, e.g. polyethylene.

Interactions of aliphatic crystallites present in two different soils with chosen organic compounds were described in previous chapters in detail. The general pattern of interaction abilities of these crystallites and the resulting implications important for immobilization of organic chemicals in SOM are discussed in the following text. The application of four solvents (water, methanol, acetone and water) did not allow to apply statistical methods and to evaluate the quantitative contribution of individual interactions. However, on the bases of structural changes observed in this work and structure of aliphatic crystallites proposed from available literature (e.g., Chefetz et al., 2004; Turner et al., 2013), a general patter of interaction abilities of aliphatic crystallites can be determined. Considering that all applied solvents were able to interact with aliphatic crystallites and deliver chosen pollutant into their structures, although the solvents differed strongly in their interaction abilities. As can be seen in the Table S1 in the Annex, hexane cannot interact via H-donor and H-acceptor forces, however it possesses relatively big molecular volume (the volume of McGowan parameter) proposing good abilities to interact via Van der Walls forces (Abraham et al., 2002; Abraham and al-Hussaini, 2003; Israelachvili, 2011). In contrast, water has high H-donor and H-acceptor interaction abilities and small molecular volume. In spite of the differences in interaction abilities of water and hexane, both solvents are able to interact with aliphatic crystallites. This is in line with the suggested structure of aliphatic crystallites in SOM that is proposed to contain oxidized aliphatic chains possessing functional groups.

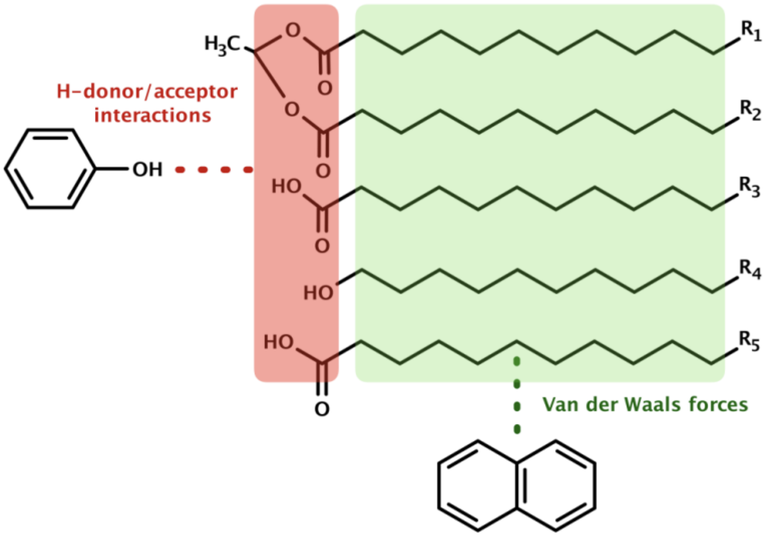

*Fig. 5.1 The proposed main interactions between organic molecules and aliphatic crystallites. Ordered carbon chains possessing functional groups (hydroxyl, carboxyl and ester group) represent a residue of crystalline biopolymer e.g., suberan or cutan. The green area shows a methylene part of the biopolymer without functionalities, interacting mainly via Van der Waals forces. The red background shows a part interacting via H-donor and H-acceptor forces. It is proposed that both, organic molecules with and without functional groups, as shown on phenol and naphthalene, are able to interact and penetrate different parts of aliphatic crystallites. The presented diagram is based on the proposed structure of subran and cutan provided by Turner, Hartman and Hatcher (2013) and Sachleben et al., (2004).*

Similarly to aliphatic crystallites, the presence of organic molecules in SOM influences properties of WaMB connecting individual molecular segments. The relation between the interaction abilities of organic molecules and the stability of WaMB were tested in the chapter 3. For evaluation of these interaction abilities, interaction parameters from LSER theory were used. The WaMB stability was assessed via temperature of WaMB disruption (T*) reflecting its thermal stability. As experiments with nine different solvents and two spiking chemicals showed, WaMB is less stable in the environment with H-donor and H-acceptor interaction abilities than WaMB in the environment without these abilities. Indeed, only the mentioned two interaction parameters were determined to be relevant for WaMB stability (see the table S4 in the Annex II). These results are in agreement with the computer modeling study performed by Aquino et al. predicting low WaMB stability in environments with a high dielectric constant (Aquino et al., 2011). Aforementioned results are thus in accordance with the hypothesis H2.

