

---

**FINAL REPORT - LONG-TERM EXCHANGE VISIT**  
**MOLTER PROGRAMME – ESF**

---

|                  |   |
|------------------|---|
| Reference number | 3696  |
| Project title    | Stabilization of SOM in Umbric Ferralsol of South Brazil: characterization by $^{13}\text{C}$ -NMR and their relationship with mineral components |
| Dates of visit   | 01.06.2012 - 30.11.2012   |
| Applicant        | Marta Velasco Molina<br>Departamento de Edafología y Química Agrícola<br>Universidade de Santiago de Compostela, 15782, Spain                     |
| Host             | Dr. Anne Berns<br>Forschungszentrum Jülich GmbH, ICG-4<br>52425 Jülich, Germany   |

---

### **Purpose of the visit**

With the performed study I intended to contribute to our knowledge of the impact of climate, vegetation and mineralogy on the content and composition of soil organic matter (SOM) in Umbric Ferralsols by the use of solid-state cross polarisation (CPMAS)  $^{13}\text{C}$  NMR spectroscopy. A special emphasis was given to the impact of charred material and the content of iron and aluminium oxides.

The aim of the stay was to increase my theoretical knowledge about solid-state  $^{13}\text{C}$  CPMAS NMR spectroscopy. This included in particular the importance of acquisition parameters which are relevant for obtaining reliable spectra and how NRM data can be applied in soil science studies.

The suggested research was conducted to complement data already obtained in the frame of my Doctoral Thesis and to improve their interpretation and reliability.

### **Description of the work carried out during the visit**

During my visit of the Forschungszentrum Jülich, Germany, Dr. Anne Berns supervised my activity and provided an intense training on basic theoretical knowledge of NMR spectroscopy which allowed me an independent use of the NMR spectrometer of the facility.

I analyzed the organic matter of Umbric Ferralsols of Southern Brazil, derived from locations described in Table 1. Prior to the visit, soil material of each horizon of two profiles was collected, dried at room temperature, subsequently sieved at 2 mm and homogenised.

Table 1. Description of study areas

| Profile | location  | altitude | climate | annual mean rainfall | annual mean T <sup>a</sup> | vegetation                              |                     |
|---------|-----------|----------|---------|----------------------|----------------------------|---|---------------------|
|         |           | m        | Köppen  | mm                   | °C                         | original                                | current             |
| P5      | Viracopos | 660      | Cwa     | 1372                 | 21,4                       | subtropical savanna                     | protected area      |
| P18     | Chapecó   | 632      | Cfa     | 1954                 | 18,9                       | subtropical moist forest with Araucaria | agricultural (mate) |

Selected samples were analysed by solid-state <sup>13</sup>C NMR spectroscopy (Unity Inova NMR Spectrometer 300 MHz), operating with a spinning speed of 8 kHz. A Fourier transformation was applied. Aside from routine CPMAS NMR spectra, Bloch decay experiments and relaxation time measurements were performed to adapt the acquisition parameters to the requirements of the samples.

To improve the quality of the solid-state <sup>13</sup>C NMR spectra the samples were demineralised with hydrofluoric acid solution. This treatment increases the concentration of organic matter and minimises mineralogical interferences, for example by paramagnetic compounds. In order to identify contributions of black carbon, the HF-treated samples were subjected to chemical oxidation (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 60 °C, 6h). The aromatic C content remaining in the residue was assigned to charred material and quantified by NMR spectroscopy (Knicker *et al.*, 2007).

In order to analyse the NMR data, an intensive training of the specific software (MestReNova) was carried out.

Further, I was instructed in the use of statistical tools (multivariate statistic analysis) to study the relationship between C content, quality of the SOM, mineral fractions and other environmental variables that can influence SOM formation (climate, geology, vegetation,...).

## Description of the main results obtained

### *Soil parameters*

The studied soils are acid (pH ≈ 5.0) and their pH values increase with depth. They are mainly clayey. The soil from Viracopos (P5) shows a high clay content of 43 - 58 % and a sand contribution of 41 - 50 %. The proportion of clay in the soil from Chapecó (P18) is between 69 and 78 % and its silt contribution is with 18 - 27 % higher than that of P5. The latter is a dark

brown (7.5YR) and reveals the same colour along the profile. The soil P18 is reddish (2.5YR and 10R).

During sampling, charred residues were found in the soil from Viracopos. They were distributed irregularly and present at all depths along the profile. Further to soil regions with more elevated density were detected between 65-80 cm and 100 cm in depth.

Due to the fact that the analysis and interpretation of the data is still in process, the data shown below have to be considered preliminary.

