Depletion of soil organic carbon and nitrogen under *Pinus taeda* plantations in Southern Brazilian grasslands (*Campos*)

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**Summary**

Establishment of pine (*Pinus* spp.) plantations on grasslands could increase carbon (C) sequestration to counteract increased atmospheric carbon dioxide concentrations. In the grasslands of the southern Brazilian highland (*Campos*), large areas have been converted to *Pinus* plantations over the last 30 years. In order to assess the impact of this land-use change on the amount and composition of soil organic matter (SOM), we investigated a grassland pasture site (G), and both an 8-year-old (P8) and a 30-year-old (P30) plantation with *Pinus taeda*. Soil samples down to 45 cm were analysed for texture, pH, soil organic carbon (SOC) and total nitrogen (N\(_{\text{tot}}\)) concentrations. Chemical composition of SOM was determined by using cross-polarization magic angle spinning (CPMAS) \(^{13}\text{C}\) NMR spectroscopy. We analysed for stable C isotope (\(\delta^{13}\text{C}\)) and assessed the lignin composition by CuO oxidation. Additionally, contents of pyrogenic organic material (PyOM) were determined because the *Campos* is regularly burnt. Both pine plantations revealed relatively small SOC concentrations in the mineral soil of 72.6 mg g\(^{-1}\) (P8) and 56.8 mg g\(^{-1}\) (P30) and N\(_{\text{tot}}\) concentrations of 4.0 mg g\(^{-1}\) (P8) and 2.9 mg g\(^{-1}\) (P30) for the A horizon, while grassland showed significantly (\(P < 0.01\)) larger contents of 100.2 mg g\(^{-1}\) for SOC and 5.9 mg g\(^{-1}\) for N\(_{\text{tot}}\). Accumulation of litter layers suggests decreased input of organic material into the mineral soil under pine, which was confirmed by the \(\delta^{13}\text{C}\) values and lignin composition. Smaller contents of vanillyl- (V), syringyl- (S), and cinnamyl (C)-phenols, smaller ratios of S/V and C/V, and smaller ratios of acidic to aldehydic forms of V and S phenols indicated a high degree of decomposition of residual grass-derived SOM in the upper part of the mineral soil (0–10 cm) under pine plantations. This was confirmed by CPMAS \(^{13}\text{C}\) NMR spectroscopy, showing an increasing Alkyl C/O-Alkyl C ratio at the same depth. No significant changes in the contents of PyOM could be detected, but all sites tended to show the greatest concentrations at deeper soil depths > 15 cm, indicating a vertical relocation of PyOM. The results suggest that decomposition of residual SOM originating from grassland species contributes to the decrease of SOC and N\(_{\text{tot}}\) and to an acidification in the topsoil under pine plantations. We also suggest that slow litter decomposition and incorporation and the absence of fires at the plantations are additional reasons for the reduced amount of SOM. Depletion of SOM and the acidification of the topsoil may reduce the availability and supply of nutrients and diminish the C sequestration potential of the mineral soil.

**Introduction**

Plantation forests established on agricultural land are regarded as an important means to reduce atmospheric carbon dioxide (CO\(_{2}\))

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Gifford, 2002; Ross et al., 2002). However, when considering different tree species, it seems that under hardwoods soil C generally increases, whereas under plantations with softwoods, particularly Pinus species, soil organic C (SOC) is lost (Guo & Gifford, 2002; Paul et al., 2002). Several mechanisms have been discussed to account for this decline, but few studies provide objective evidence for the processes assumed to occur. In tropical and subtropical regions, where large parts of natural savannas and grasslands were converted to plantations with Pinus spp. during the previous 30 years (Le Maitre, 1998), data on the impact of these afforestations on SOM properties are scarce (Lilienfein et al., 2000; Zinn et al., 2002). The grasslands in the south Brazilian highlands (Figure 1), commonly referred to as Campos, belong to a region where large areas of grassland under pasture were afforested, mainly with Pinus spp. (Goldammer, 1993). In contrast to the adjacent Pampa biome, the Campos is a mosaic of natural grasslands and different forest types and occupies approximately 13.7 million ha (Nabinger et al., 2000). As Overbeck et al. (2007) recently pointed out, large parts of the Campos have been transformed to pine plantations because economic returns are greater than for cattle production. Therefore, the Campos area is decreasing at a rate of 135 000 ha per year (Carvalho, 2006) and has lost approximately 25% of its area in the last 30 years as a consequence of conversion to cash crops and pine plantations (Nabinger et al., 2000; Overbeck et al., 2007). However, no studies concerning the impacts of these land use changes on soil properties are available.

As soil organic matter (SOM) has a particular importance for soil fertility in tropical and subtropical soils, any decline would result in a significant degradation of these soils. Recent studies of the Campo area clearly indicated that such a decline of SOC and total nitrogen (N$_{\text{tot}}$) can be induced by stopping prescribed burning at the end of the winter (Knicker et al., 2008a). Other studies demonstrate that burning is an important process to maintain SOC contents in grasslands (Lal, 2004; Chen et al., 2005; Dai et al., 2006). However, no studies are available that report to what extent the decline of SOM is reduced by plantation of pines after burning has been stopped. Therefore, we investigated the effect of afforestation with Pinus taeda on former grassland from the Campos in Rio Grande do Sul, Brazil. Both 8-year-old (P8) and 30-year-old (P30) pine plantations were sampled and the chemical composition, analysed by solid-state $^{13}$C NMR and determination of stable isotope ratios ($\delta^{13}$C) and lignin oxidation products, was compared with that of native grassland soil (G). The content of pyrogenic organic matter (PyOM) was measured by chemical oxidation with acid potassium dichromate. The hypotheses were: that (i) there is a change in the concentration of SOC and composition of SOM as a result of afforestation and (ii) that there are direct effects caused by planting pines and indirect effects induced by the absence of vegetation fires in pine plantations. We investigated the mechanisms responsible for the possible changes.

