Condensation degree of burnt peat and plant residues and the reliability of solid-state VACP MAS $^{13}$C NMR spectra obtained from pyrogenic humic material

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Abstract

Charred organic matter is assumed to contain heavily condensed polycyclic aromatic domains with a considerable proportion of core carbons. To examine their possible underestimation using variable amplitude (VA) cross polarization (CP) magic angle spinning (MAS) $^{13}$C nuclear magnetic resonance (NMR), the condensation degree of a peat subjected to thermal oxidation at 350 °C for up to 180 s was examined by means of elemental analysis and various NMR techniques. For comparison, commercially available barbeque charcoal and charred organic residues collected from a fire-affected soil from Southern Spain were analyzed. The atomic H/C ratios of the aromatic moiety of the chars revealed that on average every second to third C is connected to a proton. Dipolar dephasing NMR data confirm the high extent of and are in agreement with relatively small clusters of six aromatic rings connected by approximately two bridging CS. Alternatively, benzanthracene-like structures with two to five bridging CS are possible. The CP time ($T_{CH}$) and the $^1$H and $^{13}$C spin lattice relaxation times in the rotating frame ($T_{1\text{pH}}$, $T_{1\text{pC}}$) of the chars suggest the presence of crystalline and amorphous domains. Both fractions fulfill the condition $T_{CH} < T_{c} < T_{1\text{pH}}$ which is required for C-detection with the CP-technique. Reliability of the CP-technique was supported by experiments with standards consisting of charred material and untreated peat mixed in defined ratios. The analysis of $^{13}$C spin lattice relaxation indicated saturation of some $O$-alkyl and alkyl C in the Bloch decay (BD) NMR spectrum of the untreated peat. This may explain its higher aromatic C intensity compared to the respective CP MAS NMR spectrum.

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1. Introduction

After wildfires, charcoal together with charred plant residues are introduced into the soil system. The charring process is accompanied by drastic chemical alteration of the litter, which is manifested in the transfer of biologically available structures such as carbohydrates, proteins and lipids into relatively inert aromatic macromolecules (Almendros et al., 2003). Therefore, beside influencing the long-term C sequestration, the input of charred residues into soils is expected to have a major
impact not only on the quality and quantity of the organic matter but also on the whole humification processes.

Solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy represents a potentially attractive method for revealing such alteration. As a non-destructive method $^{13}$C NMR allows the characterization of insoluble heterogeneous mixtures which are widely excluded from analysis by means of wet chemical approaches. The emphasis of this technique is not only to determine the gross chemical composition of the material under study via a chemical shift assignment but also a quantitative correlation between the different signal intensities and the relative contribution of the respective C types to the total organic C content. In general, solid-state $^{13}$C NMR spectra of soil organic matter are obtained with the cross polarization magic angle spinning (CPMAS) technique (Wilson, 1987). This technique increases the sensitivity of $^{13}$C by magnetization transfer from the $^1$H to the $^{13}$C spin system during a contact time $\tau_c$. During this time the intensity of the $^{13}$C signal is built up with the polarization transfer time $T_{CH}$ by exciting both $^1$H and $^{13}$C spin systems according to the requirements of the Hartmann–Hahn condition. A fast $T_{CH}$ occurs for $^{13}$C nuclei with strong dipolar $^1$H–$^{13}$C interactions. However, for carbons with large C–H internuclear distances and for C in groups with high molecular mobility the proton-dipolar interactions are weakened, which increases their $T_{CH}$. Organic matter subjected to combustion transforms into condensed structures (Freitas et al., 1999; Schmidt and Noack, 2000; Baldock and Smernik, 2002). At high heat intensities, condensation is expected to result in aromatic clusters with a considerable proportion of core C for which the distance to the next proton exceeds the length of three to four bonds. Carbons with such long distances to the next proton were found to be under represented by means of solid-state CPMAS $^{13}$C NMR (Alemany et al., 1983a; Smernik et al., 2002).

The observed intensity is also affected by the relaxation behaviour of the proton reservoir during spin lock. The faster the so called proton spin relaxation in the rotating frame ($T_{1pH}$) the lower the magnitude of the magnetization that can be transferred to the $^{13}$C spin system within a certain contact time $\tau_c$. In consequence, after having passed through a maximum, the $^{13}$C-intensity is decreases with increasing $\tau_c$ and a $^{13}$C signal is only observed if the condition $T_{CH} < \tau_c < T_{1pH}$ is fulfilled.

For charcoal it was suggested that the polycyclic aromatic structures tend to stabilize organic free radicals formed during combustion (Freitas et al., 1999; Smernik et al., 2002), providing efficient relaxation sinks. Only if their contribution to relaxation is negligible or approximately the same for all C nuclei observable in the spectrum can one expect quantitative results (Mehring, 1983; Wilson, 1987). In addition, the loss of organic material during charring can result in a relative accumulation of inorganic paramagnetic compounds that can interact with the organic structures and decrease $T_{1pH}$ to an extent that CP becomes inefficient.

In A horizons of Australian soils up to 30% of the total C were suggested to consist of charcoal (Skjemstad et al., 1999). Applying Bloch decay (BD), a technique in which the $^{13}$C is directly excited and intensity loss due to inefficient CP is avoided, indicated that only $\sim$27% of charcoal-derived aromatic C is detected by the CPMAS technique. This finding is supported by spin counting experiments using glycine as reference (Smernik and Oades, 2000a).

On the other hand, no appreciable differences between the relative contribution of aromatic C in charred material were observed for a peat heated to 500 °C for 1 h under nitrogen atmosphere (Freitas et al., 1999). After increasing the temperature to 900 and 1000 °C the use of the CP technique was completely unsuccessful. Comparably, no CPMAS $^{13}$C NMR signal was obtainable from lignite coke (Abelmann et al., 2005). For the latter the low atomic H/C ratio of 0.1 suggests a highly condensed structure in which most of the protons are too far from most carbons for efficient CP. From those reports it may be inferred that char in fire-affected soil organic material may only prevent the acquisition of quantifiable solid-state CPMAS $^{13}$C NMR spectra, if a high amount of highly condensed aromatic structures is formed during the vegetation fire.

Beside using atomic O/C and H/C ratios, information on the condensation degree of aromatic structures can be obtained with dipolar dephasing NMR spectroscopy (Alemany et al., 1983a; Wilson, 1987). This technique involves a brief interruption of the $^1$H-decoupling between $\tau_c$ and acquisition, which allows $^1$H spins to interact with $^{13}$C nuclei causing a broadening of the $^{13}$C signals (dephasing). With increasing interruption delay $\tau$, the intensity of the broadened signal diminishes with the dephasing time constant, $T_{dd}$, and consequently will become indistinguishable from the noise in the corresponding CPMAS $^{13}$C NMR spectrum. Carbons in close vicinity of H and in groups with low mobility have strong dipolar interactions and thus show fast dephasing (Alemany et al., 1983b; Wilson, 1987) as described by

$$I(\tau) = I_{DG} \cdot \exp \left( \frac{-\tau^2}{T_{ddG}^2} \right),$$

where $I(\tau)$ is the experimentally determined signal intensity, $I_{DG}$ represents the intensity at $\tau = 0$ s and $T_{ddG}$ is the dephasing time constant of the fast dephasing fraction (Gaussian).

