

## Effect of land use on organic matter's quality evaluated by $^{13}\text{C}$ NMR

Santos, DC<sup>a\*</sup>; Silva, WTLS<sup>b</sup>; Kunde, RJ<sup>c</sup>; Flores, CA<sup>d</sup>; Pillon, CN<sup>d</sup>

<sup>a</sup>UFPEl, Campus Universitário s/nº, Caixa Postal 354, CEP 96010-900, Capão do Leão, RS, Brasil;

<sup>b</sup>Embrapa Instrumentação Agropecuária, Rua XV de Novembro 1452, CEP 13560-970, São Carlos, SP, Brasil; <sup>c</sup>UCPel, Rua Félix da Cunha, 412, CEP 96010-000 Pelotas, RS, Brasil;

<sup>d</sup>Embrapa Clima Temperado, Rodovia BR 392, km 78, Caixa Postal, 403, CEP 96001-970, Pelotas, RS, Brasil;

\*E-mail: santos.daianec@gmail.com

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### Introduction

On the western border of Rio Grande do Sul, there are extensive areas on sandy desertification process. One of the strategies for sustainable use of sandy soils of this region, the Pampa Biome, is the implementation of agrosilvopastoral systems and/or the afforestation with eucalyptus.

In this context, it was aimed to evaluate the effect of these systems on the quality's changes of the organic matter's (OM) physical fractions of an Ultisol, in the city of Alegrete-RS. The installation of the experiment occurred in 2002. From the installation time until now, there has not been any type of fire event. However, prior the installation there is no knowledge about fires occurring in these areas. The soil sampling, in the layer of 0.000 to 0.025 m, was performed in 2007 in: an area under homogenous eucalyptus forest (FH); an agrosilvopastoral system (AS); and in a native grassland (NG), that was used as a reference area. The soil of the area is a Typic Eutrophic Ultisol. The particle size distribution, in the layer from 0.00 to 0.26 m, was 900 g kg<sup>-1</sup> sand, 30 g kg<sup>-1</sup> silt and 70 g kg<sup>-1</sup> clay.

It was performed density physical fractionation of OM [1], using a solution of sodium polytungstate of 2.0 Mg m<sup>-3</sup>. The energy dispersion by ultrasound was 250 J mL<sup>-1</sup>.

The samples of free light fraction (FLF) and occluded light fraction (OLF) were treated with an aqueous solution of 10% of HF, to perform the  $^{13}\text{C}$  nuclear magnetic resonance (NMR) analysis.

### Results and Discussions

The  $^{13}\text{C}$  NMR spectra of the FLF's and OLF's samples showed themselves similar on the different systems evaluated (Figure 1). In the region between 25-35 ppm, the signal of C alkyl is a methylene, derived from long chain aliphatics. In the region of C O-alkyl (60-

110 ppm), one can observe two distinct peaks. The peak at 72-75 ppm is assigned to cellulose and at 105 ppm is derived from hemicellulose and other carbohydrates. The signal's strength between 160-230 ppm corresponds, in part, to the carboxyl groups of organic acids [2].

The different soil's treatment showed a predominance of substituted C alkyl groups (C O-alkyl/C di-O-alkyl + C N-alkyl/C methoxyl), whose proportion varied from 41% to 50%; followed by C alkyl group (27% to 34%). The aromatic structures (C aryl + C-phenyl) contributed approximately with 11% of the composition of the samples, the carboxyl groups with 8% and carbonyl with 6%.

The high percentages of substituted C alkyl groups in the examined systems indicated the abundance of proteins and polysaccharides-like structures present in OM. Considering that these components are easily decomposed, because they are preferentially attacked by microorganisms, the OM can be considered of low decomposition degree [3].

