# *Pinus* afforestation in South Brazilian highlands: soil chemical attributes and organic matter composition

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ABSTRACT: In the last three decades, exotic tree species are being introduced in the natural pastures of the highlands located at the northeastern part of Rio Grande do Sul State (RS), Brazil. This alteration of land use may impart drastic changes in the soil attributes. In this context, this work aimed to evaluate the impact of *Pinus taeda* afforestation on soil chemical attributes and organic matter (SOM) composition in *Leptosols* from *Campos de Cima da Serra*, RS. Soil samples under eight year old (Pi8) and 30 year old (Pi30) *Pinus* plantations and under native pasture (NP) were studied. Contents of exchangeable cations and of micronutrients and soil pH were determined. The SOM composition was investigated by means of elemental analyses and FTIR spectroscopy. The soil under pasture had a higher content of nutrients and of SOM in comparison to *Pinus* soils, reflecting the higher input and decomposition rate of the below ground added residue in the grassland environment. The SOM in pasture soils showed a higher content of carbohydrate and of structures derived from microbial metabolism. Besides the depletion of nutrients and of SOM, *Pinus* afforestation affected the SOM quality: following afforestation, the proportion of chemically recalcitrant structures and of carboxylic groups increased, whereas N-containing groups decreased.
Key words: FTIR spectroscopy, humification, exchangeable cation, pastures, recalcitrance

## Florestamento com *Pinus* em solos de altitude do Sul do Brasil: atributos químicos e matéria orgânica do solo

RESUMO: Nas três últimas décadas, o cultivo de espécies exóticas vem sendo introduzido nas áreas de pastagem de solos de altitude localizados na região nordeste do Estado do rio Grande do Sul. Essa alteração de uso do solo pode causar mudanças drásticas nos atributos do solo. Avaliou-se o impacto do florestamento com *Pinus Taeda* nos atributos químicos e na composição da matéria orgânica (MOS) de *Neossolos Litólicos* dos *Campos de Cima da Serra*, RS. Foram estudadas amostras de solo sob plantação de *Pinus* há oito (Pi8) e há 30 anos (Pi30) e sob pastagem natural (NP), sendo determinados os teores de cátions trocáveis e de micronutrientes e o pH do solo. A composição da MOS foi investigada por análise elementar e espectroscopia de FTIR. O solo sob pastagem apresentou maior teor de nutrientes e de MOS comparativamente aos solos sob *Pinus*, refletindo a maior taxa de decomposição de resíduos subsuperficiais em ambiente de campo. A MOS apresentou maior proporção de carboidratos e de estruturas de origem microbiana nos solos sob pastagem natural. Além da depleção de nutrientes e de MOS, florestamento com *Pinus* afetou a qualidade da MOS: ao longo do tempo a proporção de estruturas quimicamente recalcitrantes e de grupos carboxílicos aumentou, enquanto a de grupos nitrogenados diminuiu.
Palavras-chave: espectroscopia de FTIR, humificação, cátion trocável, pastagens, recalcitrância

## Introduction

The afforestation of a degraded land with exotic trees has been a strategy lately used to improve soil quality, promote C sequestration and simultaneously produce an economic return. However, information regarding changes to soil C resulting from afforestation in non-degraded areas are few and conflicting and, besides the plantation type, the kind of soil and the climate may affect the soil organic matter (SOM) content after the plantation establishment (Paul et al., 2002; Jandl et al., 2007). For *Pinus* plantations, a maintenance of the initial soil C content has been observed in the first eight years in subtropical highland pasture (Baretta et al., 2005), while in a New Zealand pasture soil C stocks tended to decrease in the long term (more than 17 years) (Groenendijk et al., 2003).

*Pinus* afforestation in the *Campos de Cima da Serra* (Rio Grande do Sul State, Brazil) displays a unique scenario, since the pastures are still productive and through their adequate management, forage quality and yield can

be increased, providing sufficient income for profitable cattle farming (Heringer and Jacques, 2002). The soils are shallow (mostly Leptosols, Umbrisols and Cambisols), strongly acid (pH around 4.2) and alic, with high contents of SOM in the surface layer (higher than 4%) (Silva et al., 2008). Additionally, their SOM presents a low level of humification, estimated by its high proportion of C-O alkyl groups (51 to 59%) (Dick et al., 2008), in comparison to the values usually observed for Oxisols from the same latitude (Dick et al., 2005). Consequently, soil disturbance or alteration of the C dynamic balance due to a change of vegetation may cause a reduction in SOM and soil quality as already observed by the introduction of agriculture on former pastures in the subtropics (Dieckow et al., 2005).

