Restructuring of biogeochemical interfaces: Role of cations and heat treatment

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Abstract

The main objective of this study is to evaluate the impact of temperature and cation sorption on important physical and structural parameters of soil organic matter of a mineral soil and a peat. Sieved soil samples (< 2 mm) were stored under constant conditions (rel. humidity 31%, T = 20 °C) for at least 6 weeks. Matrix characteristics, surface properties and sorption characteristics are subjected to slow and continuous changes lasting for weeks and months. Dynamics in the field are expected to induce comparable processes affecting interfacial and bulk properties, which are, however, up to now unknown. Unravelling these processes will help to develop a mechanistic understanding of functioning of soil organic matter as biogeochemical interface with respect to wettability, sorption and biodegradation of organic chemicals.

Key words

soil organic matter, cations, aging, wettability, temperature treatment, sorption, soil pollutants, kinetics

Introduction

Interfacial and matrix properties of soil samples are subjected to slow and continuous changes lasting for weeks and months (Schaumann 2006).They are further affected by temperature, storage conditions and cation content. Dynamics of these factors in the field are expected to induce comparable processes, which are, however, up to now unknown. Unravelling these processes would help to develop a mechanistic understanding of functioning of soil organic matter as biogeochemical interface with respect to wettability, sorption and biodegradation of organic chemicals. Temperature treatment is expected to (i) accelerate the processes in soil and (ii) induce irreversible changes in the samples. Therefore, samples treated with different temperatures are expected to be different even after long storage times. The specific objective of this joint study is to understand the interplay between SOM-cation interactions, physicochemical aging and sorption of organic chemicals. We expect to observe cross-linking effects of cations (Schaumann, Lang *et al.* 2006) and aging effects (Schaumann 2006) resulting in increased matrix rigidity, contact angle and sorption capacity. Temperature treatment is expected to (i) accelerate the aging and restructuring processes in soil and (ii) induce irreversible changes in the samples

Material & methods

Sample preparation and cation and temperature treatment. The samples were taken from 2 sites, Totes Moor (sapric peat, "SP") and Lakwiese (Glyinc Podzol, "LW") and air-dried. The peat samples were ground after drying. All samples were sieved to < 2 mm and stored for at least 6 weeks at 31% RH and 20°C prior to cation treatment. For cation treatment, the samples were shaken for 3 hours with the ratio by weight of 1/10 for LW and 1/25 for SP. The following solutions were used: **control**: H2O dest., **"H⁺"**: H2O dest. + 30 g Amberlite®IR hydrogen form in gaze bags (PP-149/34), **"Na"**: 0.01 M NaCl, **"Ca"**: 0.01 M CaCl₂, **"Al"**: 0.01 M AlCl₃. Samples were shaken for 3 hours in a rotary shaker, filtered with a Büchner funnel and dried at 25 °C for 4 days and gently homogenized to destroy aggregates and crusts developed during drying. Subsamples were subjected to temperature treatment as follows: **"25"**: No further treatment, **"40"**: 2*12h in sealed bottles at 40°C, **"60"**: 2*12h in sealed bottles at 60°C, **"105"**: 0.5 h at 105°C in sealed bottles.

Then, the samples were stored isothermally at 20°C and 31% relative humidity for 1,2,4, 6 and 8 weeks. Samples were investigated for matrix properties, surface properties and sorption characteristics directly before and after the temperature treatment and after each point of time during aging. For the contact angle measurements, were heated after cation treatment described above to 40, 60, and 105 degrees in a drying oven for 24 hours and also fractionated into fraction < 63 µm. Samples were stored in PE containers and contact angle measurements were conducted within 2 days after storage. Repeated contact angle measurements were made after 8 and 12 weeks, respectively.

Matrix characteristics

Matrix rigidity was assessed by Differential Scanning Calorimetry (DSC) in terms of the glass transition-like step transition temperature (T*) as described by Hurrass & Schaumann (2005). The proton NMR relaxation time indicates the mobility of proton containing molecules. The shorter the relaxation time, the stronger water is bound or the smaller the pores are in which the water is confined. We determined transverse relaxation time T2 at 7.5 MHz with a Bruker minispec mq 7.5 employing the Hahn Spin Echo method. Longitudinal relaxation times were determined at 20 MHz using a fast field cycling relaxometer as described by Conte *et al*. (2009). Thermal decomposition profiles were analyzed with DSC in a ramp of -50°C to 550 °C with 10 K min^{-1} heating and synthetic air as purge gas (50 mL min^{-1}). DSC measured the energy transformation in the samples occurring during heating. In this experiment, the combustion process was monitored. This analysis gives insight into organic matter quality under the influence of the respective sample treatment with respect to thermal stability.