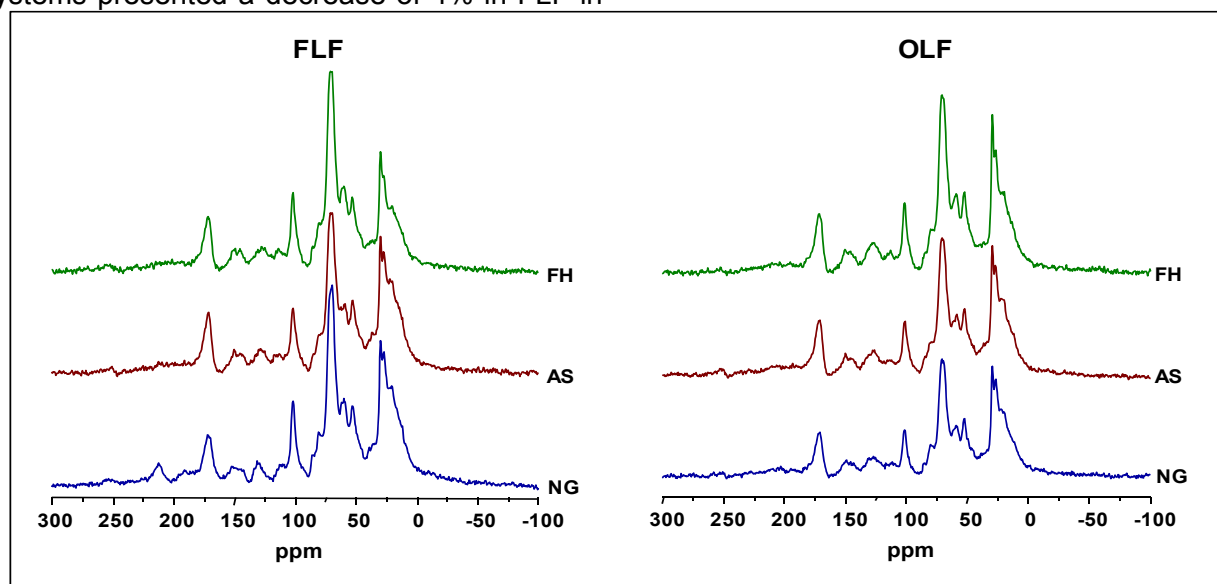
Analyzing the chemical composition of the OM on the FLF, the proportions of C O-alkyl/C di-O-alkyl + C N-alkyl/C-methoxyl ranged from 42% to 50% for the AS and FH. For C alkyl, these ratios ranged 27-34% for the FH and the AS respectively. Possibly the greatest abundance of substituted C alkyl in the FLF of FH could be explained by the differences in chemical composition (recalcitrance) of crop residue and through its relationship with the environment, where the decomposition occurs. With respect to aromatic structures (C-aryl + C-phenyl), the chemical composition of the two systems were similar, approximately 10%.

These higher proportions observed in C O-alkyl/C di-O-alkyl + C N-alkyl/C methoxyl in comparison to the aromatic structures, demonstrate that carbohydrates are the soil main organic constituents, even though they have low molecular recalcitrance. This fact associated with the aromatic compounds, that corresponds to a smaller proportions, is an

indication that the colloidal and the physical protection of the OM, are overlapping the magnitude of recalcitrance's protection [4].

In the OLF, there was a similar proportion of C's functional groups found in comparison to those found in FLF. However, on average the systems presented a decrease of 4% in FLF in

relation to the one in OLF, for the grouping of substituted C alkyl, showing decreases of aliphatic structures, such as polysaccharides and carbohydrates, from FLF to the OLF, agreeing with [5].



**Figure 1.**  $^{13}\text{C}$  NMR spectroscopy of the free light fraction (FLF) and the occluded light fraction (OLF) of organic matter of an Ultisol under different use systems in the layer of 0.000 to 0.025 m. FH = Forest homogeneous eucalyptus; AS = Agrosilvopastoral System between rows and NG = native grassland.

**Table 1.** Percentage distribution of functional groups of C determined through  $^{13}\text{C}$  NMR spectroscopy in the free light fraction (FLF) and occluded light fraction (OLF) of the organic matter of an Ultisol under different use systems, in the layer of 0.000 to 0.025 m.

Systems*	Distribution of C types / chemical shifts (ppm)						
	C-alkyl 0 - 45	C N-alkyl C-Methoxyl 45 - 60	C-O-alkyl C-di-O-alkyl 60 - 110	C-aromatic 110 - 140	C-phenolic 140 - 160	C-carboxyl 160 - 185	C-carbonyl 185 - 230
FLF							
FH	27	13	37	7	4	7	5
AS	34	11	31	7	4	8	5
NG	32	12	34	5	4	7	6
OLF							
FH	31	12	32	8	4	8	5
AS	32	11	30	8	5	8	6
NG	33	9	32	8	4	8	6

\*FH - Forest homogeneous eucalyptus; AS – System agrosilvopastoral between rows e NG - native grassland.

## Conclusion

This work allows us to infer that: i) there is a tendency of increasing proportion of C O-alkyl like structures in homogeneous eucalyptus forest, compared to the agrosilvopastoral system and the native grassland and ii) the absence of significant differences in the C types distribution in the free light fraction and occluded light fraction, for all systems, suggests relatively low capacity for physical protection of the organic matter in this soil.

The analyzed fractions do not show evidence of charred material.

<sup>1</sup>Conceição, P.C. et al. 2008. *Rev. Bras. Ci. Solo*, 32, 541.

<sup>2</sup>Kögel-Knabner, I. 2002. *Soil Biol. Bioch.*, 34, 139.

<sup>3</sup>Dick, D.P. et al. 2008. *Rev. Bras. Ci. Solo*, 32, 2289.

<sup>4</sup>Diekow, J. *Estoque e qualidade da matéria orgânica do solo em função de sistemas de culturas e adubação nitrogenada no sistema plantio direto*. 2003. 164f. Tese – UFRGS, Porto Alegre.

<sup>5</sup>Köbl, A.; Kögel-Knabner, I. 2004. *J. Plant Nutr. Soil Sci.*, 167, 45.