A recent study developed on highland soils under 8 and 30 year old plantations in the *Campos de Cima da Serra,* RS, indicated that the conversion of pasture to *Pinus* decelerated the input of organic matter into the soil; therefore, there was a decrease in the soil C stocks and promoting a relative enrichment with a more recalcitrant SOM (Wiesmeier et al., 2009). To complement the cited study, our main objective was to investigate the impact of *Pinus* afforestation on the soil chemical attributes and organic matter composition of the highland soils studied by Wiesmeier et al. (2009), using as reference the original condition under a native pasture. In order understand the lability of the SOM we investigated the sample behavior against demineralization with HF treatment and tested the FTIR indexes proposed by Gerzabek et al. (2006).

## Material and Methods

The study area belongs to the *Campos de Cima da Serra* region, northeastern of Rio Grande do Sul State, and is located at 1224 to 1287 m a.s.l. (28°35' S, 49°52' W to 28°39' S and 49°55' W). The climate is temperate with high precipitation (annual mean rainfall of 2,468 mm) and moderate temperature (annual mean of 14.4°C), with a short dry period of less than 2 months in the summer and up to 15 days with frost during winter (Moreno, 1961).

Soil samples were collected from three different layers down to 15 cm (0 to 5 cm, 5 to 10 cm and 10 to 15 cm) in Leptosols (IUSS Working Group WRB, 2006) (*Neossolos Litólicos* according to Embrapa (2006)) in three sites: native pasture (mainly *Paspalum notalum* and *Paspalum plicatum*) grazed with 2 animals $ha^{-1}$ and not fire affected in the last 22 years (NP); 8 year old (Pi8) and 30 year old (Pi30) *Pinus taeda* monoculture. Both plantation areas have been under native grassland before afforestation, which is the original native vegetation in the studied areas (Baretta et al., 2005). At each site, three soil pits at a distance of 10 to 30 m were probed. In each open pit three samples from the inner walls were collected in order to make a composite replicate sample for each sampled depth. The two *Pinus* plantations were located about 2 km apart and the native pasture area was about 4 km far from the *Pinus* forests. Soil samples (three field replicates) were air dried and ground to pass a 2.0 mm sieve.

Soil chemical analyses were performed according to Tedesco et al. (1995). Soil pH was measured in distilled water ($pH_{H2O}$) in a soil: solution ratio of 1:2.5. Exchangeable cations $Ca^{+2}$, $Mg^{+2}$ and $Al^{+3}$ were extracted with 1.0 M KCl solution, while for exchangeable $K^+$ the Mehlich 1 solution was employed. The effective cation exchange capacity ($CEC_E$) was calculated by the sum of the exchangeable cations ($Ca^{+2}$, $Mg^{+2}$ and $K^+$) and ($H^+ + Al^{+3}$) and the saturation of the $CEC_E$ by Al was calculated. The contents of micronutrients $Mn^{+2}$, $Zn^{+2}$ and $Cu^{+2}$ were obtained by extraction with DTPA (*Diethylene triamine pentaacetic acid*) 0.005 mol $L^{-1}$ (pH 7.3) solution.

Composite soil samples, made up from the three field replicates, were treated with 10% (v $v^{-1}$) HF solution (Gonçalves et al., 2003). Briefly, 10 g of soil were weighed into a 50 mL polyethylene flask, to which 30 mL of HF solution were added and the closed beaker was manually shaken for 30s. The beaker was mechanically shaken during 2 h, centrifuged for 10 min (3,000 rpm) and the supernatant was removed and appropriately discarded. This procedure was repeated eight times and thereafter the solid residue (concentrated SOM) was washed three times with distilled water to remove residual HF, and finally oven dried at 40°C.