The decay of the fraction $I_{DG}$ with weak dipolar interaction (Lorentzian) such as highly mobile C but also
2. Experimental

2.1. Charred plant residues

As representative of charred plant residues, (i) a commercially available charcoal (Montana, Germany) from beech wood and (ii) charred plant particles picked up from the Ah horizon of a fire-affected Cambisol located at 217 m.a.s.l. in the Sierra de Aznalcóllar, Southern Spain, were analyzed. This soil, developed under typical Mediterranean pine forest dominated by *Pinus pinaster* Aiton, suffered a severe fire five years before sampling in June 2001. The charred plant residues were hand-picked and divided into material in which plant features were still recognizable and into amorphous blackish charred particles of no discernable origin. Additionally, a sample from the Ah horizon was collected (fire-affected soil: FA) after removing the litter layer. Control soil material (FU) from the Ah horizon of a neighbour fire-affected Cambisol (205 m.a.s.l.; UTM 29S 0737845,4161836) with comparable properties was also sampled. A brief description of these soils is given in Knicker et al. (2005). To improve the sensitivity for the NMR analysis and to remove paramagnetic components, the soil samples were extracted five times with 10% (w/w) hydrofluoric acid at room temperature. The C and N contents were measured in duplicate by dry combustion (975 °C) using an Elementar Vario EL microanalyzer detecting N as N₂ and C as CO₂.

2.2. Preparation of charred peat samples

Samples from the sapric peat from a deposit located at Buyo (Galicia, Northern Spain) were used for laboratory-controlled heating experiments. Details on the physico-chemical characteristics of this peat and the preparation of its chars are published elsewhere (Almendros et al., 1994, 2003). In brief, 1 g of homogenized peat was heated in triplicate in porcelain boats at 350 °C for variable periods (60, 120, 150 and 180 s) in a ceramic tubular electric furnace (Wosthoff o.H.G, Bochum, Germany) operating at atmospheric pressure and under a 625 ml min⁻¹ suction flow. A membrane pump connected to a soda-lime column was used to supply CO₂-free air to the oxidation tube. After the progressive oxidation times the boats were extracted from the furnace and cooled in a desiccator with P₂O₅. The heated samples were weighed, corrections were done for the atmospheric moisture (independently calculated from samples heated at 100 °C overnight), and their elemental composition was determined with a Carlo Erba CHNS-O-EA1108 microanalyzer.

2.3. Preparation of peat-char mixtures

To test the detectability of aromatic C in charred material with the VACP MAS ¹³C NMR technique, the untreated peat material was mixed with charred material. Two mixtures with 150 and 300 mg peat charred for 150 s (peat 150 s) per 1 g sample mixture were prepared. Additionally, mixtures containing 107, 199, 344, 513, 600, 636, 666 and 714 mg barbeque char per 1 g sample mixture were analyzed. The peat charred for 150 s still contains alkyl C (25%) and was assumed to represent char produced during a medium intense vegetation fire. The organic C of the barbeque charcoal, on the other hand, is almost completely aromatic which is expected for charred plant residues formed during an intense fire.

2.4. VACP MAS ¹³C NMR measurements

The ¹³C NMR spectra were acquired with a Bruker DSX 200 spectrometer at a resonance frequency of 50.32 MHz using a zirconium rotor of 7 mm outer diameter with KEL-F caps. The CP magic-angle spinning (MAS) technique (Pines et al., 1973; Schaefer and Stejskal, 1976) was applied with a spinning speed of 6.8 kHz and using a ramped ¹H-pulse amplitude (variable amplitude; VA) during the contact time, t_c = 1 ms to circumvent spin modulation during Hartmann–Hahn condition (Peersen et al., 1993; Cook et al., 1996). Between 5000 and 8000 scans were accumulated using a pulse delay, d, between 300 and 500 ms. According to inversion recovery experiments those delays were longer than five times the ¹H spin lattice relaxation times (Table 1) which is required to avoid saturation. Prior to Fourier
transformation and depending on the signal-to-noise ratio, line broadenings between 10 and 75 Hz were applied. The $^{13}$C-chemical shifts were calibrated relative to tetramethylsilane (0 ppm). The relative distribution of carbons in different structures was determined by integrating the signal intensity in various chemical shift regions assigned to carboxyl/carbonyl/amide/C (220–160 ppm), aromatic/olefinic C (160–110 ppm), O-alkyl C (110–60 ppm), N-alkyl/methoxyl C (60–45 ppm) and alkyl C (45–0 ppm).

Owing to 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 ppm) and the carboxyl C signal (220–160 ppm) occurred at a frequency distance of the spinning speed at both sides of the central signal. They were considered 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 0–45 ppm. The integral of the side band between 276 and 323 ppm was doubled and added to the carboxyl signal (160–220 ppm), but subtracted from the intensity of the alkyl C region (0–45 ppm).

For the fresh peat, the peat 150 s and the barbeque charcoal, the CPMAS $^{13}$C NMR measurements were performed four times to determine the reproducibility. For the peat material the time span between the first and the fourth measurements was 4 years. For the barbeque charcoal the period between the measurements was 4 weeks.

### 2.5. Dipolar dephasing NMR spectroscopy

For the dipolar dephasing (DD) experiments, delay times, $\tau$, varying from 10 to 120 $\mu$s were introduced between Hartmann–Hahn contact $t_c$, and acquisition in which the decoupler was switched off. On both, the $^1$H and $^{13}$C channel, in the middle of the evolution period 180$^\circ$ pulses were added to remove linear phase distortions. For quantification, the intensity of the aromatic C region between 160 and 110 ppm was determined as a function of $\tau$ and the curve was fitted by combining Eqs. (1) and (2) using

$$I(\tau) = I_{0\ell} \cdot \exp \left(-\frac{-\tau}{T_{ddl,i}}\right) + I_{0G} \cdot \exp \left(-\frac{-\tau^2}{T_{ddG}}\right).$$  \hspace{1cm} (3)

Applying this technique, $^1$H–$^1$H dipolar interactions and interference between MAS and dipolar fluctuations could lead to dipolar echoes (Newman, 1992a). These modulations were obvious for spinning side bands of the aromatic and carbonyl C, but were not observed for the respective parent signal. Thus, the signal intensity of the spinning side bands was not included in the calculations. To avoid distortion of the dephasing decay by the impact of rotational echoes, occurring at integral multiples of the spinner period, the upper limit of $\tau$ was set to 110 $\mu$s. This value corresponds to 75% of one rotor period.

### 2.6. Variable contact experiments

The CP dynamics were determined by measuring the $^{13}$C magnetization as a function of $t_c$. The CP-behaviour is modulated by several nuclei interactions and physicochemical sample properties and at high magnetic fields and spinning speeds, these modulations can obscure the results (Mehring, 1983). In a recent study it was shown that for coals, the interfering fluctuations are best considered with the use of the original fundamental Mehring term and assuming a two component system (Abelmamn et al., 2004). Accordingly, our data were fitted using the Mathcad 2000 Professional software and applying the following equations:

$$I(t_c) = \sum \frac{I_{0i}}{a_{+i} - a_{-i}} \left[ \exp \left( -a_{+i} t_c \frac{T_{CH,i}}{T_{HH,i}} \right) - \exp \left( -a_{-i} t_c \frac{T_{CH,i}}{T_{HH,i}} \right) \right],$$

$$a_{+i} = a_0 \left( 1 + \frac{1}{1 - \frac{b_i}{a_0}} \right),$$

$$a_{-i} = a_0 \left( 1 - \frac{1}{1 - \frac{b_i}{a_0}} \right),$$

$$b_i = \frac{T_{CH,i}}{T_{HH,i}} \left( 1 + \frac{T_{CH,i}}{T_{pC,i}} \right) + \frac{T_{CH,i}}{T_{pC,i}},$$

$$a_0 = \frac{1}{2} \left( 1 + \varepsilon \frac{T_{CH,i}}{T_{HH,i}} + \frac{T_{CH,i}}{T_{pC,i}} \right),$$

$$\varepsilon = \frac{N_S S(S + 1)}{N_I (I + 1)}.$$  \hspace{1cm} (4)

Here, where $I(t_c)$ is the $^{13}$C-intensity measured at $t_c$, $I_{0i}$ the equilibrium $^{13}$C-magnetization of the component $i$. 