*C content and its relationship to Fe and Al*

The elemental analysis show that in P5, the total C ( $C_T$ ) content ranged between 41 and 7  $g\ kg^{-1}$  and are decreasing gradually with depth (Figure 1.a), which is expected in this kind of soils (Ker, 1997). The data reflected a high capacity to stock C. The content of  $C_T$  followed a similar behaviour in P18, but with slightly lower values ( $36 - 5\ g\ kg^{-1}$ ).

The total iron ( $Fe_T$ ) content remains constant until the bottom horizon, whereas the total aluminium ( $Al_T$ ) content increases slightly along the profile of Viracopos (Figure 1.a). The minimum vertical variation of Fe is classical in Ferralsols and the behaviour of Al points to the high presence of gibbsite into the clay fraction of the deeper horizon (Eswaran & Tavernier, 1980).

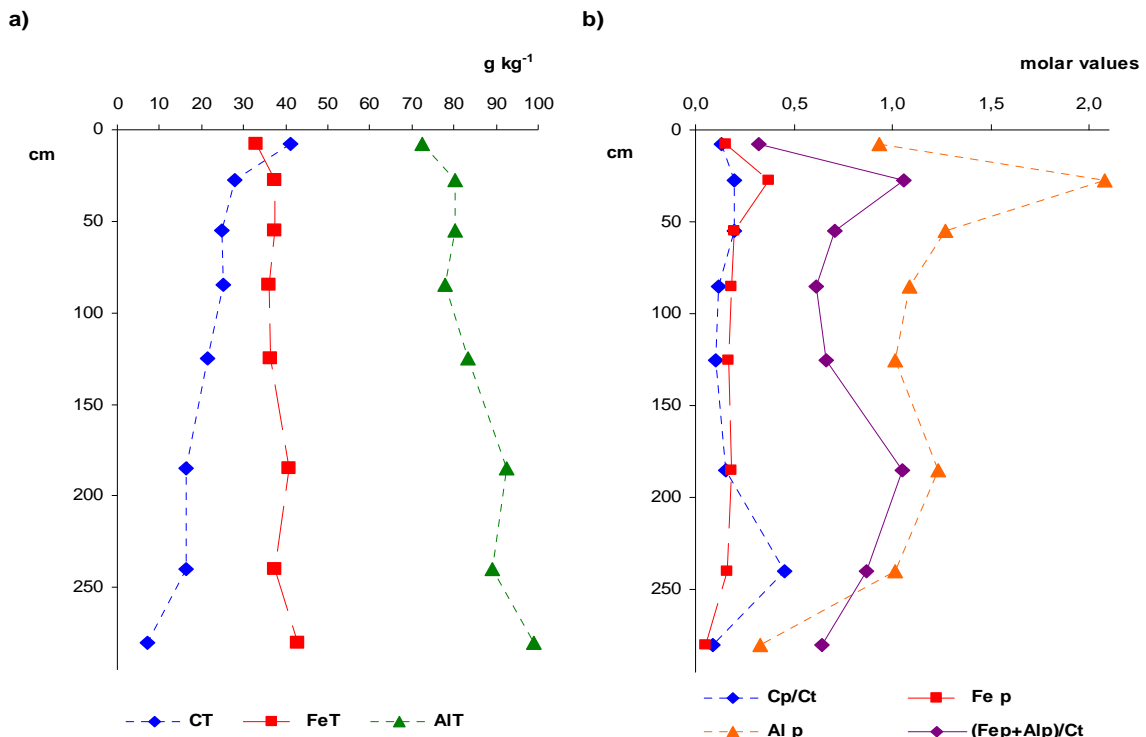


Figure 1. Total content of C, Fe and Al ( $g\ kg^{-1}$ ) in the bulk soil (a), and content of Fe and Al extracted with pyrophosphate ( $mol\ kg^{-1}$ ) and ratios with C (molar relation) (b) of the Viracopos soil (P5) as a function of soil depths.

The Al and Fe forms that are strongly complexed with organic matter can be extracted with a sodium pyrophosphate solution (USDA, 1996). The ratio  $(Al_p+Fe_p)/C$  was above the limit of 0.03 proposed by Nierop *et al.* (2002) throughout the profile of the both soils which points towards the existence of organic-metallic compounds. Most tentatively, they precipitated due to saturation of adsorption site (Figure 1.b).

#### *Characterization of soil organic matter*

Figure 2 shows the solid-state  $^{13}C$ -NMR spectra of the samples from P18. Whereas the spectra of the top horizons showed sufficiently high signal to noise ratios for integration, no spectra could be obtained from the deeper horizons.