The total C and N contents, before and after the HF treatment ($C_{HF}$ and $N_{HF}$) were determined by dry combustion (975°C) in triplicate (Perkim Elmer 2400). The C content was assigned exclusively to SOM, as all soil samples were carbonate free. The enrichment in C and in N content after HF treatment ($C_E$ and $N_E$, respectively) was calculated by dividing the element content in the treated sample by its content in the untreated sample. The recovery of C after HF treatment ($C_R$) was calculated using the following equation: $C_R (\%) = M_R(\%) \times (C_{HF}/C)$, where $M_R$ is the percentage mass remaining after HF treatment in the freeze-dried sample. The recovery of N after HF treatment ($N_R$) was calculated likewise. To elucidate possible selective losses in organic matter, the factor R, which is the ratio between the C/N relation before and after the treatment ($C/N_{HF}$), was calculated (Dick et al., 2005).

Fourier Transformed Infrared (FTIR) spectra of the SOM were recorded (Shimadzu FTIR 8300) in KBr pellets (sample: KBr ratio of 1:100) previously dried under vacuum for 24 h. The operating range was from 4,000 to 500 $cm^{-1}$ with a 4 $cm^{-1}$ resolution and an acquisition of 32 scans per sample, which were corrected against the spectrum of ambient air as background. The absorption bands were assigned following Tan (2003) and Farmer (1974). An aromaticity index was calculated by dividing the intensity of absorption around 1,630 $cm^{-1}$ by the intensity of absorption at 2,920 $cm^{-1}$ (Chefetz et al., 1996). The intensity value was obtained from the equipment's software, after establishing a baseline between 1,696 and 1,530 $cm^{-1}$ and between 3,000 and 2,800 $cm^{-1}$, respectively. For obtaining the FTIR aromaticity index, three spectra replicates were acquired. In order to compare the spectra among the samples, relative absorbance intensities of the main peaks were calculated by dividing the corrected in-

tensity of a distinct peak (e.g. around 2,920, 1,720, 1,630, 1,540 and 1,070-1,030 cm$^{-1}$) by the sum of the intensities of all studied peaks and multiplying it by 100% (Gerzabek et al., 2006). The parameters for the determination of a given peak intensity, besides the peaks at 1,620 and 2,940 cm$^{-1}$, were as follows: Base 1/peak/Base 2 (all in cm$^{-1}$) 1800/1720/1700; 1560/1540/1490; 1190/1070/900.

The data analyses were performed following a split-plot design. The vegetation types (NP, Pi8, Pi30) were considered as treatments, i.e. the main plots. The depths were considered as sub-treatments (sub-plots) (Vieira, 2006; Richards et al., 2007). The soil chemical attributes were submitted to variance analysis using general linear models (GLM) considering the interaction between treatment and depth. Prior to ANOVA the data normal distribution and homogeneity of variance were checked. The mean values were tested by Tukey HSD to compare differences ($p < 0.05$). To verify possible correlations between different attributes, the Pearson correlation test was employed.

## Results and Discussion

The soil samples were highly acidic (4.1 ≤ pH-H$_2$O ≤ 4.6) and no difference between treatments and depths were observed (Table 1). This behaviour is typical for lowly weathered highland soils from Southern Brazil, and is usually associated with the occurrence of a considerable amount of organic acids, which accumulate in the soil due to the slow decomposition and mineralization of the vegetal residues in comparison to soils from warmer and drier climates (Silva et al., 2008).

As already observed by Wiesmeier et al. (2009), the greatest values for C content were found in the samples under native pasture and a sharp decrease of this attribute with soil depth was observed (Table 1). The samples under *Pinus* showed lower C contents in comparison to the NP samples, in particular, in the 0-5 cm layer, and its decrease with depth was comparatively smoother. These results evidence the higher input of underground and easily decomposable residues to the soil, mainly in the upper layer, provided by a pasture system, as compared to P*inus*. The monoculture produces a great amount of needles, which, due to its high content of chemically recalcitrant structures, are comparatively more resistant to the microbial decomposition in this ecosystem and, thus, accumulate on the soil surface (Muscolo et al., 2005). In fact, as assessed by $^{13}$C NMR CPMAS spectroscopy, the litter under *Pinus* consists approximately of 47% of C as carbohydrate-like structures and 22% of C in alkyl chains, while grass residues presented 56% of C as N/O alkyl groups and 15% of C alkyl