<table>
<thead>
<tr>
<th></th>
<th>Carboxyl/carbonyl/amide C</th>
<th>O/C-aryl C</th>
<th>C/H-aryl C</th>
<th>O/N-alkyl C</th>
<th>alkyl C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat 0 s</td>
<td>25 (220–160 ppm)</td>
<td>19 (160–140 ppm)</td>
<td>18 (140–110 ppm)</td>
<td>34 (110–60 ppm)</td>
<td>17 (60–45 ppm)</td>
</tr>
<tr>
<td>peat 150 s</td>
<td>19 (25 ppm)</td>
<td>19 (23 ppm)</td>
<td>18 (21 ppm)</td>
<td>34 (32 ppm)</td>
<td>17 (46 ppm)</td>
</tr>
<tr>
<td>Burnt soil</td>
<td>17 (51 ppm)</td>
<td>17 (47 ppm)</td>
<td>18 (42 ppm)</td>
<td>34 (46 ppm)</td>
<td>17 (42 ppm)</td>
</tr>
</tbody>
</table>
S, I the spin quantum numbers of $^{13}$C ($S = 1/2$) and $^1$H ($I = 1/2$). $N_S$ and $N_I$ are the number of $^{13}$C and $^1$H nuclei, respectively. The nuclei number is taken into account by $e$, which approximately becomes zero for a $^1$H-$^{13}$C spin system under extreme dilution of $^{13}$C ($N_I \gg N_S$). Recent studies by Abelmann et al. (2004) indicated that $T_{1\text{H}}$ determination by variable spin lock experiments with fixed $t_c$ discriminate either against the fast or the slow fraction. Therefore, this technique was not considered.

2.7. Bloch decay NMR spectra

The BD MAS NMR spectra were recorded with $d = 60$ s, using a 90°-$^{13}$C pulse. After accumulation of 1000 up to 3000 scans the spectra were processed with a line broadening of 100 Hz, subtracting the background signal caused by the probe and the Kel-F caps as shown in Fig. 1.

The $^{13}$C spin lattice relaxation time, $T_{1C}$, was indirectly determined with a CP pulse sequence. A $\pi/2$ is inserted on the $^{13}$C channel after $t_c$ followed by a delay period, $\Delta$, during which the $^{13}$C nuclei relax. Afterwards, a BD step is added, to detect the residual $^{13}$C magnetization. The delay period $\Delta$ was varied from 1 ms to 270 s and 500 s.

3. Results

3.1. Chemical composition of the charred material

Heating the peat at 350 °C caused C losses ranging from 17% to 50% for the samples treated for 150 and 180 s (Table 2; Almendros et al., 2003). The changes of the chemical composition with heating time are depicted by the solid-state $^{13}$C NMR spectra in Fig. 1 and their intensity distributions are listed in Table 3. For the fresh
peat and the peat 150 s, the standard deviations of the relative intensities in the different regions obtained from four independent measurements performed over a time frame of four years are included. With the exception of the carboxyl/carbonyl/amide C region (13% and 14%), the standard deviations ranged from 0 to 11%. Those low values indicate high reproducibility of the NMR measurements even after periodical readjustment of the instrumental setup.

Thermally induced dehydration and selective degradation of carbohydrates and proteinaceous structures are responsible for the accumulation of newly-formed aromatic constituents (160–110 ppm) (Almendros et al., 2003). O-substituted and some quaternary aryl C contribute to the signal intensity in the region from 160 to 140 ppm, whereas between 140 and 110 ppm signals of both protonated and C-substituted aryl C are expected. The ratio \( R_a \) between the intensity in the region O/C-aryl C (160–140 ppm) and that in the region of aryl C (140–110 ppm) shows no major alteration with increasing charring (Table 3). Bearing in mind that the atomic O/C ratio (Table 2) decreased from 0.47 in the fresh peat to 0.11 in the peat 180 s, the concomitant increase of the intensities in both aromatic C chemical shift regions is unlikely to be caused by the accumulation of phenolic C groups. The broadening and melting of the two signals in the aromatic region with increasing treatment time rather points to the removal of hydroxyl or methoxyl groups and the synthesis of a heterogeneous mixture of various C-bridged aryl C structures. Intensity between 160 and 140 ppm, however, may also derive from oxygenated C in benzofuran structures (Fig. 2) produced during charring of carbohydrates (Baldock and Smernik, 2002).

The formation of condensed aromatic structures by the charring process may also be concluded from the upfield shift of the peak maximum of the aromatic signal from 129 ppm in the spectrum of the fresh peat to 126 ppm in the spectrum of the peat heated at 350°C for 150 s and that for 180 s. Comparable heat-induced shifts were observed elsewhere (Freitas et al., 1999; Baldock and Smernik, 2002; Czimczik et al., 2002) and can be explained by the transformation of protonated aromatic C occurring in lignins or tannins (129 ppm).

---

### Table 2

<table>
<thead>
<tr>
<th>Oxidation time at 350 °C (s)</th>
<th>C (mg g⁻¹)</th>
<th>H</th>
<th>N</th>
<th>O⁺</th>
<th>Ash (mg g⁻¹)</th>
<th>C-loss (%)</th>
<th>Atomic ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat 0 s</td>
<td>420</td>
<td>46.1</td>
<td>12.0</td>
<td>262</td>
<td>260</td>
<td>0</td>
<td>1.32</td>
</tr>
<tr>
<td>Peat 60 s</td>
<td>416</td>
<td>43.4</td>
<td>12.1</td>
<td>250</td>
<td>279</td>
<td>8</td>
<td>1.25</td>
</tr>
<tr>
<td>Peat 120 s</td>
<td>444</td>
<td>32.0</td>
<td>13.2</td>
<td>193</td>
<td>318</td>
<td>14</td>
<td>0.87</td>
</tr>
<tr>
<td>Peat 150 s</td>
<td>467</td>
<td>31.8</td>
<td>14.9</td>
<td>137</td>
<td>349</td>
<td>17</td>
<td>0.82</td>
</tr>
<tr>
<td>Peat 180 s</td>
<td>403</td>
<td>23.8</td>
<td>13.7</td>
<td>60</td>
<td>500</td>
<td>50</td>
<td>0.71</td>
</tr>
<tr>
<td>Barbeque charcoal</td>
<td>823</td>
<td>32.6</td>
<td>2.4</td>
<td>n.d.</td>
<td></td>
<td></td>
<td>0.48</td>
</tr>
</tbody>
</table>

\( ^a \) Calculated by difference and under consideration of the ash content.