Contact angle

Contact angle was determined by Wilhelmy plate method (WPM) and by sessile drop method (SDM). For contact angle measurement via WPM (CA_{WPM}), samples were fixed on a rectangular glass slide completely covered by double sided adhesive tape and suspended from the balance of a Dynamic Contact Angle Meter and Tensiometer (DCAT 21, DataPhysics, Filderstadt, Germany), and contact angle was determined as descibed by Bachmann *et al*. (2000). For contact angle measurement via SDM (CA_{SDM}), a thin layer of the soil sample was attached to one side of a glass microscope slide using double sided adhesive tape (Bachmann, Ellies *et al.* 2000). CA_{SDM} was calculated from the tangent to the three-phase contact point associated with the ellipse that best fitted the drop shape (Bachmann, Ellies *et al.* 2000; Diehl and Schaumann 2007).

Sorption characteristics

Batch trials according to the OECD Guideline 106 were conducted in 0.01M CaCl$_2$-solution at soil-to-solution ratios of 1:10 (LW) and 1:20 (FS). The model xenobiotics, Naphthalene and Naphthalene-2,7-diol, were added at 10µmol/L and sorption kinetics were recorded at time steps of 0.5, 1.0, 2.0, 4.0, 8.0, and 24 h. Kinetics in each of the two soils were tested with and without cation treatment using NaCl, and after additional heat treatment at 40 and 60°C, respectively, and aging for 0, 2, and 4 weeks.(= 24 soil variants). In another experiment, the radiolabel xenoestrogen compound Nonylphenol was used to determine sorption properties of treated and aged soils. Directly after the temperature treatment (40, 60 or 100°C) and after 2 and 4 weeks of storage 2 g of controls and sodium chlorite treated samples were used for sorption experiment in Teflon chambers. The soil was separated in one half-chamber by membrane with MWCO 1 kDa of the Nonylphenol water solution (soil:liquid 1:5) using NaN$_3$ to prevent microbial activity. After 22 h of shaking on over-head shaker the aliquot of pure radioactive solution was mixed with scintillation cocktail (Ultima Gold LSC-cocktail, Packard Bioscience, USA) and analyzed for 14C activity by liquid scintillation counting (Beckmann LS 6000 TA). Based on the measurements the carbon normalised partition coefficient (Koc) was calculated.

Zeta potential of dispersible colloids.

Colloids were extracted with doubly deionised water (soil/solution ratio 1:10). After shaking for 16 h the samples were centrifuged (cut off 1 µm for particles with the density of 2 g cm^{-3}) and the zeta potential and the size distribution of the colloids was determined with a Zetasizer 2000 (Malvern Instruments) and photon correlation spectrometer (Malvern).

Results & discussion

The temperature treatment has strong effects on matrix rigidity, contact angle and sorption characteristics, and cation treatment shows significant differences in OM thermal decomposition profiles.

Figures 1 A and B show that the same sample can significantly increase its contact angle by the simultaneous impact of temperature and Al^{3+}. The coarse fraction 2000-63 µm is more hydrophobic than the total soil and less affected by the described impact factors. We also observed an effect of aging, since all samples showed larger contact angles after 2 months, especially after treatment with higher valent cations Ca^{2+} and Al^{3+} (data not shown) . These changes obviously also affect the sorption characteristics (Figures 1E and 1F), since with increasing time the corresponding K_{oc} value increased for the investigated samples LW and SP, respectively. Comparably, we observed strong effect of the temperature treatment on matrix rigidity expressed by the step transition temperature (Figure 1C), while the cation effect was significantly less expressed.
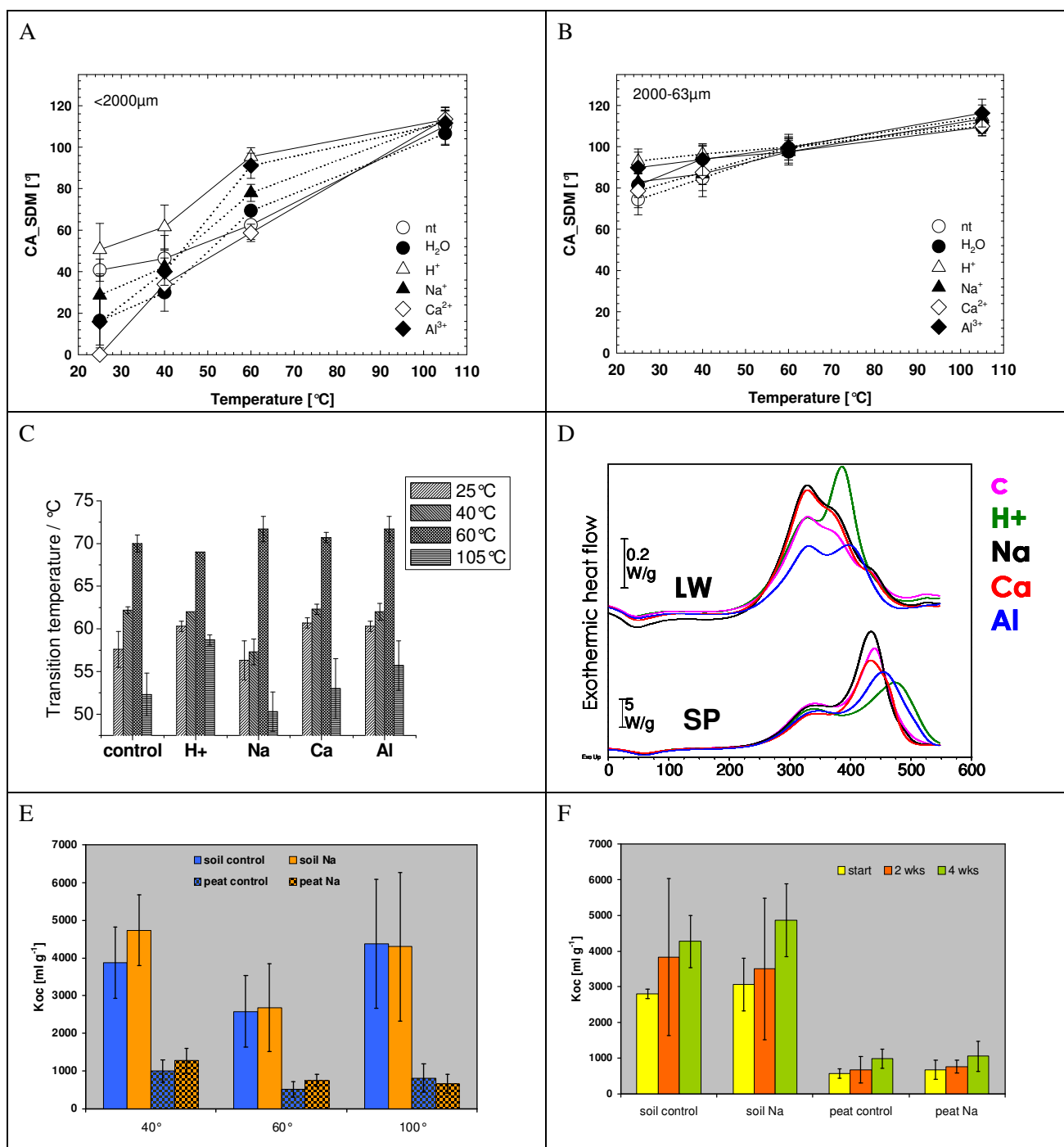