Table 1 – Soil pH, contents of C and N, C/N ratio, contents of exchangeable Ca, Mg, K and Al, effective cation exchange capacity (CEC$_E$), Al saturation, and contents of micronutrients Zn, Cu and Mn of the studied *Leptosols* under native pasture (NP), 8 years old (Pi8) and 30 years old (Pi30) *Pinus* plantations (n = 3).

| Sample | NP | | | Pi8 | | | Pi30 | | |
|---|---|---|---|---|---|---|---|---|---|
| Depth (cm) | 0-5 | 5-10 | 10-15 | 0-5 | 5-10 | 10-15 | 0-5 | 5-10 | 10-15 |
| pH-H$_2$O | 4.4 | 4.3 | 4.4 | 4.3 | 4.3 | 4.4 | 4.1 | 4.4 | 4.6 |
| | ———————————— g kg$^{-1}$ ———————————— | | | | | | | | |
| C | 137 Aa | 70 Bb | 59 Cc | 74 Ca | 65 Cb | 64 Bc | 84 Ba | 71 Ab | 6.3 Bc |
| N | 9.7 Aa | 6.4 Ab | 5.8 Ac | 6.8 Ba | 5.0 Bb | 4.5 Bc | 6.0 Ca | 4.7 Cb | 0.44 Bc |
| C/N | 14 Ba | 11 Cb | 10 Cc | 11 Cc | 13 Bb | 14 Ba | 15 Ab | 15 Aa | 14 Bc |
| | ———————————— mmol$_c$ kg$^{-1}$ ———————————— | | | | | | | | |
| Ca | 17 Aa | 6 Ab | 4 Ab | 1 Ba | 1 Ba | 2 Ba | 1 Ba | 1 Ba | 1 Ba |
| Mg | 9 Aa | 3 Ab | 2 Ab | 2 Ba | 1 Ba | 2 Aa | 2 Ba | 1 Ba | 1 Aa |
| K | 1870 Aa | 860 Aab | 590 Ab | 600 Aa | 470 ABab | 380 Bb | 460 Aa | 340 Ba | 240 Ba |
| Al | 57 Ca | 74 Aa | 76 Aa | 90 Ba | 86 Ab | 82 Ac | 110 Aa | 100 Ab | 90 Ac |
| CEC$_E$ | 90 Bb | 95 ABa | 94 Aa | 92 Ba | 90 Ba | 86 Aa | 110 Aa | 100 Ab | 94 Ac |
| | ———————————— % ———————————— | | | | | | | | |
| Al$_{saturation}$ | 64 Bb | 86 Ba | 91 Aa | 95 Aa | 96.4 Aa | 96 Aa | 97 Aa | 97 Aa | 97 Aa |
| | ———————————— mg kg$^{-1}$ ———————————— | | | | | | | | |
| Zn | 6.5 Aa | 2.6 Ab | 1.4 Ac | 2.1 Ba | 1.4 Ab | 1.0 Ac | 1.0 Ba | 1.0 Aa | 0.8 Aa |
| Cu | 1.3 | 1.1 | 0.9 | 2.4 | 1.2 | 0.9 | 1.3 | 1.1 | 1.2 |
| Mn | 88 Aa | 22 Ab | 19 Ab | 23 Ba | 3.5 Ab | 2.5 Ab | 3.0 Ba | 2.5 Aa | 1.5 Aa |

Excepting for Cu content, all attributes showed significant interaction between treatment and depth (Fischer test, $p < 0.05$); Samples with the same capital letters do not differ between treatments in each depth; Samples with the same small letters do not differ between depths in each treatment (Tukey test, $p < 0.05$).

(Wiesmeier et al., 2009). Furthermore, litter decomposition releases high amounts of polyphenols and tannins, which inhibit microbial activity and, thus, also slow down the litter humification (Badiane et al., 2001). Similar to C, N content diminished with depth and the values under *Pinus* were lower than under NP. The C/N ratio tended to be greater in the Pi30 samples, indicating a relative impoverishment of N groups after afforestation.