### Table 3

<table>
<thead>
<tr>
<th>Carboxyl/ carbonyl/ amide C</th>
<th>O/C-aryl C</th>
<th>C/H-aryl C</th>
<th>O/N-alkyl C</th>
<th>Alkyl C</th>
<th>( R_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>220–160 ppm</td>
<td>160–140 ppm</td>
<td>140–110 ppm</td>
<td>110–60 ppm</td>
<td>60–45 ppm</td>
<td>45–0 ppm</td>
</tr>
<tr>
<td>Peat 0 s</td>
<td>9.6 ± 1.4</td>
<td>7.3 ± 0.4</td>
<td>18.3 ± 0.9</td>
<td>25.5 ± 0.9</td>
<td>6.1 ± 0.4</td>
</tr>
<tr>
<td>Peat 60 s</td>
<td>12</td>
<td>9</td>
<td>21</td>
<td>22</td>
<td>6</td>
</tr>
<tr>
<td>Peat 120 s</td>
<td>11</td>
<td>14</td>
<td>29</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>Peat 150 s</td>
<td>13.2 ± 1.8</td>
<td>14.4 ± 0.2</td>
<td>37.3 ± 0.2</td>
<td>7.3 ± 0.4</td>
<td>3.7 ± 0.4</td>
</tr>
<tr>
<td>Peat 180 s</td>
<td>12</td>
<td>19</td>
<td>49</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>Unburnt soil</td>
<td>12</td>
<td>8</td>
<td>17</td>
<td>34</td>
<td>8</td>
</tr>
<tr>
<td>Burnt soil</td>
<td>12</td>
<td>8</td>
<td>25</td>
<td>25</td>
<td>7</td>
</tr>
<tr>
<td>Charred plant residue</td>
<td>5</td>
<td>11</td>
<td>46</td>
<td>13</td>
<td>6</td>
</tr>
<tr>
<td>Charred particle</td>
<td>12</td>
<td>16</td>
<td>53</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Barbeque char</td>
<td>3</td>
<td>7</td>
<td>76</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

\( R_a = \text{intensity (140–110 ppm)/intensity (160–140 ppm)} \). The values of the samples peat 0 and 150 s are given as means of four measurements \((n = 4)\) with the respective standard deviation.

\( ^a \) Standard deviation.
Fig. 2. Structures of various aromatic compounds exhibiting atomic H/C ratios (based on the aromatic portion only) between 1 and 0.33. The ratio of protonated and nonprotonated aromatic C as determined by Dipolar Dephasing NMR spectroscopy is given as $f_{\text{aH}}/f_{\text{aC}}$. The chemical shifts are given according to Pruski et al. (1990), Baldock and Smernik (2002), Kalinowski et al. (1984).
(Fig. 2) into polyaromatic hydrocarbons. The chemical shift of non-protonated core carbons in, e.g., coronene is expected at 119 ppm, the exterior carbons at 126 ppm, and the protonated carbons at 123 ppm (Pruski et al., 1990). Alternatively, the shift may be due to the heat-induced increase in the concentration of delocalized electrons around carbons in graphite-like crystallites as was recently observed for peat subjected to temperatures up to 1000 °C under nitrogen atmosphere (Freitas et al., 1999). On the other hand, if such structures were present in higher concentrations, the acquisition of NMR spectra would have been hindered due to the electronic properties of the graphitic domains. They can lead to a reflection of the excitation pulse (skin effect).

The transformation of biogenic C to aromatic compounds during natural charring is also revealed in the spectra of charred plant material found in the A horizon of a fire-affected soil from the Sierra del Aznalcóllar (Southern Spain; Fig. 3). The aromaticity is more expressed for the particles charred to a degree to which the plant morphological features were no longer discernable by eye (charred particles) than for the charred material still attributable to plant remains (Knicker et al., 2005). The solid-state $^{13}$C NMR spectrum of the latter shows distinguishable signals in the $\theta$-alkyl C region. The clear signal at 20 ppm is assignable to methylene carbons in the short chains, whereas CH$_3$ in $\alpha$-position to an aromatic ring or those in terminal position of alkyl chains resonate at 20 and 15 ppm, respectively. The occurrence of such charred particles in the soil FA is responsible for its higher aromatic C content if compared to that of the control soil FU. According to the solid-state $^{13}$C NMR spectrum of the barbeque charcoal the charring intensity was high enough to remove most of the alkyl residues (Table 3).
3.2. Impact of charring on $T_{1H}$

Baldock and Smernik (2002) detected a decrease in the relaxation times $T_{1H}$ and $T_{1QH}$ with increasing temperature during charring of wood. This was not evidenced for our samples, although shorter $T_{1H}$ were observed for aromatic C and carboxyl/carbonyl/amide C (17–25 ms) than for O-alkyl C and alkyl C (32–51 ms), irrespective of the material (Table 1). Comparable values were obtained for humifying plant residues (Knicker et al., 1996, 1997). The different behaviour with respect to the observation of Baldock and Smernik (2002) may be due to the fact that we determined $T_{1H}$ for each chemical shift region, while in their work, this variable is given as an average of the total organic C.

In the material heated at low temperatures, this average value is dominated by the slowly relaxing components (O-alkyl C). At high charring degrees mostly aromatic C with fast $T_{1H}$ survives and determines the average value.

3.3. Elucidation of the condensation degree with the atomic H/C ratios

For a preliminary elucidation of the condensation degree of aromatic structures formed during charring by a medium to high intensity fire, the atomic H/C ratios of the peat, its heat-treated residues and the barbeque charcoal were calculated (Table 2). The atomic H/C ratio = 1.3 of the thermally untreated peat indicates that most C is either directly bound or connected through an OH group to at least one H. Namely, all C should be visible using the VACP MAS technique. With prolonged heating time, the atomic H/C decreases and reaches a value of 0.71 for peat heated for 180 s. This is in accordance with ongoing dehydration and condensation reactions during charring. Assuming each C in the region between 90 and 0 ppm to be bound to two H, this leaves an atomic H/C ratio of approximately 0.52 for the remaining C in the carboxyl/carbonyl/amide and aromatic C region of the spectrum of peat heated 180 s. Therefore, almost every second C in these C regions is connected to a proton. Even for the barbeque charcoal the atomic H/C = 0.48 is high enough to conclude that a substantial fraction of the aromatic C is protonated. Fig. 2 shows examples of possible aromatic structures with atomic H/C ratios ranging from 1 to 0.3, including linear as well as graphite-like condensation of aromatic rings. In ring clusters such as coronene the maximal distance of the inner core C from the next proton comprises three bonds. Increasing the cluster size to ten rings, 6% of the total aromatic C are four bonds away from the next proton and may already be affected by inefficient CP. However, even for this structure, the expected loss is far below the amount of 70% determined...
to be invisible in CPMAS $^{13}$C NMR spectra of charcoal of spin-counting experiments with glycine (Smernik and Oades, 2000b).