**Materials and methods**

**Study area and sampling**

The research was conducted in the highlands (Planalto – Campos de Cima da serra) in the northeast of Rio Grande do Sul, southern Brazil (28°35’ – 39°S, 49°51’ – 57°W) at an average altitude of 1280 m above sea level. Climate is characterized as a transition between subtropical and temperate conditions, with a mean annual temperature of 14.5°C, large precipitation (annual values of 1800–2000 mm), a short dry period of less than 2 months in the summer and up to 15 days with frost during winter (Nimer, 1979).

![Figure 1 Map of South America showing the location of the Campos (adapted after Hueck, 1966) and the study area.](image-url)
The soils are classified as Leptosols with Ah thickness of 25 cm and as Umbrisols with Ah of 30 cm (IUSS Working Group WRB, 2006), derived from acid volcanic rocks. The diverse vegetation (3000–4000 phanerophytic species) of the grassland in the south Brazilian highland is composed of tropical, continental and temperate species belonging to the families Poaceae, Cyperaceae, Asteraceae, Apiaceae, Fabaceae and Ericaceae, with a large proportion of C4-grasses (Behling, 1997). For the grassland studied, fire was used as a management tool approximately every 2 years after the winter season to remove grass and shrub biomass, to stimulate the regrowth after the winter and to supply nutrients. Further information concerning the Campos region is presented by Overbeck et al. (2007).

Soil material was taken from the A horizon of a grassland pasture (site G) and two former grassland sites, that were converted into Pinus taeda plantations 8 (site P8) and 30 years (site P30) before sampling. Samples were split into depth increments of 0–5 cm, 5–10 cm, 10–15 cm, 15–25 cm (30) cm and from 25 (30) to 45 cm (C horizon). At each site, four profiles separated by a distance of 10–30 m were sampled. Additionally, grass material (Gr) from site G, and also pine needle litter (N) and plant material, respectively, were placed in Teflon vessels and oxidized with 15 ml 2M NaOH, 250 mg CuO, 50 mg Fe(NH4)2(SO4)2 - 6H2O and 50 mg glucose in a pressure bomb (Groteklaes, Ju¨lich, Germany) at 172°C for 2 hours under a N2 atmosphere. Ethylvanillin was added after oxidation as an internal standard in order to control the recovery of lignin monomers, which is usually in the range of 60–75% (Dignac et al., 2005). The solution was quantitatively transferred to glass beakers, adjusted to pH 1.8–2.2, and the generated lignin-derived phenols were cleaned by C18 columns (International Sorbent Technology, Hengoed, UK). The eluate was dried under N2 and silylated for gas chromatographic analysis. Determination of CuO oxidation products was carried out with a HP GC 6890 gas chromatograph, equipped with a SGE BPX-5 column and a flame ionization detector (FID) in the split mode (1:10). The oven temperature was programmed from 100°C (held for 2 minutes), to 172°C with a linear increase of 8°C min-1, and to 184°C at a rate of 4°C min-1. The final temperature of 300°C was reached at a rate of 10°C min-1.

Curoxidation yields a suite of phenolic oxidation products composed of vanillyl (V), syringyl (S) and cinnamyl (C) units with aldehydic, ketonic and acidic side chains. V-type phenols are derived from coniferyl alcohol that is generated from gymnosperm lignin (Ko¨gel-Knabner, 2002). They consist of concentrations of vanillin, acetovanillione and vanillic acid. S-type phenols are the sum of syringaldehyde, acetosyringone and syringic acid and originate from sinapyl alcohol units. In angiosperms, the lignin is built up from equal amounts of coniferyl and sinapyl alcohol (Johansson et al., 1986). C-type compounds consist of ferulic and p-coumaric acid components.

Solid-state CPMAS 13C NMR spectroscopy

Prior to the NMR spectroscopic analysis, two samples from each site were enriched in SOM by depleting the paramagnetic

Analysis of the δ13C isotope ratios

The stable C isotope ratios were measured for four samples from each site by a CHN auto analyser coupled to an isotope ratio mass spectrometer (VG Sira 10, VG Isotech, Middlewich, UK). The laboratory reference was calibrated against the international standard Vienna Pee Dee Belemnite (VPDB). Carbon isotope ratios were expressed in the delta notation for δ13C with units of per thousand (‰), which is the difference in the 13C/12C ratio between a sample and the VPDB standard:

$$\delta^{13}C = \left( \frac{^{13}C / ^{12}C_{\text{sample}}}{^{13}C / ^{12}C_{\text{VPDB}}} - 1 \right) \times 1000. \quad (1)$$

Lignin quantitative analysis

Lignin contents were analysed for two samples from each site using a modified method of the alkaline CuO oxidation method (Hedges & Ertel, 1982). Approximately 200 mg or 50 mg of soil and plant material, respectively, were placed in Teflon vessels and oxidized with 15 ml 2 m NaOH, 250 mg CuO, 50 mg Fe(NH4)2(SO4)2 - 6H2O and 50 mg glucose in a pressure bomb (Groteklaes, Ju¨lich, Germany) at 172°C for 2 hours under a N2 atmosphere. Ethylvanillin was added after oxidation as an internal standard in order to control the recovery of lignin monomers, which is usually in the range of 60–75% (Dignac et al., 2005). The solution was quantitatively transferred to glass beakers, adjusted to pH 1.8–2.2, and the generated lignin-derived phenols were cleaned by C18 columns (International Sorbent Technology, Hengoed, UK). The eluate was dried under N2 and silylated for gas chromatographic analysis. Determination of CuO oxidation products was carried out with a HP GC 6890 gas chromatograph, equipped with a SGE BPX-5 column and a flame ionization detector (FID) in the split mode (1:10). The oven temperature was programmed from 100°C (held for 2 minutes), to 172°C with a linear increase of 8°C min-1, and to 184°C at a rate of 4°C min-1. The final temperature of 300°C was reached at a rate of 10°C min-1.