They are dominated by a signal at 30 ppm in the region assigned to alkyl C in lipids and amino acids (45 - 0 ppm). Other major intensities are observed between 110 and 45 ppm, in the region of O/N-alkyl C (carbohydrates, amino acids) and carboxyl C (220 to 160 ppm). The missing of a clear signal in the region between 160 and 110 ppm (signal derives from aromatic or olefinic C) indicates that in this soil lignin has minor contributions to its aromatic C content. The contribution of aromatic C with depth may be explained with charcoal contributions. However, applying chemical oxidation with acid potassium dichromate could not confirm this

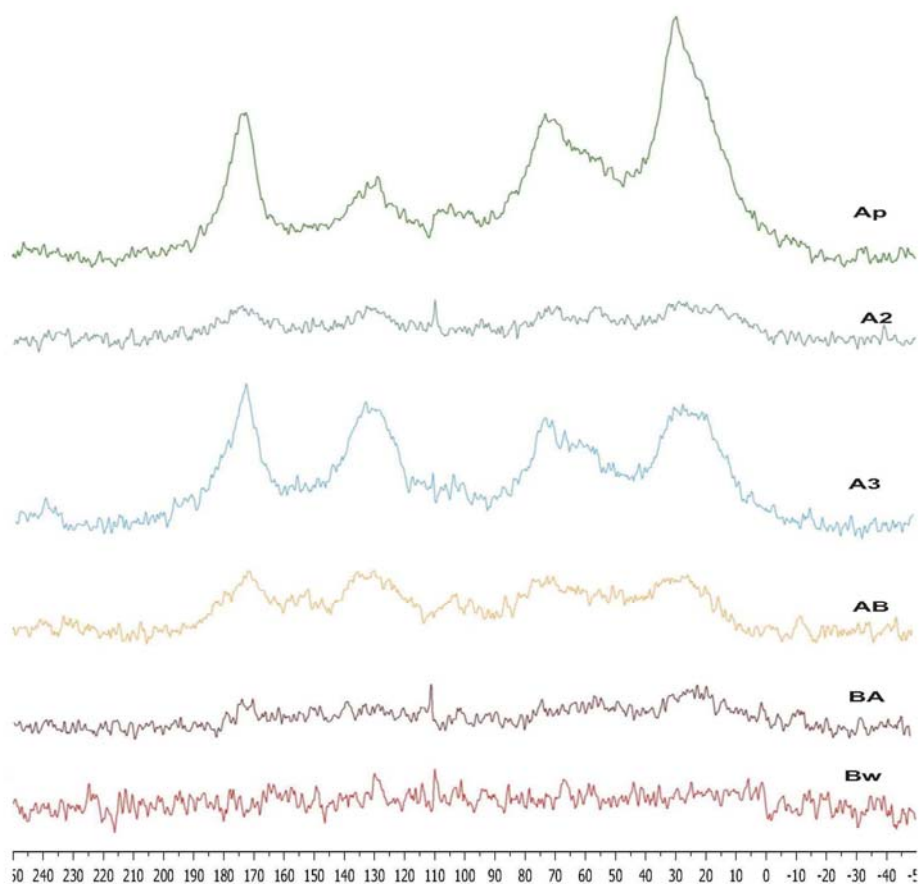


Figure 2.  $^{13}C$  CPMAS NMR spectra of Chapecó soil (P18).

assumption. In the profile P5, however, between 12 and 83% of the total C resisted the harsh chemical treatment, confirming the presence of charcoal residues already visually observed during sampling.

## References

- Eswaran, H. & Tavernier, R.. 1980. Classification and Genesis of Oxisols. *In*: Then, B. K. G. (Ed). Soils with variable charge. New Zealand Society of Soil Science.
- Ker, J.C.. 1997. Latossolos do Brasil: uma revisão. *Geonomos* 5, 17-40.
- Knicker, H., Müller, P., Hilscher, A.. 2007. How useful is chemical oxidation with dichromate for the determination of "Black Carbon" in fire-affected soils?. *Geoderma* 142, 178-196.
- Nierop, K.G.J., Jansen, B., Verstraten, J.M.. 2002. Dissolved organic matter, aluminium and iron interactions: precipitation induced by metal/carbon ratio, pH and competition. *Science of the Total Environment* 300, 201-211.
- USDA. 1996. United States Department of Agriculture. Soil survey laboratory methods manual. V.3. *Soil Survey Investigation Report* 42.

## Future collaboration with host institution (if applicable)

Presently, the applicant is preparing her doctoral thesis and several publications in collaboration with the host supervisor. Further collaborations are planned with respect to post-doctoral work and the development of new projects.

## Projected publications / articles resulting or to result from the grant

The results generated are intended to be presented during 2013 at the International Meeting on Organic Geochemistry (IMOG), at the European Geosciences Union (EGU) and/or at the Meeting of the Spanish Society of Soil Science (SECS).

It is intended to summarize the data for a publication in an international peer reviewed journal. It will focus on the stabilization of SOM in umbric Ferralsol and their relationship with mineral components.