### 3.4. Elucidation of the condensation degree with dipolar dephasing experiments

Fig. 4 shows the dipolar dephasing behaviour of the aromatic C (160 to 110 ppm) in the untreated peat, the peat heated for 180 s and the charcoal. Table 4 lists the respective dipolar dephasing parameters calculated for the fresh and the charred peat, the FA and FU soils, the charred plant residues and the barbeque charcoal. All samples exhibited $T_{ddL}$ between 22 and 27 μs for the fast dephasing fraction of aryl C (160–110 ppm). These time constants are in the range reported for non-mobile protonated aryl C in soil organic matter and coals (Wilson et al., 1983, 1984; Hatcher, 1987, 1988). Most of the reported data were obtained with a MAS rate between 3 and 5 kHz. Faster spinning, however, decreases the magnitude of the $^{13}$C–$^1$H coupling and thus longer $T_{ddG}$ but, also longer $T_{ddL}$ are, expected (Newman, 1990). The proportion of aryl C with strong \(^1\)H-interaction within the aromatic units is expressed by $f_{aH}$. With increasing heat treatment the proportion of $f_{aH}$ increases from 35% for the untreated peat to 46% and 42% in the samples heated for 150 and 180 s, respectively, possibly due to cleavage of the lignin polymer or demethoxylation of the monomers. The charred residues found in the A horizon of soil FA, but also the barbeque charcoal show comparably higher proportions of $f_{aH}$ between 43% and 51%. These proportions are higher than those reported for charcoal derived from red gum wood chips with BD dipolar dephasing experiments (22%; Smernik and Oades, 2001) but in close agreement with the atomic H/C ratios determined for the aromatic C content of the peat heated for 180 s (calculated for carbonyl and carboxyl C: 0.52) and the barbeque charcoal (0.48). The latter values strongly supports the reliability of our DD measurements. Important to note is that the high values of $f_{aH}$ indicate that in the charred peat and plant residues and also in the barbeque charcoal almost every second aryl C is directly connected to neighbouring H. This is in a clear contrast to a supposedly highly condensed graphitic-like structure of aromatic moieties in plant remains produced during vegetation fires.

The proportion of aryl C with weak interactions with \(^1\)H, corresponding to condensed, linked and/or C-substituted aryl C (Table 3) is expressed by $f_{aC}$. These non-protonated CS account for 65% of the total aromatic C contributing to the signal intensity between 160 and 110 ppm in the VACP MAS $^{13}$C NMR spectrum of the untreated peat. Their $T_{ddL}$ (185 μs) represents the average value of all slowly dephasing aryl C, comprising those which are only two bonds away from the next proton up to those which are larger distances away and experience even weaker dipolar interactions. Comparing our results with those reported in the literature one has to bear in mind that spinning speed and applied pulse sequence affect the magnitude of $T_{ddL}$. Using the same pulse sequence suggested by Alemany et al. (1983a) as in the present study but at lower spinning speeds, $T_{ddL}$ between 100 and 230 μs were measured for phenolic C in isolated lignin preparations and coalified wood (Wilson et al., 1983; Hatcher, 1987, 1988). Non-protonated carbons in coals resulted in longer $T_{ddL}$ between 200 and 300 μs.

As mentioned above, $T_{ddL}$ represents an average value and one has to consider its dependence on the used pulse sequence (Smernik and Oades, 2001). However, if the same conditions were used for one sample set, the dipolar dephasing constants of the respective samples certainly can be compared to reveal trends. Under those circumstances, if charring had resulted in a considerable enlargement of the average of some hypothetical graphite-like ring cluster size, the impact of core C with weak dipolar interactions should have increased. This would have led to a prolongation of the average $T_{ddL}$. The fact that for our sample no major alteration of $T_{ddL}$ occurred evidences that graphite-like clusters were not formed in considerable amounts during the production of the chars under controlled laboratory heating. They were also not present in high amounts in the barbeque charcoal or the char collected from the soil after the passage of the wildfire (Table 3).

Calculating $f_{aH}/f_{aC}$, as an indicator for the protonation degree of the polyaromatic clusters, shows a slight increase from 0.55 for the untreated peat to 0.73 for the peat 180 s. The barbeque charcoal exhibits an even higher value of ca. 1. The $f_{aH}/f_{aC}$ of the charred residues found in soil FA are 0.75 and 0.94. With respect to the structures depicted in Fig. 2 the determined $f_{aH}/f_{aC}$ for the untreated peat is in accordance with aromatic C in lignin moieties. Prolonged charring cleaves their β-O-4-ethers and leads not only to dehydroxylation and demethoxylation but also decarboxylation of oxidized lignin components. The respective sites may be replaced by C–C linkages, a reaction which is in competition with protonation due to dehydroxylation. Such processes, previously suggested to occur during coalification (Hatcher, 1988) will not considerably alter $f_{aH}/f_{aC}$. However, during charring new but protonated aromatic units are formed by the cyclization and dehydration of aliphatic C. Their accumulation could explain the decrease in the atomic H/C ratio of the bulk sample with a concomitant relative increase in the protonation degree of the aromatic C to values between 0.7 and 1. For the charred residues those values, in combination with the respective atomic H/C ratios, limit the appropriate structures to simple linear condensed aromatic rings or to small cluster-like structures. Assuming that
at least one bridging C has to be present to connect two aromatic clusters, the average cluster size is unlikely to exceed a number of six condensed rings.

### 3.5. Impact of charring on the CP dynamics

The next step of our study was to examine the impact of charring on the CP dynamics of aromatic C. Therefore, variable contact time experiments were conducted and the intensity plotted against the contact time, \( t_c \). A two-component fit [Eq. (4)] with a fast and a slow relaxing proportion (Table 5) and including the complete Mehring term as suggested by Abelmann et al. (2004) was used.

While \( T_{CH} \) and \( T_{1PC} \) characterize the individual chemical and/or crystallographic sites in a solid, \( T_{1PH} \) is influenced by the efficiency of spin diffusion and represents a volume property averaged over a distance of approximately 2–30 nm (Botto et al., 1987; Newman, 1992b; Kolodziejski and Klinowski, 2002). Thus, changes in the average mobility should be indicated by a change in this parameter. However, alteration of the concentration of both the organic and inorganic radicals would also affect relaxation.

Fig. 5 shows the CP dynamics for the signals in the aryl C region (160–110 ppm) of the solid-state \(^{13}\)C NMR spectra of peat, charred peat material and the barbeque charcoal. During the relatively fast increase in the signal intensity, oscillations are visible for all samples. In crystalline domains, CP can proceed through transient harmonic oscillations (Mueller et al., 1974; Kolodziejki and Klinowski, 2002). For the peat materials and the charcoal, relatively short \( T_{CH} \) between 21 and 35 \( \mu \)s were found for approximately 60–76% of their aryl C. For the soil FA, \( T_{CH} \) is 60 \( \mu \)s. No trend with increasing charring intensity is discernable. These transfer times are shorter than those reported for protonated aromatic reference substances (100–182 \( \mu \)s; Alemany et al., 1983b) but are expected for \(^{13}\)C with strong dipolar interactions with \(^1\)H in crystalline domains in which oscillating CP behaviour drastically shortens \( T_{1CH} \) (Muller et al., 1974).

Between approximately 25–40% of the aryl C in the samples are attributable to the fraction with long \( T_{CH} \) between 290 and 619 \( \mu \)s. Such times are in the range observed for non-protonated aromatic C in coals (Botto et al., 1987; Abelmann et al., 2004) but are much shorter than those assumed for \( T_{1PH} \) determinations for charred wood (\( T_{CH} \) between 1 and 5 ms) (Smernik et al., 2002). If charring increases the cluster size of graphite-like aromatic domains, it should also increase the average \(^1\)H–\(^{13}\)C distance because proportionally more C will occur in the core than at the surface. This would result in diminishing CP efficiency and thus in an increase of the average \( T_{CH} \). But within our sample set, the shortest \( T_{CH} \) were obtained for the peat 180 s (290 \( \mu \)s) and the barbeque charcoal (204 \( \mu \)s), which is clearly against an increase with increasing charring of the size of any graphitic-like structure. This observation rather supports our results obtained from the dipolar dephasing experiments. A possible explanation for the shortening of \( T_{CH} \) may be a decrease in the mobility of smaller polyaromatic domains by formation of C bridges between the individual clusters.