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Solid-state CPMAS 13C NMR spectroscopy

Prior to the NMR spectroscopic analysis, two samples from each site were enriched in SOM by depleting the paramagnetic
components by removing mineral components with hydrofluoric acid (HF) (Gonçalves et al., 2003). For each sample, 10–15 g of ground soil material was weighed into 100 ml plastic bottles and 50 ml of 10% HF solution was added. After shaking for 2 hours, the samples were centrifuged for 10 minutes at 3008 g and the supernatant was discarded. This procedure was repeated five times and after this the samples were washed with 50 ml deionized water to remove residual HF and freeze-dried.

The solid-state cross-polarization magic angle spinning (CPMAS) $^{13}$C NMR spectra were obtained on a Bruker DSX 200 spectrometer (Karlsruhe, Germany) operating at a $^{13}$C resonance frequency of 50.3 MHz. Demineralized samples were packed into zirconium dioxide rotors with a diameter of 7 mm and spun with 6.8 kHz at the magic angle. All measurements were carried out with a ramped $^1$H pulse during a contact time of 1 ms to avoid Hartmann-Hahn mismatches. Between 5000 and 300 000 scans with pulse delays between 250 and 300 ms were applied. Before Fourier transformation, line broadenings of 50–100 Hz were used to improve the signal-to-noise ratios. The relative distribution of C forms in different structures was determined by integrating the signal intensity in various chemical shift regions assigned to carboxyl/carbonyl/amide C (220–160 p.p.m.), aromatic/olefinic C (160–110 p.p.m.), O-alkyl C (60–45 p.p.m.) and alkyl C (45–0 p.p.m.). Because of insufficient averaging of the chemical shift anisotropy at a spinning speed of 6.8 kHz, spinning side bands of the aromatic C signal (140–110 p.p.m.) and the carboxyl C signal (220–160 p.p.m.) occurred at a frequency distance of the spinning speed on both sides of the central signal. They were accounted for by adding their intensities to that of the parent signal as described in Knicker et al. (2005). One side band of the carboxyl C is found in the region 276–323 p.p.m. Assuming that the second side band for carboxyl C between 0 and 45 p.p.m. is equal in size, the integral of the side band between 0 and 45 p.p.m. was doubled and added to the carboxyl signal (160–220 p.p.m.), but subtracted from the intensity of the alkyl C region (0–45 p.p.m.). The chemical shift scale was referenced to tetramethylsilane (= 0 p.p.m.) and adjusted with glycine (COOH; 172.8 p.p.m.).

**Determination of pyrogenic organic material (PyOM)**

For quantification of PyOM, a modified method of chemical oxidation with acid dichromate (Wobach & Anders, 1989) followed by solid-state CPMAS $^{13}$C NMR spectroscopy of the chemical oxidation resistant elemental C (COREC) was used according to the method of Knicker et al. (2007, 2008b). For two samples from each site approximately 200 mg of plant material or 500 mg of HF-treated soil samples were weighed into 100 ml plastic bottles and oxidized with 50 ml of 0.1 M K$_2$Cr$_2$O$_7$/2 M H$_2$SO$_4$ solution for 6 hours at 60°C in an ultrasonic bath. Afterwards, the oxidation residues were washed five times with deionized water and freeze-dried. Determination of the C concentration of the oxidized sample was carried out by dry combustion on a Vario Max CNS elemental analyzer (Hanau, Germany) and COREC was expressed in percentage of the initial C content after mass balance calculation. The COREC content obtained for each sample was multiplied with the relative intensity of the aryl C region from solid-state CPMAS $^{13}$C NMR spectra. A correction factor $f$ was applied to take account of PyOM losses induced by the chemical oxidation. This correction factor was obtained by calculating the contribution of the aromatic proportion of COREC to the total C of charcoal produced from the native vegetation at the study site (Knicker et al., 2008a). The resulting values represent an index for the content of PyOM (Rumpel et al., 2006; Knicker, 2007).

**Statistical analysis**

All statistical analyses were carried out using SPSS 16.0 (SPSS Inc., Chicago). Normal distribution and homogeneity of variances for the measured properties were tested by using the Kolmogoroff-Smirnoff test. To determine the significance of differences between the grassland and the pine plantations a one-way analysis of variance (ANOVA) combined with post hoc tests (LSD, Tukey and Scheffe) was applied.

**Results and discussion**

**Soil characteristics and pH**

The A horizons at all sites showed comparable textures, with large clay contents between 46.5 and 58.2%, silt contributions from 32.6 to 48.2% and small amounts of sand of 6.7 to 17.3% (Table 1). Topsoils had relatively small bulk densities between 0.72 and 0.77 g cm$^{-2}$, which is in the range reported for adjacent grassland soils from the Campos (Dümmig et al., 2007). For the layer between 0 and 5 cm, the pH was 4.1 for the grassland soil. This value significantly ($P < 0.01$) decreased to 3.7 in the topsoil of the 8 year-old plantation and to 3.6 at the 30 year-old plantation, which is lower than that recently determined for Campo sites at which burning had stopped $c$. 22 years ago (Knicker et al., 2008b). These changes were not detected at depth.

