

Application of ^1H HR/MAS NMR to Soil Organic Matter Studies

L. A. Colnago, L. Martin-Neto

Embrapa Instrumentação Agropecuária, São Carlos, SP, Brazil

M. G. Pérez*

Embrapa Instrumentação Agropecuária, São Carlos, SP; Universidade de São Paulo
Instituto de Química de São Carlos, SP, Brazil
marta@cnpdia.embrapa.br

C. Daolio, A. G. Ferreira

Universidade Federal de São Carlos, SP, Brazil

O. A. Camargo, R. Berton

Instituto Agrônomo de Campinas, Campinas, SP, Brazil

W. Bettiol

Embrapa Meio Ambiente, Jaguariúna, SP, Brazil

Keywords: ^1H HR/MAS NMR, soil organic matter

Abstract: *NMR is a powerful technique that allows the characterization of organic matter (OM) components directly in whole soils, providing important information on those complex materials with irregular structures and strong physical and chemical links to mineral matter. The aim of the present work is to evaluate the application of proton high-resolution magic angle spinning nuclear magnetic resonance (^1H HR/MAS NMR) to soil organic matter studies. The use of ^1H HR/MAS NMR allows studying aliphatic hydrogens in humin, humic acids and the granulometric fraction with higher carbon content. It is worth noting that humin is the insoluble component of soils, cannot be studied using liquid NMR, and has a tight association with metals and minerals that interfere in solid state NMR even after strong HF treatment. This technique seems to be a new option in OM studies, opening new possibilities for evaluating effects of agricultural managements.*

NMR is a powerful technique that allows the characterization of organic matter (OM) components directly in whole soils, providing important information of those complex materials with irregular structures and strong physical and chemical links to mineral matter. ^{13}C solid state NMR is the technique most currently used for the characterization of OM of soils because it allows the study of humic substances including insoluble fractions and humin. It is also suitable for examination of OM without any chemical treatment.¹

OM contributes to most chemical, physical and biological properties of soils. It is very important to elucidate the structure of humic substances as much as it is to evaluate

qualitative and quantitative changes that take place in OM soil caused by agricultural management systems.²

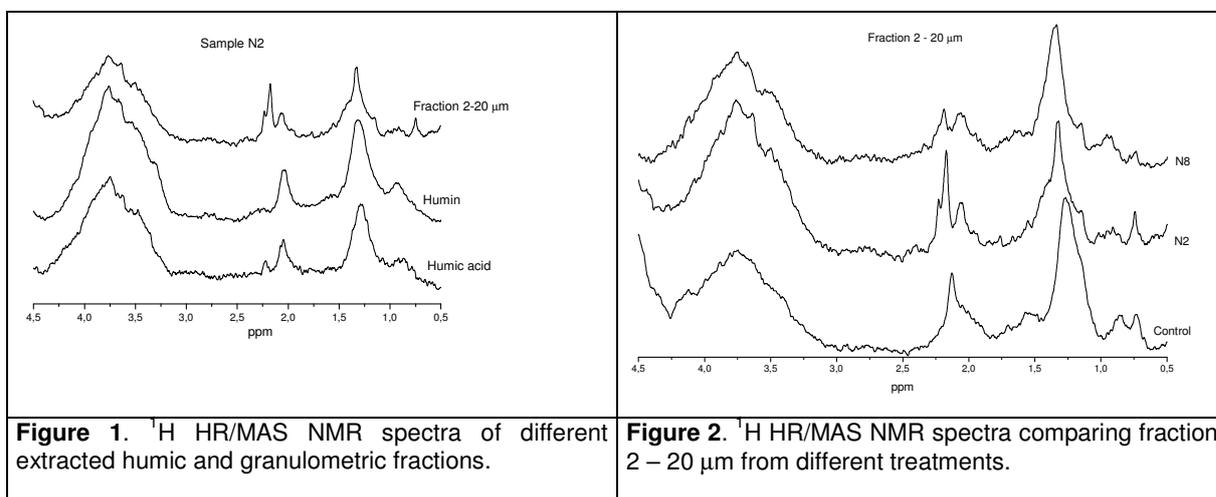
Aggregates are the structural units of soils. In tropical soils, aggregates consist of minerals, mainly iron and aluminium oxides, and organic compounds;³ they also contribute to soil properties such as structural stability, resistance to erosion, water infiltration and retention, thermal properties, and arrangement of pores that influence water and oxygen availability. Aggregates thus control stability of OM against biological attack. Therefore, it is very important to study the distribution of OM within the mineral matrix of soil (granulometric fractions), where there is a tight association