For the crystalline part, \( T_{1PH} \) between ca. 6 and 10 ms were determined. A trend with respect to charring intensity is not observable. Thus, if charring resulted in an increase of the radical concentration, it had no impact on \( T_{1PH} \). For the amorphous portion (long \( T_{CH} \)) of the aryl C in the fresh peat and its charred residues, comparably short \( T_{1PH} \) were determined, indicating efficient spin diffusion between those two domains. A further important finding is that both for the fast and slow cross polarizing fractions, the condition \( T_{CH} < t_c < T_{1PH} \) is fulfilled.

### Table 5

Cross polarization parameters calculated under consideration of a two-components system

<table>
<thead>
<tr>
<th></th>
<th>( I_S )</th>
<th>( I_L )</th>
<th>( T_{CHS} ) (( \mu )s)</th>
<th>( T_{CHL} ) (( \mu )s)</th>
<th>( T_{1PHS} ) (ms)</th>
<th>( T_{1PHL} ) (ms)</th>
<th>( T_{1PS} ) (ms)</th>
<th>( T_{1PC} ) (ms)</th>
<th>SSD</th>
<th>me</th>
<th>CD</th>
<th>mef</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat 0 s</td>
<td>72</td>
<td>28</td>
<td>26</td>
<td>512</td>
<td>8.3</td>
<td>8.1</td>
<td>2.0</td>
<td>10.6</td>
<td>0.004</td>
<td>0.036</td>
<td>0.975</td>
<td>0.985</td>
</tr>
<tr>
<td>Peat 60 s</td>
<td>61</td>
<td>39</td>
<td>24</td>
<td>363</td>
<td>4.8</td>
<td>13.6</td>
<td>2.2</td>
<td>10.7</td>
<td>0.010</td>
<td>0.035</td>
<td>0.969</td>
<td>0.987</td>
</tr>
<tr>
<td>Peat 120 s</td>
<td>74</td>
<td>26</td>
<td>30</td>
<td>430</td>
<td>11.5</td>
<td>4.2</td>
<td>2.1</td>
<td>10.4</td>
<td>0.016</td>
<td>0.077</td>
<td>0.972</td>
<td>0.984</td>
</tr>
<tr>
<td>Peat 150 s</td>
<td>74</td>
<td>26</td>
<td>35</td>
<td>619</td>
<td>9.2</td>
<td>10.3</td>
<td>0.8</td>
<td>6.1</td>
<td>0.052</td>
<td>0.094</td>
<td>1.000</td>
<td>0.944</td>
</tr>
<tr>
<td>Peat 180 s</td>
<td>76</td>
<td>24</td>
<td>27</td>
<td>290</td>
<td>7.4</td>
<td>6.8</td>
<td>0.8</td>
<td>4.9</td>
<td>0.027</td>
<td>0.062</td>
<td>0.982</td>
<td>0.989</td>
</tr>
<tr>
<td>Barbeque charcoal</td>
<td>74</td>
<td>26</td>
<td>21</td>
<td>204</td>
<td>5.6</td>
<td>17.1</td>
<td>2.0</td>
<td>21.0</td>
<td>0.012</td>
<td>0.036</td>
<td>0.985</td>
<td>0.991</td>
</tr>
<tr>
<td>Burnt soil</td>
<td>87</td>
<td>13</td>
<td>60</td>
<td>997</td>
<td>19.9</td>
<td>18.3</td>
<td>2.5</td>
<td>11.9</td>
<td>0.098</td>
<td>0.124</td>
<td>0.975</td>
<td>0.985</td>
</tr>
<tr>
<td>Unburnt soil</td>
<td>50</td>
<td>50</td>
<td>36</td>
<td>677</td>
<td>7.3</td>
<td>5.9</td>
<td>0.2</td>
<td>11.0</td>
<td>0.032</td>
<td>0.100</td>
<td>0.953</td>
<td>0.959</td>
</tr>
<tr>
<td>Glycine 176 ppm</td>
<td>50</td>
<td>50</td>
<td>291</td>
<td>1713</td>
<td>79.6</td>
<td>31.6</td>
<td>1186</td>
<td>2816</td>
<td>0.054</td>
<td>0.071</td>
<td>1.003</td>
<td>0.973</td>
</tr>
<tr>
<td>Glycine 42 ppm</td>
<td>62</td>
<td>38</td>
<td>22</td>
<td>536</td>
<td>24.8</td>
<td>21.6</td>
<td>15.6</td>
<td>33.1</td>
<td>0.003</td>
<td>0.020</td>
<td>0.970</td>
<td>0.969</td>
</tr>
</tbody>
</table>

\( I_S \) and \( I_L \) are the relative contribution of the fractions with short and long cross polarization times (\( T_{CHS}, T_{CHL} \)), \( T_{1PHS} \) and \( T_{1PHL} \) represent the respective \(^1\)H spin lattice relaxation times in the rotating frame and \( T_{1PS} \) and \( T_{1PC} \), the \(^{13}\)C spin lattice relaxation times in the rotating frame. SSD gives the square standard deviation; me, the maximal error; CD, the coefficient of determination and mef, the model efficiency.
Depending on the molecular flexibility, $T_{1qC}$ is determined by static interactions or by spin-lattice processes. For the crystalline proportion, relatively short $T_{1qCS}$ of 2 ms were found for the untreated peat and peat 120 s. Prolonged heating decreased this value to 0.8 ms, although for the barbeque charcoal again a value of 2 ms was determined. For the amorphous moiety, values between 5 and 21 ms were calculated, which are in the same magnitude as the corresponding $T_{1qHL}$. Thus for these carbons, spin-lattice processes may determine the relaxation. However, here again the peat 150 and 180 s show faster $T_{1qCS}$ than the other samples. Possibly this is caused by an increase in organic radicals.

Due to the fact that CP and spin lattice relaxation in the rotating frame are time-dependent processes that occur simultaneously, at any $t_c$, it is impossible to observe all carbons with a CP experiment. At each $t_c$, relaxation has already decreased the signal intensity and incomplete CP does not detection of all carbons. The differing CP behaviour of the various C groups in a heterogeneous mixture represents an additional difficulty with respect to quantification. In order to circumvent those difficulties for soil organic matter samples, a $t_c$ is chosen, at which the intensity loss for each C group is comparable (Wilson, 1987). Thus, although not all CS are detected, those which are observed reflect a distribution that is representative for that occurring in the whole sample. For soils, $t_c = 1$ ms is commonly used to reach this goal (Wilson, 1987). However, for some coals it was found that considerable underestimation of the aromatic C can occur.

To elucidate a possible underestimation of aromatic C in charcoal and charred soil organic matter, the proportions of carbon that are detectable at $t_c = 1$ ms for the different C groups were calculated using the $I_0$ calculated according to Eq. (4). For all samples, between 80% and 85% of the aromatic C in the chemical shift region between 160 and 110 ppm are detectable at $t_c = 1$ ms (Table 6). Recoveries between 74% and 87% of the alkyl C (45–0 ppm), 75% and 85% of the O-alkyl C and 78–
93% of carboxyl/carbonyl/amide C (220–160 ppm) were calculated. Accordingly, a slight overestimation of the aromatic C and of the carboxyl/carbonyl/amide C is expected.