Acidification of the topsoil after conversion of grasslands to forests with Pinus species is a common phenomenon throughout the world (e.g. in New Zealand (Ross et al., 2002), Ecuador (Farley & Kelly, 2004) and in the Cerrado region in Brazil (Lilienfein et al., 2000)). The acidification of topsoils may be ascribed to the input of pine needle residues, which had a lower pH-value of 3.6 compared with grass (pH of 4.2). As well as the direct input of organic acids from the coniferous litter through leaching, a decrease in the pH-value can be induced by increased soil respiration and enhanced nitrification coupled with net nitrate losses, as frequently observed after afforestation with pine (Parfitt et al., 1997; Scholes & Nowicki, 1998).
Alteration of organic C and N contents

Compared with adjacent grasslands in South America (Alvarez & Lavado, 1998) and other grassland ecosystems (e.g. Steffens et al., 2008), the A horizon of the Campos of our study area had large SOC and Ntot contents of, respectively, 136 mg g⁻¹ and 8.2 mg g⁻¹ in the topsoil (0–5 cm) decreasing to 63.4 mg g⁻¹ and 3.5 mg g⁻¹ in depths of 15–25(30) cm (Figure 2). For the C horizon, values of 21.7 mg g⁻¹ for SOC and 1.3 mg g⁻¹ for Ntot were determined. Afforestation with Pinus taeda resulted in a significant (P < 0.01) decrease of SOC down to 88.6 mg g⁻¹ and of Ntot to 4.7 mg g⁻¹ in the top 5 cm after 8 years. Under P30, the SOC concentration of the 0–5 cm soil layer declined to almost half (72.7 mg g⁻¹) of that in the G site. A large depletion was also observed for Ntot of 3.7 mg g⁻¹. In comparison, stopping burning 22 years previously on adjacent grassland sites resulted in lower depletion of C and N to 89 mg g⁻¹ and 7 mg g⁻¹ in the top 5 cm, but in comparable C concentrations at 15 to 25 (30) cm depth (Knicker et al., 2008a). Mean SOC concentrations of the A horizon were 28% and 43% smaller for P8 and P30, respectively, and mean Ntot concentrations 32% and 51% smaller when compared with the G treatment (Figure 3).

Table 1 Soil texture, bulk density (BD), C/N ratio and pH values of the studied samples (Standard deviation (±) of four replications)

<table>
<thead>
<tr>
<th>Location</th>
<th>Horizon</th>
<th>Depth /cm</th>
<th>Clay /%</th>
<th>Silt /%</th>
<th>Sand /%</th>
<th>BD /g cm⁻³</th>
<th>C/N</th>
<th>pH (CaCl₂)/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (Grassland)</td>
<td>Ah</td>
<td>0–5</td>
<td>51.2</td>
<td>42.0</td>
<td>6.7</td>
<td>0.73</td>
<td>16.6 ± 0.4</td>
<td>4.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>5–10</td>
<td>53.1</td>
<td>37.0</td>
<td>9.9</td>
<td>16.6 ± 0.3</td>
<td>4.0 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10–15</td>
<td>49.1</td>
<td>35.7</td>
<td>15.2</td>
<td>17.5 ± 0.3</td>
<td>3.9 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15–30</td>
<td>47.2</td>
<td>35.6</td>
<td>17.3</td>
<td>20.6 ± 2.9</td>
<td>4.1 ± 0.1</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Cv</td>
<td>30+</td>
<td></td>
<td></td>
<td></td>
<td>18.8 ± 0.9</td>
<td>4.2 ± 0.0</td>
<td></td>
</tr>
<tr>
<td>P8 (Pinus taeda 8 years)</td>
<td>Ah</td>
<td>0–5</td>
<td>58.1</td>
<td>35.0</td>
<td>6.9</td>
<td>0.77</td>
<td>18.9 ± 0.9</td>
<td>3.7 ± 0.1</td>
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<td></td>
<td>5–10</td>
<td>58.2</td>
<td>34.0</td>
<td>7.8</td>
<td>18.0 ± 0.8</td>
<td>3.9 ± 0.1</td>
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<td>10–15</td>
<td>56.6</td>
<td>34.7</td>
<td>8.7</td>
<td>18.1 ± 0.6</td>
<td>3.9 ± 0.0</td>
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<tr>
<td></td>
<td>15–25</td>
<td>55.6</td>
<td>32.6</td>
<td>11.8</td>
<td>18.4 ± 1.0</td>
<td>4.0 ± 0.0</td>
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<tr>
<td></td>
<td>Cv</td>
<td>25+</td>
<td></td>
<td></td>
<td></td>
<td>20.0 ± 9.3</td>
<td>4.0 ± 0.0</td>
<td></td>
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<tr>
<td>P30 (Pinus taeda 30 years)</td>
<td>Oe</td>
<td>15–6</td>
<td></td>
<td></td>
<td></td>
<td>31.7</td>
<td>3.2</td>
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<td>Oa</td>
<td>6–0</td>
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<td>33.1</td>
<td>2.5</td>
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<tr>
<td></td>
<td>Ah</td>
<td>0–5</td>
<td>46.5</td>
<td>44.5</td>
<td>9.0</td>
<td>0.72</td>
<td>19.7 ± 0.7</td>
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<td>5–10</td>
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<td>41.5</td>
<td>10.3</td>
<td>18.8 ± 0.5</td>
<td>3.8 ± 0.1</td>
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<td></td>
<td>10–15</td>
<td>49.4</td>
<td>40.2</td>
<td>10.4</td>
<td>18.6 ± 0.8</td>
<td>3.9 ± 0.1</td>
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<td></td>
<td>15–25(30)</td>
<td>47.4</td>
<td>40.8</td>
<td>11.9</td>
<td>20.1 ± 2.3</td>
<td>4.0 ± 0.1</td>
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<tr>
<td></td>
<td>Cv</td>
<td>25(30)+</td>
<td>30.2</td>
<td>39.0</td>
<td>30.8</td>
<td>20.5 ± 4.3</td>
<td>4.0 ± 0.1</td>
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<tr>
<td>N (Pine needles)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>120.5</td>
<td>3.6</td>
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<tr>
<td>Gr (Grass)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>42.3</td>
<td>4.2</td>
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</table>

