



New understanding of cross-polarization dynamics in amorphous and heterogeneous natural organic substances

P. Conte (1) and A. E. Berns (2)

(1) Dipartimento di Ingegneria e Tecnologie Agro-Forestali (DITAF), Università degli Studi di Palermo, v.le delle Scienze 13, 90128 Palermo, Italy (pellegrino.conte@unipa.it / Fax: +39 091-484035), (2) Forschungszentrum Jülich GmbH, Institute of Chemistry and Dynamics of the Geosphere, Institute 4: Agrosphere, 52425 Jülich, Germany

Two humic acids were extracted from a soil (soil-HA) and a coal (coal-HA) and variable contact time (VCT) NMR experiments were performed. We verified that the classical monotonic cross-polarization (CP) mechanism was unable to explain the shape of the VCT curves. For this reason a non-monotonic model providing two different CP rates was built and used to fit the VCT data. The non-monotonic model fitted the experimental results better than the classical one. The two cross-polarization rates from the new non-monotonic model were associated with different proton-to-carbon transfer rates. The first one was a fast H→C energy transfer due to protons directly bound to carbons, whereas the second was associated to a slow H→C magnetization transfer mediated by local segmental motions. According to this new model, different humic domains were differentiated. In fact, we suggested that soil-HA was made mainly of rigid domains containing both aromatic and carboxylic moieties, bound to fast moving domains containing alkyl, C-O and C-N groups. On the other hand, coal-HA was made by a rigid aromatic domain surrounded by a very mobile domain containing alkyl and COOH groups. We suggest that the non-monotonic CP model should be used for interpreting the cross-polarization dynamics of humic substances if the classical monotonic model fails to fit the experimental VCT results.