3.6. Experiments with standards obtained mixing the original samples

So far, the experiments indicate that it should be possible to obtain quantifiable spectra from soil organic matter containing charred residues. However, all the presented tests involve the CP sequence. If there is indeed a fraction of aromatic C with $T_{CH}/c$, this proportion will remain undetected and thus will not be considered in those tests. In order to determine the detectability of carbons in CP experiments, spin counting with glycine is often suggested (Smernik and Oades, 2000b). It is based on the approximation that at $t_c = 1$ ms all glycine C is seen by CPMAS $^{13}$C NMR. However, in our experiments, at $t_c = 1$ ms, the CP of carboxyl C is still incomplete and only 70% of this C type is seen (Table 6, Fig. 6). The low detectability of the former is best explained by its long $T_{CH}$ of 0.291 ms (50%) and 1.713 ms (50%), respectively (Table 5). Because the required approximation was not valid in our study, glycine was not used as reference. Alternatively, mixtures with known amounts of fresh peat and charred peat (sample heated for 150 s) or barbeque charcoal were prepared (Table 7). Using the intensity distribution of their spectra and their C content, a summed spectrum can be calculated. A considerable amount of undetectable C would be indicated by a significant discrepancy between the intensity distribution in the calculated sum spectrum and the spectrum obtained by direct measurement of the mixture.

Table 6
Relative recovery (%) of C intensity in the different chemical shift regions of the solid-state $^{13}$C NMR spectra of the VCT experiments acquired at a contact time $t_c = 1$ ms as it was calculated by Eq. (4) using a two components fit

<table>
<thead>
<tr>
<th>Carboxyl/carbonyl/amide C</th>
<th>Aryl C</th>
<th>O/N-alkyl C</th>
<th>Alkyl C</th>
</tr>
</thead>
<tbody>
<tr>
<td>220–160 ppm</td>
<td>160–110 ppm</td>
<td>110–60 ppm</td>
<td>60–45 ppm</td>
</tr>
<tr>
<td>Peat 0 s</td>
<td>78*</td>
<td>82</td>
<td>79</td>
</tr>
<tr>
<td>Peat 60 s</td>
<td>93*</td>
<td>85</td>
<td>79</td>
</tr>
<tr>
<td>Peat 120 s</td>
<td>85</td>
<td>75</td>
<td>85*</td>
</tr>
<tr>
<td>Peat 150 s</td>
<td>81</td>
<td>81</td>
<td>79*</td>
</tr>
<tr>
<td>Peat 180 s</td>
<td>81</td>
<td>81</td>
<td>79*</td>
</tr>
<tr>
<td>Unburnt soil</td>
<td>87*</td>
<td>72</td>
<td>79</td>
</tr>
<tr>
<td>Burnt soil</td>
<td>89*</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Charred particle</td>
<td>77</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>Barbeque charcoal</td>
<td>84</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>Glycine</td>
<td>70</td>
<td>81</td>
<td>79</td>
</tr>
<tr>
<td>Average (without glycine)</td>
<td>87</td>
<td>81</td>
<td>79</td>
</tr>
</tbody>
</table>

For the values marked with asterisks the results derive from a one component fit since this fit resulted in better model efficiency (mef) and coefficient of determination (CD).
For the peat/charred peat mixtures (peat 1 and 2) almost identical values were obtained for the calculated and measured intensity distribution (Fig. 7). A comparable result was obtained for the peat/barbeque charcoal mixtures with charcoal portion between 50% and 71% (charcoal 4–8), comprising >89% of the aromatic C content of the sample (Fig. 8). With decreasing charcoal content, however, the difference between the calculated and measured aromatic C content increases, although it is still in the 10% error range. This increasing difference in aromatic proportion with decreasing charcoal input is astonishing since, due to the diminishing impact of the aromatic C from the char on the total C, an opposite trend would be expected. Thus, it seems more likely that this discrepancy is caused by the overestimation of aromatic C relative to O-alkyl and alkyl C at $t_c = 1\,\text{ms}$ in the reference CPMAS $^{13}$C NMR spectrum of the untreated peat.

For comparison, the calculations were also conducted for the peat/barbeque charcoal mixtures under the assumption that only $\sim 30\%$ of the charcoal C is visible with CPMAS (Smernik and Oades, 2000a). Fig. 8 shows that in this case for the mixtures tested the measured aromatic C content was higher than the calculated values. The underestimation of the calculated values with respect to the measured data were 9% for the sample with the lowest amount of charcoal and around 20% for those with charcoal concentrations higher than 30%. Those observations demonstrate that, at least for our sample set, a detectability of char C of only 30% is certainly an underestimation.

### 3.7. Bloch decay NMR

A further test for the reliability of solid-state CPMAS $^{13}$C NMR spectra represents BD MAS NMR which is independent upon losses due to CP. However, a background noise, deriving from the probe or from the KEL-F caps on the rotor may occur and obscure the intensity distribution. In general the broad background signal such as it is shown in Fig. 1 is subtracted from the respective spectrum.

Figs. 1 and 3 include BD MAS $^{13}$C NMR spectra of selected samples. They were obtained with $d = 60\,\text{s}$, which is in the range reported for other published BD MAS $^{13}$C NMR spectra of organic matter in soils, sediments, and peat.

---

**Table 7**

Sample description of the peat/charred peat 150 s and the peat/barbeque charcoal mixtures

<table>
<thead>
<tr>
<th></th>
<th>Proportion of char in the mixture (mg g$^{-1}$)</th>
<th>Proportion of char C on total C of the mixture (mg g$^{-1}$)</th>
<th>Contribution of aromatic C from char to aromatic C of the mixture (%)</th>
<th>Recovery of aromatic relative to calculated values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat 1</td>
<td>150</td>
<td>164</td>
<td>28</td>
<td>98</td>
</tr>
<tr>
<td>Peat 2</td>
<td>300</td>
<td>317</td>
<td>48</td>
<td>95</td>
</tr>
<tr>
<td>Charcoal 1</td>
<td>107</td>
<td>187</td>
<td>43</td>
<td>88</td>
</tr>
<tr>
<td>Charcoal 2</td>
<td>199</td>
<td>321</td>
<td>61</td>
<td>90</td>
</tr>
<tr>
<td>Charcoal 3</td>
<td>344</td>
<td>501</td>
<td>77</td>
<td>89</td>
</tr>
<tr>
<td>Charcoal 4</td>
<td>513</td>
<td>668</td>
<td>87</td>
<td>96</td>
</tr>
<tr>
<td>Charcoal 5</td>
<td>600</td>
<td>741</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td>Charcoal 6</td>
<td>636</td>
<td>770</td>
<td>92</td>
<td>96</td>
</tr>
<tr>
<td>Charcoal 7</td>
<td>666</td>
<td>792</td>
<td>93</td>
<td>99</td>
</tr>
<tr>
<td>Charcoal 8</td>
<td>714</td>
<td>826</td>
<td>94</td>
<td>99</td>
</tr>
</tbody>
</table>
ments and coals (Botto et al., 1987; Skjemstad et al., 1996). Fig. 9 depicts the difference between the intensity distribution obtained by the CP- and by the BD-technique for the fresh peat, the peat 180 s and the soil FA. The slightly lower aromatic C and alkyl C content of the BD MAS spectrum of peat 180 s, with respect to the VACP MAS spectrum is counterbalanced by a higher carboxyl C contribution. A comparable result
was obtained for the charred particle found in soil FA (Knicker et al., 2005) and for charred wood buried during the eruption of the Vesuvius in ancient Pompeii in 79 AD (Simpson and Hatcher, 2004). Performing the same comparison on the sample of the HF-treated soil FA and the fresh peat sample, with respect to the VACP MAS NMR spectra, a clear increase in the relative intensity in the aromatic C and carboxyl C region at the expense of O/N-alkyl and alkyl Cs is observed for the BD MAS NMR spectra. This result is in accordance with BD MAS/CP MAS comparisons of char containing soil organic matter given in the literature and could confirm the low detectability of char with the CP-technique. However, to the knowledge of the authors, the fresh peat material did not contain considerable amounts of charcoal. Thus, another reason should be responsible for the differing results. A frequent cause for unreliable NMR data are saturation effects, caused by pulse delays, which are too short for a complete relaxation between the pulses. Such saturation may occur in particularly for the carbohydrate fraction. In recent studies, for cellulose in office paper and for polystyrene $T_{1C}$ of 53 and 136 s were measured, respectively (Pichler et al., 2000). For the crystalline domains in cotton a $T_{1C} = 266$ s is reported (Teea¨ar and Lippmaa, 1984). Polyethylene even reached a $T_{1C} = 449$ s (Pichler et al., 2000). Thus, if comparable compounds are present in the soil organic material, the required pulse delays are much longer than those commonly applied.