Also the structural mobility of SOM is influenced by the presence of organic molecules in SOM matrix. The structural mobility of SOM associated with WaMB was analyzed as a change of heat capacity (C*) during a WaMB disruption (see chapter 3). The mobility was influenced mostly by four interaction parameters in total (see the figure 5.2). The most significant influence showed the volume of the interacting molecules represented by the volume of McGowan. This suggests that large molecules, able to interact with SOM matrix via dispersion forces, contribute to SOM rigidity. WaMB stability and molecular mobility related to WaMB are thus influenced by different interaction parameters, as it is schematically shown in figure. 5.2. In addition, the WaMB stability and molecular segment mobility showed a relation in a large data set (see the figure 8 in chapter 3) and a linear regression revealed that only 37 % of the variability of C* is affected by T*. This is in line with the finding that the mobility of

SOM molecular segments is influenced also by other factors than WaMB stability. The hypothesis H3 is thus confirmed only partially.

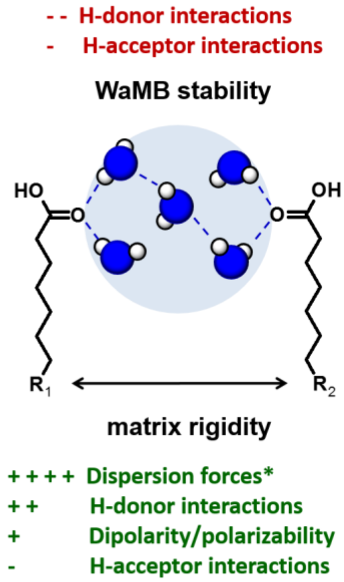

*Fig. 5.2 The influence of intermolecular interactions in SOM environment on WaMB stability and SOM matrix rigidity. Positive and negative influence is labeled via + and – sign, respectively. WaMB stability is influenced via H-donor and H-acceptor interactions with molecules forming their direct environment. The matrix rigidity is influenced via several types of interactions. *The main influence on matrix rigidity had volume of McGowan of interacting molecules, which suggests involvement of weak dispersion forces (Abraham et al., 2002; Abraham and al-Hussaini, 2003; Israelachvili, 2011).*

In previous paragraphs, it was shown that organic molecules interact with individual compartments of SOM, as exemplified on aliphatic crystallites and WaMB. It was further showed that these interactions subsequently lead to the modification of these SOM compartments and cause measurable changes of their structure and properties. In this part, the attention is paid to the sequestration potential of the chosen SOM compartments, aliphatic crystallites and WaMB.

Although the experimental approach presented in this work, do not allows to analyze the role of aliphatic crystallites in sequestration of organic molecules in SOM, a comparison of structure and properties of aliphatic crystallites with other SOM phases (e.g., glassy and rubbery phases) helps to anticipate their involvment in sequestration processes. The fundamental difference between glassy and rubbery domains is the degree of motional freedom of molecule segments, which determines the mechanisms of their interactions with extraneous molecules (Mao et al., 2002a; Mao et al., 2002b; Pignatello et al., 2006; Xing and Pignatello, 1997). The motional freedom in crystalline phases is significantly restricted and to some extend comparable with glassy phases (Schaumann, 2006; Wunderlich, 2005). This suggest that, if organic molecules penetrate crystalline phases, their mobility and sorption mechanisms can be similar with those absorbed in glassy phases. Presence of crystalline phases in SOM would thus enhance the sequestration potential. This hypothesis is in line with the assumption that a high degree of crosslinking in direct vicinity of aliphatic crystals causes non-linear sorption processes (Deshmukh, 2003). To evaluate this assumtion, further research focused on sorption processes related with aliphatic crystalline phases is needed. Since properties of individual SOM phases, including aliphatic crystallites, are directly associated with their unique structure, sorption processes should be studied in soil samples in their natural state.

In the chapter 4, a connection between WaMB characteristics and the desorption kinetics of phenol was assessed experimentally. On the bases of phenol distribution between its fast and slow desorbing fraction the hypotheses H4 was tested. The results did not support the assumption that WaMB direct phenol into specific SOM environment. However, the relation between WaMB stability and desorption time constants supported the hypothesis H5 assuming that slow desorption from pre-aged samples is caused by WaMB-based diffusion limitation in the SOM matrix. This supports the hypothesis that WaMB act as a desorption barrier hindering phenol desorption. This is in accordance with the main hypothesis that sequestration of organic chemicals is controlled by physicochemical SOM matrix aging where formation of WaMB plays a dominant role. The gradual formation of WaMB connecting individual SOM segments, subsequently leading to the restriction of phenol diffusion in SOM, is proposed and schematically shown in the figure 5.3.