between organic and mineral fractions of soil. The aim of the present work is to evaluate the application of proton high resolution magic angle spinning nuclear magnetic resonance (^1H HR/MAS NMR) to soil organic matter studies.

All measurements were performed on a BRUKER DRX400, 9.4 Tesla, equipped with a HRMAS probe, at 298K. The samples were confined in a Zirconium rotor with 4mm diameter. The homogeneity of the magnetic field was adjusted using D_2O , and TSPAd4 was used as internal reference. The following parameters were used: Bloch decay using a 90° pulse (11.8 μs), spectral window: 5208 Hz, recycle delay: 1 s, acquisition time: 3.1 s and 32 K data points. The FIDs were zero filled and filtered by an exponential function with line broadening 10 Hz.

Soil samples were collected from the superficial layer (0 - 20cm) of an Oxisol from

the experimental Station of the Embrapa - Center for Environmental Research in Jaguariuna, SP, Brazil. The field experiment evaluated different doses of sewage sludge, and the sewage sludge originated from urban wastes that had been treated at the sewage sludge treatment station of Franca, SP. The following treatments were selected: *control soil* (untreated soil) and two treatments, *N2* and *N8*, equivalent to 2 and 8 doses of N mineral fertilization. The IHSS method was used for the extraction of humic substances from soil, and a combination of wet sieving and sedimentation was used for particle size fractionation. Four fractions were separated: sand fraction $> 53 \mu\text{m}$, one clay fraction $< 2 \mu\text{m}$ and two silt fractions 2 - 20, 20 - 53 μm . All samples were treated with 10% HF solution using a soil with an acid ratio of 1:8. The results shown in Figure 1 and 2 are preliminary.



The spectra show broad band signals, probably due to the presence of polymeric materials that prevent a simple structural elucidation.⁴ All spectra showed basically the same signals, indicating the presence of the same species at different concentrations. In

the region δ 4.2 - 3.3, there is a broad band probably associated to methyl or methylene groups linked to N or O atoms⁴. The two singlets at δ 2.17 and 2.05 can be attributed to CH_2 and CH_3 groups, respectively, linked to $-\text{CONR}_2$, $-\text{COOR}$ or $-\text{COR}$. The band at δ 1.30

is mainly associated to aliphatic CH₂. In the region δ 9.5 - 6.0 no signals were observed, thus indicating that aromatic hydrogens with lower mobility are difficult to detect.

The use of ¹H HR/MAS NMR makes possible the study of aliphatic hydrogens in humin, humic acids, and the granulometric fraction with higher carbon content. It is worth pointing out that humin is the insoluble component of soils and cannot be studied using liquid NMR. It has a tight association with metals and minerals that may interfere in solid state NMR, even after strong HF treatment. Therefore, this technique seems to be a new option in OM studies, opening new possibilities for evaluating effects of agricultural managements.

Acknowledgements

The authors acknowledge EMBRAPA, FAPESP and CNPq/PACDT.

References

1. C. M. Preston, *Soil Sci.* **145** (1996), 161.
2. F. J. Stevenson, *Humus chemistry: genesis, composition, reactions*. John Wiley: New York, 1994.
3. J. Tarchitzky, P.G. Hatcher, Y. Chen, *Soil Sci.* **165** (2000) 328.
4. E. Guimarães, A. S. Mangrich, V. G. Machado, D. G. Tragheta, M. A. Lobo, *J. Braz.Chem. Soc.* **734** (2001) 12.