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Application and Reliability of Solid-State NMR in Environmental Sciences

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For the characterization of soil organic matter, a suite of analytical approaches are available. Chemical degradative methods involve an extraction scheme with which the soluble part of the mixture is isolated and analyzed by colorimetrical or chromatographic means. Macromolecular structures can be subjected to thermolytic or combined thermochemolytic degradation. Because secondary reactions (rearrangement, cracking, hydrogenation and polymerization) in a heterogeneous mixture cannot be excluded, it is obvious that conclusions regarding the original structure in the macromolecular phase have to be drawn with caution. A powerful alternative represents solid-state nuclear magnetic resonance (NMR) spectroscopy, allowing the examination of the bulk sample without major pre-treatment In environmental sciences, this technique mostly involves the isotope 13C to study the chemical composition of organic matter in soils, sediments or compost to study the temporal development of humic material or chemical alterations due to variation in environmental parameters. Due to its low sensibility solid-state 15N NMR studies on such samples are only found occasionally. The emphasis of solid-state NMR spectroscopy is not only to determine the gross chemical composition of the material under study via a chemical shift assignment but also a quantitative correlation between the different signal intensities and the relative contribution of the respective C or N types to the total organic C or N content. However, despite increasing popularity, this approach is still viewed as mysterious techniques, in particular with respect to quantification. Accordingly, the purpose of this review is to give a short overview on the possibilities and limitations of this technique in environmental science and in particular for the study of soil organic matter.

In general, solid-state 13C NMR spectra of soil organic matter are obtained with the cross polarization magic angle spinning (CPMAS) technique. This technique increases the sensitivity of 13C by magnetization transfer from the 1H to the 13C spin system during a contact time tc. However, one has to bear in mind that some molecular properties may obscure quantification. Thus, for carbons with large C–H internuclear distances (bigger than four bonds, i.e in graphite structures) and for C in groups with high molecular mobility (i.e. gas) the proton-dipolar interactions are weakened and the polarization transfer may be incomplete. The observed intensity can also be affected by interactions of the protons with paramagnetic compounds. To circumvent this problem, the samples are often demineralized with hydrofluoric acid. Alternatively, the Bloch decay, a technique in which the 13C is directly excited is used. Here, on the other hand, one has to consider long relaxation times which may lead to saturation effects.

Nevertheless, as it will be discussed within the presentation those quantification problems can be solved for most soil samples and then solid-state NMR spectroscopy represents a powerful tool for qualitative and quantitative analysis. Special techniques, such as dipolar dephasing or the proton spin relaxation editing can be used to extract additional information about chemical properties or mobility. A more detailed examination of the cross polarization behavior can be used to analyze the interaction of organic matter and paramagnetics but also for obtaining revealing properties on a molecular level. Applications involving isotopic labeling combined with both 13C and/or 15N NMR allows to follow the fate of a specific compound i.e. in a natural matrix and- if the enrichment is high enough – the use of 2D solid-state NMR techniques. In particular with respect to environmental chemistry, this combination of isotopic labeling with the use of corresponding NMR spectroscopy shows great potential for a better understanding of the kind of interaction between pollutants and natural organic matter.