In comparison to NP samples, exchangeable Ca and Mg contents were considerably lower in all *Pinus* samples, while exchangeable K differed only in samples deeper than 5 cm (Table 1). In addition to N, afforestation also caused a depletion of exchangeable nutrients, as previously observed in *Pinus* forested *Cambisols,* from the *Sul Catarinense* Plateau (Baretta et al., 2005). The contents of exchangeable Al in the 0-5 cm layer increased in the order NP< Pi8< Pi30, while no difference was detected in the deeper layers (Table 1). For the NP samples, an inverse correlation between exchangeable Al and C content was obtained ($r = -0.99$, $p < 0.02$). Since the soil pH in this treatment is homogeneous along the profile and it also lies below the pKa of Al hydrolysis (around 5.5) (Sposito, 2008), the lower content of exchangeable Al in the surface layer may be associated with the formation of insoluble Al-organic matter complexes, removing this element from the exchange sites (Haynes and Mokolobate, 2001).

The $CEC_E$ varied between 86 and 110 $mmol_c\ kg^{-1}$ and was greater in the Pi30 samples until 10 cm depth, in spite of the small values for exchangeable Ca, Mg and K (Table 1). This behavior is explained by the high content of exchangeable Al in these samples. In fact, Al saturation in all *Pinus* samples was very high (95 - 97%), while in the NP treatment the value was smaller at the 0-5 cm (64%) and increased with depth (91%). The contents of Zn and Mn in the 0-5cm layer in NP were greater than in *Pinus* samples, and did not differ among the treatments in subsurface layers. The content of Cu was very low in all analyzed samples.

The results about C content, exchangeable cations and micronutrients highlight the faster nutrient cycling under the grassland system in comparison to *Pinus* veg-

etation. The high root density under pasture, particularly in the first 5 cm, promotes the return of nutrients and C to the soil through the decaying of vegetal residues. In contrast, the root system under *Pinus* goes deeper into the soil and presents a slower turnover, leading to a lower nutrient cycling, though more uniform, along the profile.

The FTIR spectra of whole soil of pasture and *Pinus* samples presented, in general, the same pattern (Figures 1a and b). Absorption bands at 3,697 and 3,627 $cm^{-1}$ are assigned to Al-OH stretching and indicate the occurrence of kaolinite, while bands at 1,080, 1,033, 1,012 and 914 $cm^{-1}$ correspond to Si-O vibrations from kaolinite and quartz. In the *Pinus* samples' spectra (Figure 1b, Pi8 not shown), peaks at 3,530, 3,450 and 3,390 $cm^{-1}$ were identified, which are typical for the Al-OH stretching in gibbsite. The presence of kaolinite and gibbsite in *Leptosols* from South Brazilian highlands have been reported elsewhere (Silva et al., 2008).

The contents of C and N after HF treatment increased in all samples, and the resulting enrichments varied between 2.8 and 6.7 for C and between 2.8 and 4.7 for N (Table 2). With exception of sample 0-5 cm NP, $C_E$ was always greater than $N_E$; consequently, the C/N ratio of the concentrated SOM was greater than the untreated sample (Table 1). During the HF treatment a preferential loss of N occurred compared to C. The organic matter lost due to the HF treatment is believed to be from microbial origin, mainly carbohydrates that are not trapped in the micelle structure of the humified SOM and are hydrolyzed by the acid treatment (Rumpel et al., 2006). Also, this fraction includes small humic molecules that are released from its sorbed form to the solution when the mineral is dissolved by the HF acid (Dick et al., 2005; Dick et al., 2008). The R value decreased steadily with depth in the NP treatment, showing that in this environment the preferential N loss from the SOM increased in the same order. In the samples under *Pinus,* an opposite behavior was observed regarding the R value (Table 2). It seems that under pasture, the protection of N-containing structures inside the humic micelle or by organo-mineral interactions decrease in deeper layers, while in the environment under *Pinus*
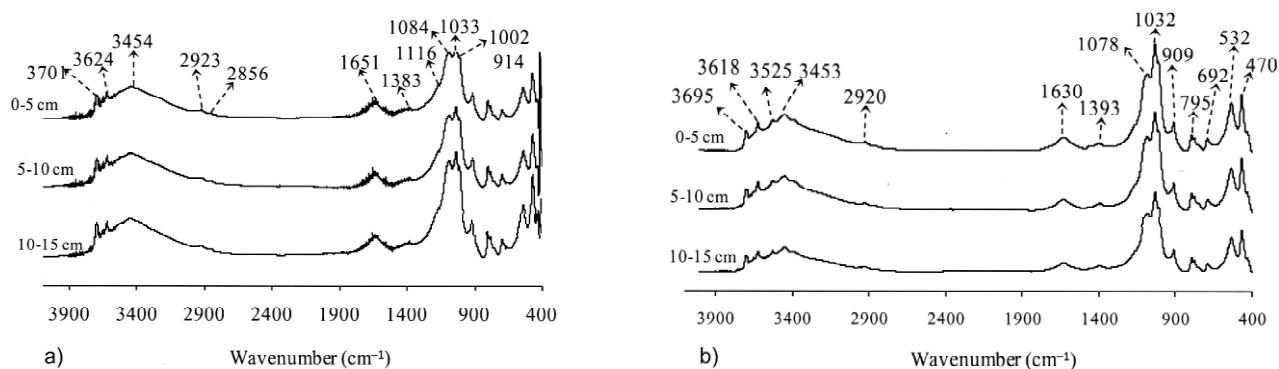


