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Interactions between cations and peat organic matter monitored with NMR wideline, static and FFC NMR relaxometry

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The molecular size of humic substances is still under debate and is believed to range up to several hundred thousands Dalton, although a number of recent studies suggest much lower molecular weights. Nowadays an increasing number of authors suggest a model of molecular aggregates. One explanation why results on the molecular mass of humic materials are contradictory, may be that individual OM molecules are linked via intermolecular interactions, by bridges of water molecules or by cations bridging cation exchange sites (Schaumann, 2006a, b). Properties of such cross-linked systems can be similar to macromolecular systems revealing covalent cross-links. In this context, multivalent cations play an important ecological role, serving as reversible cross-linking agent. Formation and disruption of such cation bridges may close or open sorption sites in soil organic matter. Although cross-linking by multivalent cations has been proposed in many studies, the cross-linking effect has not yet been demonstrated on the molecular scale.

The objective of this study was to investigate the interactions between cations and peat organic matter using NMR wideline techniques as well as static and fast field cycling (FFC) NMR relaxometry. Peat treated with solutions containing either Na^+, Ca^{2+} or Al^{3+} was investigated in air-dried state for longitudinal relaxation times (T1) and NMR wideline characteristics. T1 distributions were separated into two Gaussian functions which were interpreted to represent two proton populations belonging to two environments of differing mobility. The relaxation rates ($R1 = T1^{-1}$) in the cation treated samples spread over a range of 87-123 s^{-1} (R1a: fast component) and 32-42 s^{-1} (R1b: slow component). The rates in all treatments are significantly different from each other. <R1a> and <R1b> decrease in the order conditioned sample > desalinated sample > Na-treated sample. The treatment with multivalent cations affects R1a and R1b in different ways and needs more detailed explanation. Wideline proton NMR spectra can be used to quantify proton containing material, mainly water, based on their mobility. Spectra were decomposed into a Gaussian and Lorentzian line and changes to mobility after heat treatment indicate the water binding strength. In this study, differences in the various NMR parameters on the cation treatments will be presented and discussed with respect to the crosslinking hypothesis.