For the aryl C signal (160–110 ppm) in the BD MAS $^{13}$C NMR spectrum of the peat 180 s a short $T_{1C} = 0.3$ s was determined for 72% of the aromatic C while 28% relaxed with a $T_{1C} = 11$ s. Comparable $T_{1C}$ values of 0.3 and 13 s were measured for 55% and 45% of the aromatic C and for 70% and 30% of the carboxyl C in the untreated peat sample. For the O-alkyl region, however, $T_{1C}$ could not be calculated, since even after a delay time of 300 s the intensity was still increasing, denoting that the relaxation process is still not complete. According to rough estimations approximately 40% of the O-alkyl C exhibits such inefficient relaxation. It will be saturated at a pulse delay of 60 s, which explains its low relative intensity in the respective BD MAS $^{13}$C NMR spectrum.

4. Discussion

The intention of the present study was to assess the progressive condensation of soil organic matter and plant remains structures during charring and to relate those changes to the detectability of char in soil organic matter using VACP MAS $^{13}$C NMR spectroscopy.

The atomic H/C ratios of the aromatic portion of the chars between 0.4 and 0.6 indicate that on average every second to third carbon is connected to a proton. Assuming graphite-like aromatic ring clusters in which at least two carbons are involved in cross linking, those atomic ratios allow maximally for a ten ring system (atomic H/C = 0.38). In such structures, 6% of the C is more than 3 bonds apart from the next 1H. Increasing the cluster size to 12 rings enhances their proportion to 11%. However, as recently reported (Simpson and Hatcher, 2004) and demonstrated in this study, the comparison of BD MAS and VACP MAS $^{13}$C NMR spectra of charred material cannot confirm the presence of a higher amount of such core C. But even if such compounds are present, they would not account for the 70% of the total C in charcoal that were determined by means of spin counting with glycine to be invisible using CPMAS $^{13}$C NMR spectroscopy (Smernik and Oades, 2000a). Such high values are more likely for soot material or for lignite coke. For such samples atomic H/C ratios <0.1 were previously determined (Abelmann et al., 2005) which is in good accordance with a dominance of graphite-like domains. However, if possible at all, the acquisition of VACP MAS NMR spectra from such samples results in low resolution spectra with low signal to noise ratios (Abelmann et al., 2005).

In contrast to the atomic H/C ratio of the bulk sample, the $f_{4H}/f_{4C}$ ratio as a parameter for the protonation degree of aromatic moieties increases with charring of the peat. Thus, the loss of hydrogen is caused mainly...
by the dehydration of the aliphatic C moiety. Deprotonation and condensation of aromatic C seem to play a minor role. This assumption is supported by the fact that prolonged charring did not slow down $T_{1\text{ph}}$ or affect $T_{\text{CHL}}$. The low $f_{\text{CH}}/f_{\text{C}}$ ratio of 0.55 of the untreated peat is best explained by non-degraded lignin residues (Fig. 2). The values between 0.7 and 0.95 indicate a basic size up to naphthalene-like compounds or of clusters of maximal six condensed rings, both having up to four to five substituents. Such relatively small clusters are not consistent with the highly condensed aromatic structure commonly proposed for black carbon (Schmidt and Noack, 2000) but are in line with observations for burned forest floor samples (Czimczik et al., 2003) and laboratory burned wood (Solum et al., 1995; Baldock and Smernik, 2002; Czimczik et al., 2002).

Comparably low cluster sizes were recently determined for coals of different maturation degree (Abelmann et al., 2003; Solum et al., 2001). However, although their CP and relaxation times are comparable to those of the samples studied here, their proportion of slowly polarizing aromatic C is considerably higher (Abelmann et al., 2004). This indicates that in spite of the dominance of aromatic C for both the charcoal and the natural coal, they differ in some structural properties. According to our cross-polarization analysis, one difference is the higher proportion of crystalline domains in carbonaceous material produced by thermal alteration.

Based on our and previous studies, the presence of high proportions of large graphitic domains may be limited to soot and material produced under cooking conditions at elevated temperatures above 700 °C (Freitas et al., 1999). Under aerobic and wildfire conditions, most of the organic matter is likely to be mineralized or volatilized at those high temperatures. Thus, the input of soot or inert graphite-like structures to soil after a vegetation fire may be lower than often assumed. At least for our sample set, no indication for a high proportion of soot in the fire-affected soil from the Sierra del Aznalcóllar was revealed by the relaxation and CP data.

The CP efficiency is also affected by $T_{1\text{ph}}$ which can be considerably shortened by paramagnetic compounds. Although an increase in organic radicals with prolonged heat treatment was found using electron spin resonance spectroscopy (data not shown), a consistent trend concerning $T_{1\text{ph}}$ of aromatic C was not observable for our samples. Summarizing Table 5, for all aromatic C the condition $T_{\text{CHL}} < t_c < T_{1\text{ph}}$ is fulfilled. Together with the results of the mixing experiment, this confirms that almost all aromatic CS were efficiently cross polarized. Note that we do not state that 100% of the C is detected with CP. This is simply impossible due to losses caused by relaxation or incomplete CP. However, for the studied soil organic material and the char, the detectable C intensity of the different signals at $t_c = 1$ ms were comparable and ranged between approximately 80% and 85%.

Thus, the presented data lead to the conclusion that for soil organic materials containing charred vegetation remains but no soot, the intensity distributions obtained with VACP MAS $^{13}$C NMR at $t_c = 1$ ms should representatively reflect the chemical composition of the samples. The discrepancy between the intensity distribution in BD and VACP MAS $^{13}$C NMR spectra is likely due to saturation of some O-alkyl C and alkyl C constituents.

The small cluster size of the aromatic domains in charred plant residues may have also some implication for the stability of black carbon produced during vegetation fires. Compared to predominantly graphite-like structures, their surfaces are more likely to be microbially attacked and oxidized, e.g., by lignin degrading organisms. Oxidized char was detected in Australian soils (Skjemstad et al., 1996). In fact, aromatic clusters rich in carboxyl groups were isolated from oxidized charred residues (Hauamaier and Zech, 1995). It was concluded that such structures should also occur in fire-affected soils with subsequent high rate of oxidation. Those carboxyl groups were suggested to be involved in organo-mineral complexation (Glaser et al., 2000), but may also allow a colloidal transport into deeper horizons with the soil solution. On the other hand, they represent an attractive site for further microbial degradation. Long-term recalcitrance of charred material, therefore, may be coupled mostly to anoxic and oxygen-depleted environments.

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