Figure 1: Contact angles of the sieved (<63 µm; A) and coarse (2000-63 µm; B) fraction, DSC step transition temperature of the treated SP sample (C), thermal decomposition profiles of treated LW and SP samples (C). E, F: Nonylphenol sorption characteristics of the treated samples.

Sorption of Naphthalene and Naphthalene-2,7-diol to a different soil was enhanced in aged samples and correlated with SOM matrix rigidity and coefficients of fast soil sorption (data not shown). Therefore, we also presume clearly enhanced sorption to the aged and heated soil samples, respectively, in this experiment, since both treatments increase matrix rigidity.

The results thus indicate significant effects of temperature pre-treatment, aging and cation treatment on numerous properties which are relevant for biogeochemical interfaces. However, the cation effects on sorption characteristics and contact angle are less pronounced but not negligible. Aging effects can be observed at least for matrix rigidity, NMR relaxation times (data not shown) and for sorption characteristics as well as for contact angles. The differences are significant, and interpretation and requires further discussion. Cation treatment changes organic matter stability. But surprisingly, it appears to have lower effects on matrix rigidity and contact angle than the temperature pre-treatment. Cation effects may even disappear almost completely upon temperature treatment at 105°C. Temperature pre-treatment above 40°C was shown to have sustainable effects on contact angle, matrix rigidity, but effects were also observable in the 40°C treatment.

These partly unexpected results need to be discussed in more detail after complete evaluation. Under the impact of temperature, the sample may change its behaviour from good wettable to strongly hydrophobic, which is in line with frequent observations after wildfires.

First conclusions

Our results proof the dependence of the supramolecular properties of soil organic matter from environmental conditions and the conditions of sample storage. These properties determine the functioning of biogeochemical interfaces. To fully understand the functioning of biogeochemical interfaces the processes of aging of labile structures in organic matter have to be identified by further investigations.

Further emphasis will be laid on comparison of the findings with designed model soil compounds in all groups in order to verify hypotheses deduced from the results of this joint experiment. It should also the focus of further investigations, if the observed effects are reversible, i.e. can be reproduced after rewetting and drying like in natural soil. Combining various properties relevant for biogeochemical interface functioning in samples prepared after exactly the same protocol in various groups, this joint research will help to provide a mechanistic understanding of the relevance of labile structures in organic matter for functioning of biogeochemical interfaces. However, at the present state it might be concluded, that time, temperature as well as higher-charged cations like Al^{3+} modified the structure of the entire organic matter towards more hydrophobicity. This effect is not restricted to the surface or the interphase, since structural properties like glass transition temperature or the DSC signal of the bulk samples are also affected by the described impact factors. We conclude further that some important properties of soil samples are strongly affected by storage temperature and time.

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