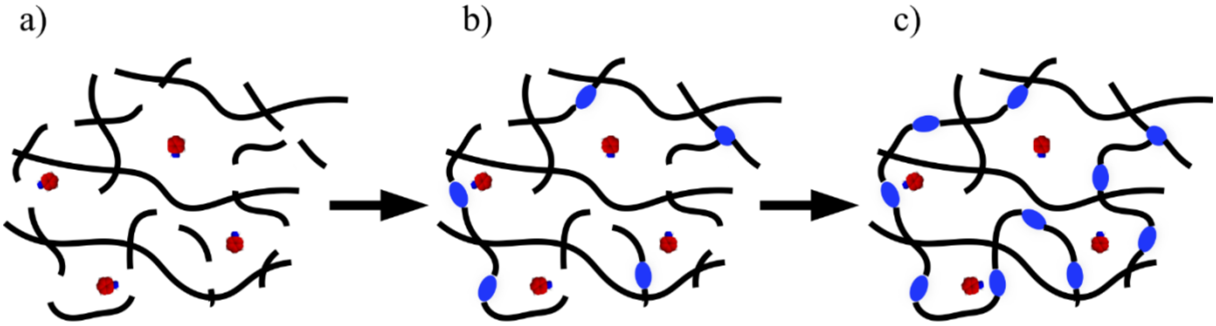

*Fig. 5.3 Proposed development of a physicochemical matrix aging contributing to the physical immobilization of phenol in SOM. Structure of SOM is represented via black curves, WaMB are depicted as blue ellipses and phenol is represented by red molecules. a) SOM matrix without WaMB that can be obtained by means of vacuum treatment. b) Formation of WaMB in SOM matrix. c) SOM matrix containing WaMB connecting individual segments that subsequently restrict diffusion of phenol molecules.*

The degree of physical immobilization of organic molecules via WaMB was assumed to be related to the ability of organic molecules to undergo H-donor and H-acceptor interactions, because molecules with these abilities decrease WaMB stability. Although, H-donor and H-acceptor interaction abilities of phenol are comparable with those of water (see the table S4 in the Annex II), WaMB are able to decelerate desorption of phenol from SOM matrix. Since molecules without H-donor and H-acceptor interaction abilities increase WaMB stability, a stronger immobilization potential of these molecules via WaMB can be expected. This suggests that WaMB are able to physically immobilize organic molecules with a broad range of interaction abilities.

### Outlook

Although WaMB and aliphatic crystallites are supramolecular assemblies strongly differing in their characteristics (e.g., molecular mass of their constituents and type of interactions acting between them), both assemblies dynamically respond to the presence of extraneous molecules and changes in environmental conditions. This observation is in accordance with the literature (e.g., Schaumann 2006a, Schaumann 2006b, Schaumann and Bertmer 2008) predicting enormous flexibility of SOM to environmental conditions, which results from SOM heterogeneity and inter- and intramolecular interactions acting between individual compartments. The findings provided in this thesis show that SOM is a highly dynamic system that evolves under the influence of environmental conditions and external factors, such as the presence of interaging molecules (e.g., small molecules penetrating SOM matrix) or temperature. SOM characteristics including sorption properties thus change with thermal history, moisture content and presence of interacting molecules. Our observations therefore suggest that fast and/or significant changes in moisture content and temperature would lead to a release of organic molecules. On the other hand, constant environmental conditions would contribute to the sequestration of organic molecules in SOM. This underlines the relevance of the intermolecular intercations and supramolecular structures for the understanding of sequstration processes in SOM.

Since WaMB are involved in the sequestration of organic chemicals in SOM, they could subsequently influence degradation processes, e.g. biodegradation, of organic chemicals in SOM. Desorption kinetics of organic molecules from soils often reveal two steps differing in desorption rate. The fast desorbable fraction is proposed to be available for microbial degradation (e.g., Cornelissen et al., 1998; Reid et al., 2000). The measurements of desorption kinetics of phenol described in this thesis, revealed a relation between WaMB characteristics and the fast and slow desorbing fraction of phenol. This suggests that WaMB might be important with regard to the biodegradation of organic molecules in soil. In the future research, the role of WaMB for bioavailability and biodegradation of organic molecules should be investigated.

