

## **NMR doesn't lie or how solid-state NMR spectroscopy contributed to a better understanding of the nature and function of soil organic matter (Philippe Duchaufour Medal Lecture)**

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“Nuclear magnetic resonance (NMR) does not lie”. More than anything else, this statement of a former colleague and friend has shaped my relation to solid-state NMR spectroscopy. Indeed, if this technique leads to results which contradict the expectations, it is because i) some parts of the instrument are broken, ii) maladjustment of the acquisition parameters or iii) wrong preparation or confusion of samples. However, it may be even simpler, namely that the expectations were wrong. Of course, for researchers, the latter is the most interesting possibility since it forces to reassess accepted views and to search for new explanations. As my major analytical tool, NMR spectroscopy has confronted me with this challenge often enough to turn this issue into the main subject of my talk and to share with the audience how it formed my understanding of function and nature of soil organic matter (SOM).

Already shortly after its introduction into soil science in the 1980's, the data obtained with solid-state  $^{13}\text{C}$  NMR spectroscopy opened the stage for ongoing discussions, since they showed that in humified SOM aromatic carbon is considerably less important than previously thought. This finding had major implications regarding the understanding of the origin of SOM and the mechanisms by which it is formed. Certainly, the discrepancy between the new results and previous paradigms contributed to mistrust in the reliability of solid-state NMR techniques. The respective discussion has survived up to our days, although already in the 1980's and 1990's fundamental studies could demonstrate that quantitative solid-state NMR data can be obtained if i) correct acquisition parameters are chosen, ii) the impact of paramagnetic compounds is reduced and iii) the presence of soot in soils can be excluded. On the other hand, this mistrust led to a detailed analysis of the impact of paramagnetics on the NMR behavior of C groups which then improved our understanding of the role of carbohydrates for organo-mineral interactions. Since decent solid-state NMR spectra cannot be obtained from graphenic components, the successful acquisition of solid-state  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra of charcoals challenged the well accepted model of their chemical nature. Application of advanced 2D NMR approaches confirmed the new view of charcoal as a heterogeneous material, the composition of which depends upon the feedstock and charring condition. The respective consequences of this alternative for the understanding of C sequestration are still matter of ongoing debates. Although the sensitivity of  $^{15}\text{N}$  for NMR spectroscopy is 50 times lower than that of  $^{13}\text{C}$ , first solid-state  $^{15}\text{N}$  NMR spectra of soils with natural  $^{15}\text{N}$  abundance were already published in the 1990's. They clearly identified peptide-like structures as the main organic N form in unburnt soils. However, in spite of their high contribution to SOM, the role of peptides in soils is far from understood. Considering the new technological developments in the field of NMR spectroscopy, this technique will certainly not stop to contribute to unexpected results.