Figure 2 Content of SOC and Ntot (mg g⁻¹) of the grassland (G) and the pine plantations (P8, P30) at different soil depths. Error bars represent standard deviation (n = 4).
Our results are in agreement with other findings of smaller SOC and N contents after conversion from grassland to Pinus spp. plantations. In general, SOC was 5–48% smaller in 7–23 year old pine forests on former grassland and N was 14 to 47% smaller (Paul et al., 2002; Ross et al., 2002; Zinn et al., 2002; Farley & Kelly, 2004). A review of over 65 publications dealing with land use change from pasture to plantations with conifers (mainly Pinus radiata) showed that SOC decreased by 12% on average, whereas in areas with higher precipitation (>1500 mm) the depletion was greater (by 23%) (Guo & Gifford, 2002).

An important reason for the SOC and N\(_{\text{tot}}\) reduction in the mineral soil could be a change in the quantity and quality of organic matter input resulting from the vegetation change from mainly grass to pines. Although pines certainly contribute to the total litter production from their roots, the proportion of vegetation residue input derived from above-ground biomass is much greater when compared with grassland species with relatively large root/shoot ratios (Jackson et al., 1996). As pine litter is more recalcitrant than the easily degradable organic matter from grasses, litter decomposition rate is reduced and detrital inputs from pines accumulate on the soil surface. This was also observed in the plantations of our study sites, where organic surface layers were up to 15 cm thick. This greater recalcitrance can be caused by oversaturation in cavities of partly decomposed pine needles, chemical inhibitors, relatively large concentrations of lignin and other phenolic compounds and non-existent needle-decomposer macrofauna (Goldammer, 1993; Scholes & Nowicki, 1998; Zinn et al., 2002).

The greater reduction of N\(_{\text{tot}}\) compared with SOC could be attributed to N-uptake by the pines and its immobilization into the above-ground biomass as was assumed for reduced N contents of soils under Pinus radiata plantations on former pastures in Australia (Birk, 1992). Furthermore, the suppression of N-fixing grassland legumes by pines and leaching of mineralized N are likely to be important contributors to the increased N-depletion, as well as a smaller N-input after the change to litter with wider C/N ratios.

In the grassland soil, the C/N ratios increased with soil depth from 16.6 at 0–10 cm to 18.8 at >30 cm (Table 1). C/N ratios of P8 were significantly \(P < 0.05\) greater in the first 10 cm with ratios of 18.0 to 18.9, but there was no significant difference beneath this region. P30 also had significantly \(P < 0.01\) greater C/N ratios of 19.7 and 18.8 at 0–5 cm and 5–10 cm, respectively. Bearing in mind that the cessation of burning resulted in a clear decrease of the C/N ratio to 13 (Knicker et al., 2008b), the marginal increase of this value for the material from the surface of the mineral soil from the afforested sites may be attributed to the alteration of litter material quality. Whereas for the vegetation of the Campos region a C/N of 34 was determined (Knicker et al., 2008b), the grass material collected from the forest floor had a C/N ratio of 42.3 and that of the pine needles was 120.5.

Changes of δ\(^{13}\)C isotope ratios after afforestation

The δ\(^{13}\)C values from the G site ranged from −14.4 to −15.7\(^{\circ}\), an isotopic signature that is characteristic of organic material derived from C4 plants with signatures ranging from approximately −9 to −17\(^{\circ}\) (Staddon, 2004). Plant δ\(^{13}\)C values were −14.6\(^{\circ}\) for Campos vegetation (C4 photosynthesis) and −29.3\(^{\circ}\) for pine needles (C3 photosynthesis), resulting in a common isotopic difference of approximately 14\(^{\circ}\) between C3 and C4 plants (Figure 4). Although organic surface layers (Oe and Oa horizons) from afforested sites exhibited characteristic δ\(^{13}\)C values derived from C3 plants (pines), soil C isotope ratios had a C4 signature ranging from −14.2 to −15.2\(^{\circ}\). The only exception was the layer from 0–10 cm at P30, where δ\(^{13}\)C had significantly \(P < 0.01\) smaller values of −18.5\(^{\circ}\) at

![Figure 3](image-url)  
**Figure 3** Mean SOC and N\(_{\text{tot}}\) concentrations (mg g\(^{-1}\)) of the A horizon from the grassland (G) and the pine plantations (P8, P30). Error bars represent standard deviation \((n = 4)\).

![Figure 4](image-url)  
**Figure 4** δ\(^{13}\)C values (\(^{\circ}\)) of plant samples (pine needle, grass) and different soil depths from the grassland (G) and the pine plantations (P8, P30). Error bars represent standard deviation \((n = 4)\).
Lignin degradation

Figure 5 shows the sum of lignin-derived phenolic CuO oxidation products vanillyl, syringyl and cinnamyl units (VSC), which can be considered as an indicator of the relative amount of lignin (Hedges & Mann, 1979). VSC values were normalized to SOC for soil and total plant C for plant samples, respectively, and expressed as mg VSC g⁻¹ C. In general, the concentrations of VSC decreased with increasing soil depth at all sites, indicating a greater degree of decomposition of lignin in the deeper soil layers (Hedges & Mann, 1979). The largest VSC content of 1.4 mg g⁻¹ C was determined in G at 0–5 cm. P8 and P30 had significantly smaller concentrations of 1.1 and 1.0 mg g⁻¹ C, respectively, although VSC-concentrations were greater for pine needles (9.5 mg g⁻¹ C) than for grass (4.3 mg g⁻¹ C). A comparable decrease of the VSC contents was also found in the topsoil of a forest with Pinus caribaea var. hondurensis in the adjacent savanna region (Cerrado) of Brazil (Zinn et al., 2002).