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# Annex I

## Supporting Information to Chapter 2

## Supplementary data: “Influence of organic chemicals on aliphatic crystallites analyzed in whole soils”

Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E (2017) Geoderma 291 pp. 40-46

doi: 10.1016/j.geoderma.2016.12.016

# Annex II

## Supporting Information to Chapter 3

## Supplementary data: “Influence of organic chemicals on water molecule bridges in soil organic matter of sapric histosol”

Ondruch, P., Kucerik, J., Steinmetz, Z., Schaumann, G.E (2017) The Journal of Physical Chemistry A, 121(12), pp. 2367-2376

doi: 10.1021/acs.jpca.6b10207

# Annex III

## Supporting Information to Chapter 4

## Supplementary data: “Influence of water molecule bridges on sequestration of phenol in soil organic matter of sapric histosol

Ondruch, P., Kucerik, J., Tunega, D., Aquino A. J., Silva N. J., Schaumann, G.E

(Submitted, 2018) The Journal of Physical Chemistry A

Supporting Information for:

# Influence of water molecular bridges on sequestration of phenol in soil organic matter of sapric histosol

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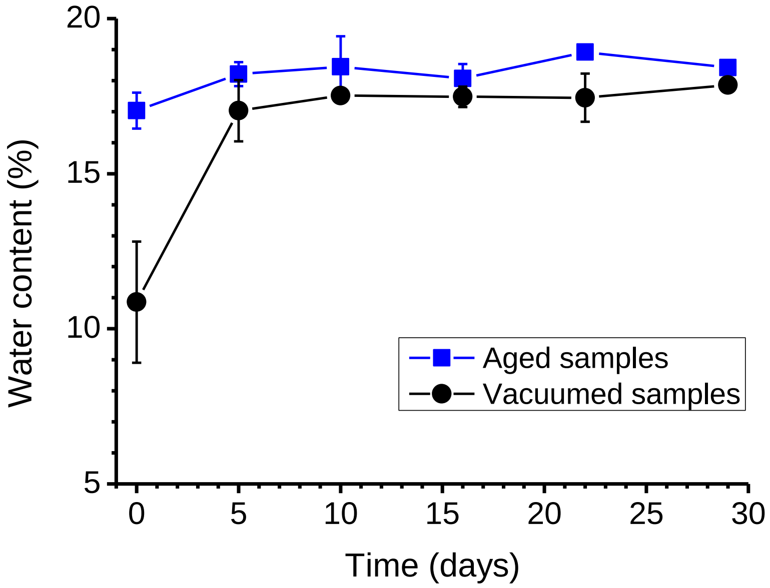