Figure 1 – FTIR Spectra of the whole soil under native pasture (a) and under 30 years *Pinus* forestation (b) from *Leptosols*.

the opposite occurs. In the sample 0-5 cm from NP, which had the highest C content, $C_E$ was 2.8 and comparable to the values obtained for highland soils from South Brazil with a similar SOM content (Silva et al., 2008). The R factor of 1.1 in this sample indicates that no relevant preferential loss either of C or N occurred due to the HF treatment (Dick et al., 2005).

The recovery of C ($C_R$) was in general low (43 to 66%) and the obtained values (Table 2) were smaller than those observed for *Ferralsols* from South Brazil (Dick et al., 2005; Dalmolin et al., 2006), but comparable to those verified for highland soils (Silva et al., 2008). In the NP environment, $C_R$ increased with depth, indicating that SOM losses due to HF treatment decreased in the same order. In comparison to the *Pinus* environments, $C_R$ in the 0-5 cm layer of NP was smaller (Table 2). Probably, the SOM in the surface layer under pasture is more associated with the mineral fraction and less recalcitrant than in the corresponding layer under *Pinus,* and thus, more susceptible to extraction by the HF treatment. For the Pi8 and Pi30 samples, $C_R$ decreased with depth, suggesting that the contribution of more labile structures to whole SOM increases in the opposite direction.

The removal of the inorganic soil matrix enabled the identification of organic functional groups of the SOM in the FTIR spectra (Figures 2a and b). The main absorption bands and their assignments are: a broad band at $3,426 \text{ cm}^{-1}$ due to stretching of OH groups (bonded and non-bonded); two bands at $2,920$ e $2,850 \text{ cm}^{-1}$ due to aliphatic C-H vibrations of aliphatic methyl and methylene groups; a band around $1720 \text{ cm}^{-1}$ due to C=O stretching of COOH groups; a peak at $1,630 \text{ cm}^{-1}$ due to C=C stretching of aromatics groups; a shoulder at $1,540 \text{ cm}^{-1}$ due to N-H bending of amide II; weak bands at $1,387 \text{ cm}^{-1}$ due to C-H aliphatic groups; a broad band at $1,245 \text{ cm}^{-1}$ due to C-O stretching and OH bending from COOH; a peak at $1,075 \text{ cm}^{-1}$ due to C-O stretching of carbohydrates, and a peak at $1,030 \text{ cm}^{-1}$ due to Si-O vibration. Since all HF treated samples were dried at pH 4.0, it is most unlikely that the contribution of the C=O stretching of carboxylate group at $1,630 \text{ cm}^{-1}$ to the total band intensity is relevant. Furthermore, the $1,245 \text{ cm}^{-1}$ peak confirms the presence of non dissociated COOH groups.

The $I_{1630}/I_{2920}$ index in the 0-5 cm layer of NP was greater than in Pi30 environment (Table 2) indicating a higher aliphatic character of the SOM under Pi30 in the surface. Conversely, in layers deeper than 5 cm greater values for $I_{1630}/I_{2920}$ index were found in Pi30, indicating an enrichment of aromaticity in the subsoil in the *Pinus* environment in comparison to native pasture.

