



Conformational behaviour of humic substances at different depths along a profile of a Lithosol under loblolly (*Pinus taeda*) plantation

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The conformation of natural organic matter (NOM) plays a key role in many physical and chemical processes including interactions with organic and inorganic pollutants and soil aggregates stability thus directly influencing soil quality. NOM conformation can be studied by solid state NMR spectroscopy with cross polarization and magic angle spinning (CPMAS NMR). In the present study we applied CPMAS ^{13}C NMR spectroscopy on three humic acid fractions (HA) each extracted from a different horizon in a Lithosol profile under *Pinus taeda*. Results showed that the most superficial HA was also the most aliphatic in character. Amount of aromatic moieties and hydrophilic HA constituents increased along the profile. Cross polarization (TCH) and longitudinal relaxation protons times in the rotating frame ($T_{1\rho}(\text{H})$) were measured and compared only for the NMR signals generated by carboxyls and alkyls. This because the signal intensity for the aromatic, C-O and C-N systems was very low, thereby preventing suitable evaluation of TCH and $T_{1\rho}(\text{H})$ values for such systems. The cross polarization times of carboxyls decreased, whereas those of the alkyl moieties increased with depth. Conversely, $T_{1\rho}(\text{H})$ values increased for both COOH and alkyl groups along the profile.

Polarization transfer from protons to carbons is affected by the dipolar interactions among the nuclei. The stronger the H-C dipolar interaction, the faster is the rate of the energy exchange. All the factors affecting the dipolar interaction strength also influence the rate of magnetization transfer. Among the others, fast molecular tumbling and poor proton density around the carbons are responsible for long TCH values. Molecular tumbling and proton density also affect $T_{1\rho}(\text{H})$ values. Namely, the larger the molecular tumbling and the proton density, the faster is the proton longitudinal relaxation rate in the rotating frame (shorter $T_{1\rho}(\text{H})$ values).

The decrease of TCH values of COOH groups along the profile was attributed to an increased rigidity of the carboxyl systems. Very likely COOH groups may form hydrogen bondings with other hydrophilic HA components that were progressively revealed at deeper depths. On the other hand, increasing of TCH values of alkyl components was explained with a progressive enhancement of branched chains number. In fact, branches may favor molecular flexibility, thereby enabling faster molecular tumbling and longer cross polarization times. Since the amount of branched chains in the alkyl moieties appeared to increase from the top to the bottom of the soil horizons, the amount of poorly protonated carbons placed in the branch nodes also increases with soil depth. For this reason, proton spin diffusion becomes more difficult and $T_{1\rho}(\text{H})$ values increase with the soil depth. Reduced protonation degree may also account for increasing $T_{1\rho}(\text{H})$ values of COOH groups.

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