**Figure S1.** Development of water content in vacuumed and aged samples.

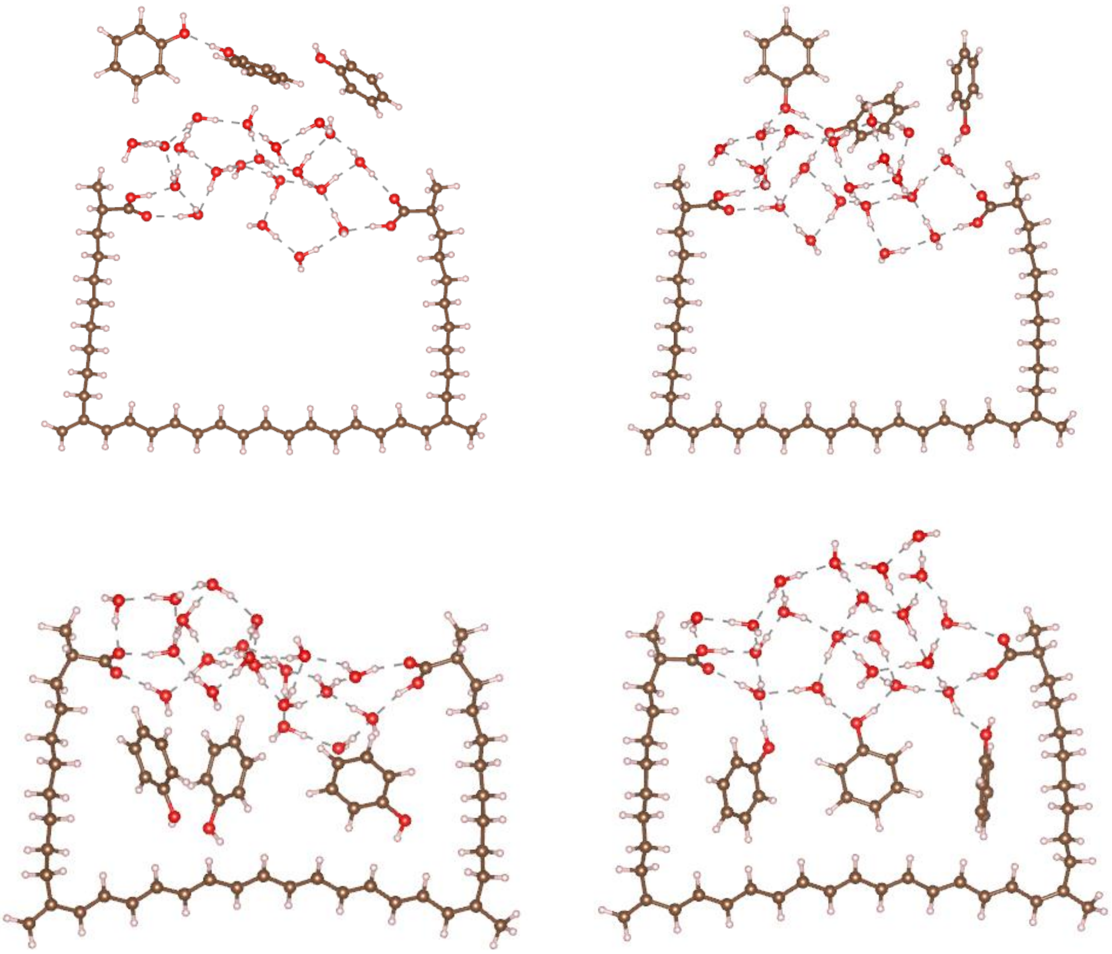

**Figure S2.** COSMO optimized geometries of phenol-WaMB-SOM with different mutual position of phenol molecules with respect to the WaMB chain (models 1-4 from left to right) in polar environment (methanol). Atom color scheme: C – brown, O – red, and H – white.

# Curriculum Vitae

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Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E (2017) Influence of organic chemicals on aliphatic crystallites analyzed in whole soils. Geoderma 291 40-46.

Ondruch, P., Kucerik, J., Steinmetz, Z., Schaumann, G.E (2017) Influence of organic chemicals on water molecule bridges in soil organic matter of sapric histosol. J. Phys. Chem. A.

## Publications in preparation

Ondruch, P., Kucerik, J., Tunega, D., Aquino, A. J. A., Nadeesha J. Silva, Schaumann, G.E, Influence of water molecular bridges on sequestration of phenol in soil organic matter of sapric histosol. (Submitted, 2018) J. Phys. Chem. A.

Kucerik, J., Ondruch, P., Mouvenchery, K. J. ,Schaumann, E. G., Role of water molecule bridges in filling of hydrophobic pores of soil organic matter under arid conditions.

**Oral presentations**

Ondruch, P., Kucerik, J., Jäger, A., Bertmer, M., Schaumann, G.E. Interaction of organic chemicals with crystalline soil aliphatic domains; German Soil science society – Annual meeting 2015, Munich, Germany

**Poster presentations**

Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E. Changes in the structure of sapric peat induced by presence of phenol; SPP 1315 – International Symposium 2014, Leipzig, Germany

Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E. Change in physical structure of a phenol-spiked sapric histosol observed by Differential Scanning Calorimetry; European Geoscience Union – General Assembly 2014, Vienna, Austria

Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E. Incorporation of organic chemicals in to the organic matter of sapric histosol observed by Differential Scanning Calorimetry; German Soil science society – Annual meeting 2013, Rostock, Germany

Ondruch, P., Jäger A., Kucerik J., Marko Bertmer, Schaumann, G.E. Incorporation of organic chemicals into the organic matter of sapric histosol observed by differential scanning calorimetry; SPP 1315 Annual Meeting - 2013, Jena, Germany