The ratios of syringyl to vanillyl units (S/V) and cinnamyl to vanillyl units (C/V) provide information not only on the source of the lignin, but also about its state of decomposition because the stability against degradation is in the order V > S > C (Hedges & Mann, 1979; Ziegler et al., 1986). The ratios of S/V and C/V decreased at the G site with increasing soil depth, which is in accordance with an increasing degradation state of lignin in the deeper soil layers, already assumed from the declining VSC contents (Figure 6). Both afforested sites, on the other hand, showed an opposite trend with the smallest S/V and C/V ratio in the upper soil layers from 0 to 5 cm and 5 to 10 cm. The older forested site (P30) had smaller ratios than the younger site (P8). Because the S/V ratio is lower (approximately 1:13) for lignin produced from gymnosperms than from angiosperms with equal amounts of S and V phenols, and only non-woody vascular plant tissues produce C-type phenols (Hedges & Mann, 1979), those observations could be explained by enhanced input of pine litter at the pine sites. Pine needles had much smaller ratios of S/V and C/V (0.067 and 0.154, respectively) compared with grass (0.414 and 0.777, respectively). However, this interpretation contrasts with the data obtained from the C isotope analysis and the VSC concentrations, which indicated only minor inputs of fresh pine litter. Thus, the decreasing ratios probably result from a more advanced degradation state of lignin derived from grass residues still present in the forest soils. Between 10 and 15 cm depth no significant differences between G, P8 and P30 were found, demonstrating that the deeper soil layers were not yet affected by the vegetation change.

The ratio of acidic to aldehydic forms of vanillyl, (Ac/Al)ᵥ, and syringyl, (Ac/Al)ₛ, are further indicators for the degree of lignin oxidation (Hedges & Ertel, 1982; Ziegler et al., 1986) and allow an assessment of its origin from gymnosperms ((Ac/Al)ᵥ (i.e. Pinus spp. in our case)) or angiosperms ((Ac/Al)ₛ (i.e. grass in our case)). (Ac/Al)ᵥ showed no significant difference between G, P8 and P30 in the topsoil from 0 to 5 cm and 5 to 10 cm and increased at all sites with soil depth (Figure 7). The latter finding is in accordance with an enhanced oxidation degree of the lignin residues depth. For the top 5 cm, (Ac/Al)ₛ was greater at the forest sites compared with the grassland. This greater proportion of acidic compounds is direct evidence for an enhanced oxidation of grass-derived SOM in the topsoil of the pine plantations. In the deeper soil layers, no significant differences between the different locations were found.

Chemical composition of SOM (CPMAS ¹³C NMR spectroscopy)

After HF treatment, all soil samples were enriched in SOC by a factor of 3.2 to 11.3 and in Nₙₐₜ by a factor of 3.2 to 11.7, whereas the greatest accumulation was at depth, especially in the C horizon. Recovery of SOC was between 51 and 78% for the A and 26 and 49% for the C horizon and for Nₙₐₜ 53 and 74% for the A and 19 and 53% for the C horizon, which is in
the range of losses during the HF treatments of the Campos soils of this region and of other studies (Goncalves et al., 2003; Dieckow et al., 2005). For the detection of possible alterations of the original organic material as a consequence of the HF treatment, the factor $R$ was calculated (Schmidt et al., 1997):

$$R = \frac{(C/N \text{ before HF treatment})}{(C/N \text{ after HF treatment})}.$$ (2)

$R$-values of between 0.9 and 1.1 for all samples plus the fact that there were no major differences between the intensity distribution in solid-state $^{13}$C NMR spectra of the grassland soils before and after HF-treatment (Knicker et al., 2008b) suggest that selective changes in the SOM did not occur during demineralization.

Table 2 lists the intensity distributions (%) in the solid-state CPMAS $^{13}$C NMR spectra of soil, litter and plant samples: representative spectra are shown in Figure 8. In all spectra, the greatest intensity was found in the chemical shift region between 60 and 110 p.p.m., which is probably assignable to O-alkyl C. The contribution of this C-class material decreased with depth and with increasing time from afforestation (i.e. in accordance with a preferential decomposition of carbohydrates and a relative decrease of the input of fresh litter residues into the upper mineral soil). The N-alkyl C region from 45 to 60 p.p.m. showed no differences between the sites investigated.

In the top 10 cm, the relative intensity in the region between 0 and 45 p.p.m., comprising signals from alkyl C in fatty acids, amino acids and alkane structures, increased slightly with time after afforestation. A similar trend can be observed for the region between 220 and 160 p.p.m., which is probably attributable to carboxylic C. The alkyl C/carboxyl C ratio, however, remained at approximately 2 to 3, demonstrating that accumulation of short-chain acids rather than the preferential preservation of long-chain lipids and alkane structures was responsible for the increase in alkyl C.
The alkyl C/O-alkyl C may be used as an index of the extent of decomposition of SOM (Baldock et al., 1992). However, this is only applicable if the source material remains constant, and processes leading to preferential sequestration of certain C-groups can be excluded. Such processes may include selective sorption onto soil minerals or preferential leaching of water soluble compounds. In the case of our study site, changes in the composition of the source material may be an additional cause for an alteration of this ratio. At site G, the alkyl C/O-alkyl C ratio was 0.54 and 0.59 for the material from the depths 0 to