The $RI_{1070}$ index, which informs about the relative carbohydrate content, varied broadly among the studied samples and, in all layers, was greater in the NP environment in comparison to Pi30 (Table 2). These results provide evidence of the more recalcitrant nature of the SOM under *Pinus*. The correlation of the $RI_{1070}$ values

Table 2 – C and N contents, C recovery, C and N enrichment and C/N ratio after HF treatment, R factor, and FTIR indexes: $I_{1630}/I_{2920}$, $RI_{2920}$, $RI_{1630}$, $RI_{1540}$ and $RI_{1070}$ of the studied *Leptosols* under native pasture (NP), 8 years old (Pi8) and 30 years old (Pi30) *Pinus* plantations (n = 3)

| Sample | NP | | | Pi8 | | | Pi30 | | |
|---|---|---|---|---|---|---|---|---|---|
| Depth (cm) | 0-5 | 5-10 | 10-15 | 0-5 | 5-10 | 10-15 | 0-5 | 5-10 | 10-15 |
| | ---------- g kg⁻¹ ---------- | | | | | | | | |
| $C_{HF}$ | 380 | 390 | 400 | 400 | 390 | 370 | 410 | 370 | 320 |
| $N_{HF}$ | 28 | 29 | 27 | 19 | 20 | 19 | 19 | 18 | 16 |
| | ---------- % ---------- | | | | | | | | |
| $C_R$ | 43 | 64 | 66 | 62 | 63 | 52 | 58 | 59 | 50 |
| $C_E$ | 2.8 | 5.7 | 6.7 | 5.4 | 6.0 | 5.8 | 5.0 | 5.2 | 5.1 |
| $N_E$ | 3.0 | 4.5 | 4.7 | 2.8 | 4.1 | 4.3 | 3.2 | 3.8 | 3.6 |
| $C/N_{HF}$ | 13 | 14 | 15 | 21 | 20 | 19 | 22 | 20 | 17 |
| R | 1.1 | 0.8 | 0.7 | 0.5 | 0.6 | 0.7 | 0.7 | 0.8 | 0.9 |
| *$I_{1630}/I_{2920}$ | 1.18 Aa | 1.20 Ba | 1.14 Ba | 1.06 ABa | 1.13 Ba | 1.28 ABa | 0.97 Bb | 1.45 Aa | 1.64 Aa |
| | ---------- % ---------- | | | | | | | | |
| *$RI_{2920}$ | 17 Aa | 14 Aa | 16 ABa | 18 Aa | 16 Aa | 19 Aa | 24 Aa | 18 Aa | 14 Ba |
| *$RI_{1720}$ | 10 Ca | 13 Aa | 12 Aa | 14 Ba | 10 Aa | 15 Aa | 17 Aa | 21 Aa | 20 Aa |
| *$RI_{1630}$ | 19 Aa | 16 Aa | 18 Ba | 19 Aab | 18 Ab | 22 ABa | 20 Ab | 25 Aa | 23 Aab |
| *$RI_{1540}$ | 2.8 Aa | 2.9 ABa | 3.1 Aa | 4.1 Aa | 1.9 Ba | 4.2 Aa | 3.6 Aa | 3.7 Aa | 3.3 Aa |
| *$RI_{1070}$ | 44 Aa | 47 Aa | 42 Aa | 36 ABa | 45 Aa | 32 ABa | 26 Ba | 25 Aa | 28 Ba |

