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Physicochemical aging mechanisms in soil organic matter assessed by NMR and DSC

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Soil organic matter (SOM) controls a variety of processes occurring at biogeochemical interfaces acting as a highly dynamic matrix. Results from previous studies showed that SOM undergoes physicochemical matrix aging. It was hypothesized that the formation and disruption of water molecule bridges are responsible for this aging process. The objective of this study was to evaluate this hypothesis using three peat samples from different sample sites in Germany: a peat from Rhinluch, 60 km northwest of Berlin, a black peat and a white peat from Fuhrberg near Hannover. The composition determined by pyrolysis field ionisation mass spectrometry was similar for the Rhinluch peat and the Fuhrberg black peat, but showed a distinctly higher carbohydrate content for the Fuhrberg white peat.

To elucidate mechanisms of physicochemical matrix aging and to evaluate the hypothesis of water molecule bridges we carried out heating-cooling events in hermetically sealed containers and measured the response by NMR and DSC as a function of time. The heating-cooling event started with heating for 10 minutes at 110 °C followed by rapid cooling and isothermal storage at 19 °C for at least four months.

All peats show a non-reversing step transition between 40 °C and 65 °C similar to transitions observed in previous studies. The black peat from Fuhrberg showed an additional step transition between 35 °C and 45 °C. The temperature of the non-reversing step transition immediately decreased by 25 °C in response to the heating-cooling event and slowly re-increased upon isothermal storage within several months. The temperature of the reversing transition showed a similar behaviour but not as strongly as the non-reversing transition.

The proton NMR in combination with line separation into Lorentz and Gauss lines was used to differentiate between the different kinds of water. In dependence of the water bridge status the portions of these lines on the total wide line spectrum change; at a higher amount of movable water the portion of the Lorentz line, as an indicator for the movable water molecules, should increase. The separation of the proton NMR wide line spectra for the Rhinluch peat into the different lines showed the expected behaviour but for the Fuhrberg black peat the opposite effect was observed.

The results of the differential scanning calorimetry support the hypothesis that water molecules bridge molecular segments of soil organic matter. The proton NMR-measurements for the Rhinluch peat also supports this hypothesis, while the NMR-results for the Fuhrberg peat are contradicting it. This contribution discusses potential explanations for these (partly unexpected) results.