<table>
<thead>
<tr>
<th>Location</th>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Carboxylic C</th>
<th>Aromatic C</th>
<th>O-alkyl C</th>
<th>N-alkyl C</th>
<th>Alkyl C</th>
<th>Alkyl C/O-alkyl C</th>
</tr>
</thead>
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<td>G (Grassland)</td>
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<td>0–5</td>
<td>9</td>
<td>16</td>
<td>43</td>
<td>9</td>
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<tr>
<td></td>
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<td>18</td>
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<td>34</td>
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<td>22</td>
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<tr>
<td></td>
<td>Cv</td>
<td>30+</td>
<td>15</td>
<td>27</td>
<td>30</td>
<td>8</td>
<td>20</td>
<td>0.67</td>
</tr>
<tr>
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<td>Ah</td>
<td>0–5</td>
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<td>37</td>
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<td>24</td>
<td>0.65</td>
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<tr>
<td></td>
<td></td>
<td>5–10</td>
<td>14</td>
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<td>8</td>
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<td>0.57</td>
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<td>17</td>
<td>23</td>
<td>34</td>
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<td>25+</td>
<td>16</td>
<td>29</td>
<td>30</td>
<td>8</td>
<td>17</td>
<td>0.57</td>
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<tr>
<td>P30 (Pinus taeda 30 years)</td>
<td>Oe</td>
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<td>37</td>
<td>9</td>
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<tr>
<td></td>
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<td>9</td>
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<td>0.87</td>
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<td>32</td>
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<td></td>
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<td>25(30)+</td>
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<td>27</td>
<td>29</td>
<td>8</td>
<td>22</td>
<td>0.76</td>
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<td>N (Pine needles)</td>
<td></td>
<td>3</td>
<td>17</td>
<td>58</td>
<td>7</td>
<td>15</td>
<td>0.26</td>
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<tr>
<td>Gr (Grass)</td>
<td></td>
<td>9</td>
<td>18</td>
<td>48</td>
<td>8</td>
<td>17</td>
<td>0.35</td>
<td></td>
</tr>
</tbody>
</table>

The alkyl C/O-alkyl C may be used as an index of the extent of decomposition of SOM (Baldock et al., 1992). However, this is only applicable if the source material remains constant, and processes leading to preferential sequestration of certain C-groups can be excluded. Such processes may include selective sorption onto soil minerals or preferential leaching of water soluble compounds. In the case of our study site, changes in the composition of the source material may be an additional cause for an alteration of this ratio. At site G, the alkyl C/O-alkyl C ratio was 0.54 and 0.59 for the material from the depths 0 to

Figure 8 Solid-state CPMAS $^{13}$C NMR spectra of the A horizon from the grassland (G) and the pine plantations (P8, P30) at different soil depths.

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5 cm and 5 to 10 cm and increased to 0.65 and 0.57 for P8 and to 0.87 and 0.82 for P30, respectively (Table 2). The data collected so far do not support an enhanced input of pine litter into the mineral soils of P8 and at P30; only minor contributions of pine-derived SOM were found. These ratios are therefore in line with the assumption that over a time scale of a few decades, pine plantations of pines on grassland lead to an enhanced degradation of residual SOM in the mineral soil derived from the grass species. This conclusion is supported by the relatively comparable chemical composition of the SOM of the top 10 cm of P30 and of a *Campos* soil of the same area that remained unburnt for the last 22 years (Knicker et al., 2008b). For the latter, it was demonstrated that stopping burning had decreased the input of fresh litter from decaying grass plants. However, down to 30 cm, P30 exhibited greater O-alkyl C and lower alkyl C contents with respect to the *Campos* soil profile, possibly because the deeper root system of pines allows the release of fresh exudates and thus the input of carbohydrate-rich organic matter at this depth.

The chemical shift region between 110 and 160 p.p.m. embraces signals of lignin and recalcitrant aromatic compounds such as pyrogenic organic matter (PyOM). For all sites, the relative contribution of aromatic C increased. Because we observed a decline in CuO-oxidation products down the soil profile, this is unlikely to be attributable to a selective preservation of lignin degradation products. However, because all sites were regularly burnt before changing to pine plantations, we tentatively suggest that the aromatic C enrichment with depth is caused by accumulation of PyOM.

**Content of pyrogenic organic material (PyOM)**

In general, PyOM accounted for 3.7 to 7.1% of organic C, but there were no marked differences between the regularly burnt grassland and the pine plantations (Table 3). The observed PyOM concentrations are in the range observed in other studies, which used the same method of chemical oxidation in combination with solid-state $^{13}$C NMR spectroscopy (e.g. Rumpel et al., 2006). However, the spectra of the oxidized material also demonstrated large contributions in the alkyl C region (Figure 9) and therefore PyOM concentrations would be over-estimated. Possibly, hydrophobic compounds such as plant waxes resisted the acid attack.

At all the sites investigated, PyOM contents tended to have greater amounts in deeper soil layers from 15 to 25(30) cm with concentrations of 6.7 to 7.1% of organic C. Normally, the largest contents of PyOM should be located in the topsoil, because after burning, fire-affected SOM accumulates at the soil surface or in the first few cm of the soil. However, PyOM was relocated from the topsoil to the deepest part of the A horizon. This is in contrast to other studies, which demonstrated the graphite-like nature of PyOM and the associated chemical and physical recalcitrance against biological degradation (Schmidt & Noack, 2000). There is rising evidence that PyOM is not as stable as assumed previously. Knicker et al. (2006) found significant charcoal contribution in the B horizon of a Spanish Cambisol only 2 years after a severe forest fire. This was explained by leaching of biochar residues that became water-soluble after oxidation and introduction of carboxylic groups. In a subtropical Acrisol from Brazil, the greatest amount of PyOM was found in the subsoil, and this was attributed to bioturbation (Dieckow et al., 2005). Such relocations may be explained by recently developed concepts that describe PyOM as a heterogeneous mixture of partly heat-altered biopolymers with domains of relatively small polyaromatic clusters, but with considerable substitution with N, O and S functional groups (Knicker et al., 2007). Such structures offer enough areas for microbial attack and thus enable faster oxidation of PyOM, which then can be dissolved and relocated vertically.