*$I_{1630}/I_{2920}$ and relative intensities (RI) showed significant interaction between treatment and depth at 5% probability according to Fischer test; Samples with the same capital letters do not differ between treatments in each depth; Samples with the same small letters do not differ between depths in each treatment by Tukey at 5% probability.
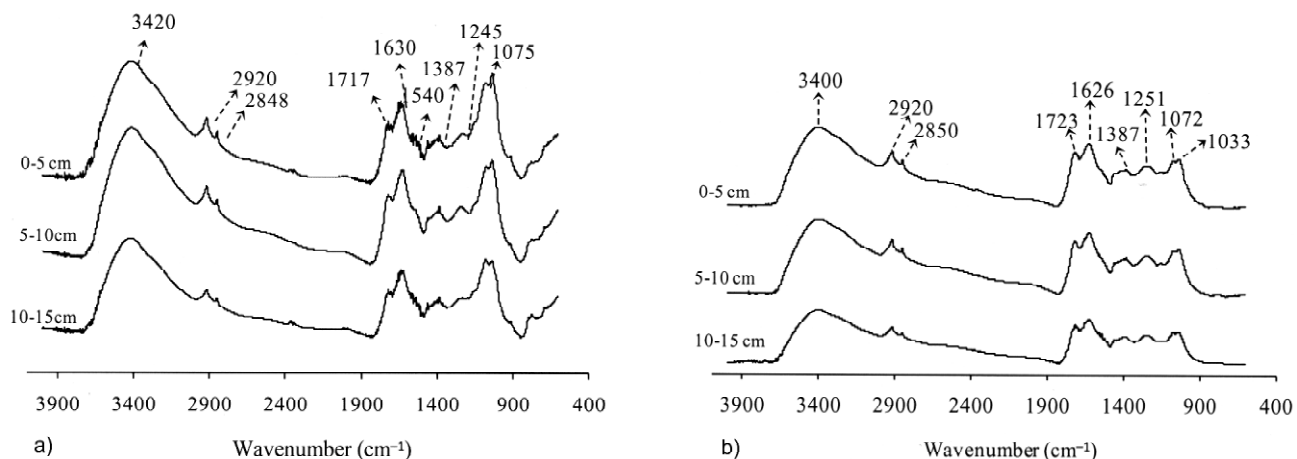
Figure 2 – FTIR Spectra of the SOM (HF-treated samples) from *Leptosols* under native pasture (a) and under 30 years *Pinus* forestation (b).

with the proportion of O-alkyl groups determined by ^{13}C NMR CPMAS in the same samples (Wiesmeier et al., 2009) was significant at $p < 0.01$ (Figure 3), suggesting that this index might be a promising tool in comparative studies of SOM composition. The $RI_{1720}$ index differed among samples only in the upper layer and indicates an increase of the SOM functionalization in the order NP < Pi8 < Pi30 (Table 2). However, when considering the mean value for a given environment, calculated from the data of the three layers, it follows that NP has a smaller value (12 ± 1.7) in comparison to Pi30 environment (19 ± 2.0). By applying the same approach to the $RI_{1630}$ index, similar behavior is observed: mean value in NP (17 ± 1.2) is smaller than in Pi30 environment (23 ± 2.2). These results indicate the presence of more aromatic organic SOM with a greater content of carboxylic groups under Pi30, and are in line with the results obtained by Wiesmeier et al. (2009) by means of ^{13}C NMR CPMAS.

The other calculated FTIR indexes, $RI_{2920}$ and $RI_{1540}$, varied narrowly and showed no consistent variation among treatments and depths. Therefore, no information regarding differences of the SOM composition among the studied environments could be obtained from them.

## Conclusions

*Pinus* afforestation depleted the soil of nutrients and of organic matter. The organic matter in pasture soils contains a greater content of less decomposed moieties, e.g. carbohydrates, and of structures derived from microbial metabolism. Following afforestation, the SOM in this environment is gradually enriched in chemically recalcitrant structures with higher functionalization, and poorer in N-containing groups.

## Acknowledgements
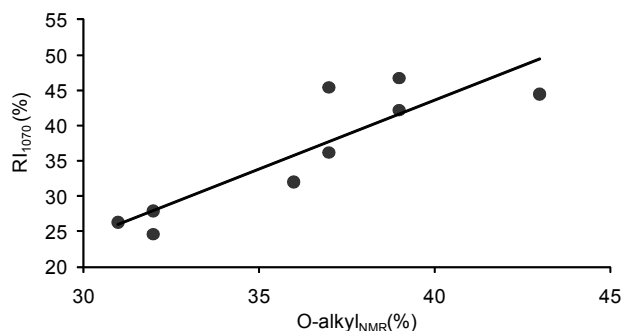
Figure 3 – Relationship between relative intensity of the band at 1,070 cm$^{-1}$ in the FTIR spectra and content of O-Alkyl groups, determined by NMR ^{13}C CPMAS (Wiesmeier et al., 2009), of the SOM (HF-treated samples) from the studied *Leptosols*.

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