### Table 3

<table>
<thead>
<tr>
<th>Location</th>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>COREC (%)</th>
<th>Aromatic C (%)</th>
<th>PyOM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (Grassland)</td>
<td>Ah</td>
<td>0-5</td>
<td>23.5</td>
<td>15.7</td>
<td>3.7</td>
</tr>
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<td>28.5</td>
<td>17.2</td>
<td>4.9</td>
</tr>
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<td>15-30</td>
<td>32.0</td>
<td>21.0</td>
<td>6.7</td>
</tr>
<tr>
<td>P8 (Pinus taeda 8 years)</td>
<td>Ah</td>
<td>0-5</td>
<td>31.9</td>
<td>19.7</td>
<td>6.3</td>
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<td>15-25</td>
<td>26.4</td>
<td>26.8</td>
<td>7.1</td>
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<tr>
<td>P30 (Pinus taeda 30 years)</td>
<td>Ah</td>
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<td>28.0</td>
<td>17.1</td>
<td>4.8</td>
</tr>
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<td>29.7</td>
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<td>15-25(30)</td>
<td>25.9</td>
<td>26.5</td>
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</table>

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Degradation of SOM and the effect of the cessation of burning

The results of $^{13}$C isotopic analysis, determination of lignin and CPMAS $^{13}$C NMR spectroscopy indicated that throughout the soil profiles of the pine plantation SOM is mainly derived from grass residues. Even after 30 years, only a small impact of pine litter residues on SOM composition was present in the top 10 cm. The low incorporation rate of pine litter may be explained by its high level of recalcitrance, leaving only partly degraded pine needle accumulating on the soil surface. Because of the decelerated input of fresh organic material, the SOC and N$_{tot}$ losses caused by degradation cannot be balanced, thus resulting in decreasing SOM with a relatively high level of humification.

Any significant degradation of residual SOM was also assumed to be responsible for decreased SOC and N$_{tot}$ contents in Pinus radiata plantations on former pastures from New Zealand, although there was no direct evidence for this (Davis, 1995; Parfitt et al., 1997). Low SOC concentrations at 0–5 cm depth from soils under forests with Pinus caribaea var. hondurensis in the Cerrado region of Brazil were explained by the site preparation with heavy ploughing to 20 cm and a low rate of pine needle litter input associated with acceleration of decomposition of remaining SOM formed under pastures (Zinn et al., 2002).

In addition, the observed decline is attributed to the absence of the formerly frequent vegetation fires. Such fires are, typically, of low intensity. The low heat conductivity of the mineral matter means that the heat intensity does not penetrate deeper than a few cm into the soil. Thus, such fires do not destroy the SOM in the mineral soil (Goldammer, 1993) and only the above-ground biomass is burnt, whereas the remaining roots die and contribute to the SOM. As below-ground biomass from grass and herb species accounts for a very large part of total biomass in grasslands, vegetation burning could be an important process in the accumulation of SOC and N in such soils (Knicker, 2007). Furthermore, there is a considerable C and N input from litter at the grassland sites because unburnt plant residues accumulate on the soil surface and the release of mineral nutrients from the ash allows the growth of herbs immediately after the fire. Thus, annual dry matter production is usually greater in regularly burnt than in unburnt grasslands (Lal, 2004). In tropical savannas of Australia, frequent burning caused greater SOC stocks, whereas fire exclusion led to smaller stocks, which was explained by a reduction in detrital input (Chen et al., 2005). Greater organic C and N concentrations in forest soils in Spain after wildfires were reported by Knicker et al. (2005). Dai et al. (2006) described greater SOC and N stocks at sites with different fire treatments compared with unburnt controls in a temperate mixed-grass savanna.

In a recent study at adjacent grassland sites, stopping burning at natural grasslands for 22 years resulted in a SOC decrease of 23% (Knicker et al., 2008b). Compared with the results from our study, where a considerably bigger SOC decrease of 43% was shown in 30-year-old pine plantations, it is obvious that both stopping burning and enhanced degradation of SOM are responsible for the observed depletion of SOC. Furthermore, no alteration in N$_{tot}$ stocks was found in grassland soils that were protected from burning for 22 years. Consequently, the considerable reduction of N$_{tot}$ reported in our study can be attributed to the plantation of pines.

Conclusions

The grassland soils of the Brazilian Campos clearly showed a considerable increase in SOM under plantations of Pinus taeda. This depletion is caused both by an enhanced degradation of SOM because of a reduced input of organic material and by stopping regular burning inside the plantations. Pine plantations in this region are primarily used for production of cellulose and harvested after < 30 years and thus the observed decline of SOM probably cannot be balanced because of a long degradation period of recalcitrant pine litter. Thus, the C sequestration potential of the mineral soil is probably reduced. As soil fertility in the weathered grassland soils is associated mainly with SOM, the demonstrated decreases are likely to reduce availability and supply of nutrients in the mineral soil.

Acknowledgements

The authors would like to thank the staff of the Laboratoire de Biogéochimie des Milieux Continentaux from INRA for

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**Figure 9** Solid-state CPMAS $^{13}$C NMR spectra after chemical oxidation from the 8-year-old afforested site (P8) at different soil depths. The grey-coloured band shows the aromatic C region.
support with $\delta^{13}$C and lignin analysis and Petra Müller (TUM) for technical assistance. This project was partially financed by CAPES (Brazil) and DAAD (Germany).

References


