

Comparison of solid-state ^{13}C NMR spectra of soil organic matter from an experimental burning site acquired at two field strengths

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Abstract. Solid-state ^{13}C cross polarisation (CP) nuclear magnetic resonance spectra were acquired for 15 soil organic matter samples on 2 different spectrometers (200 MHz and 400 MHz). Distributions of broad functional group classes—carboxyl, aryl, O-alkyl, and alkyl—were determined by integration across broad chemical shift regions. The distributions derived from the 2 spectrometers were closely correlated ($r^2 = 0.77\text{--}0.93$). Only slight biases were identified; carboxyl C contents were on average 8% lower and alkyl C contents 5% higher for spectra acquired on the 400 MHz spectrometer. These results indicate that valid ^{13}C CP spectra can be acquired at field strengths up to 400 MHz, and that spectra acquired at different field strengths can be directly comparable.

Additional keywords: soil organic matter, cross polarization, solid-state ^{13}C NMR.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy has become an important method, probably the most important method, for determining the chemical composition of soil organic matter (Preston 1996, 2001). Although there is a wealth of different NMR experiments that provide information on different aspects of organic matter chemistry, by far the most common use of NMR spectroscopy in this field is to determine the relative proportions of broad functional group classes of C types, for example, alkyl, O-alkyl, aryl, and carboxyl. This is achieved by integration across broad chemical shift regions, but the reliability of this approach is affected by (i) spinning sidebands, which can transfer signal from one C type into regions assigned to other C types, (ii) different sensitivities of different C types to cross polarisation (CP), and (iii) interference by paramagnetic species. These quantitation issues have been discussed at length, including in several recent reviews (Preston 1996, 2001; Cook 2004). Several techniques have been developed both to improve quantitation (Skjemstad *et al.* 1994; Cook *et al.* 1996; Mao *et al.* 2000, 2002; Smernik and Oades 2003) and to better gauge quantitation problems (Smernik and Oades 2000a, 2000b; Keeler and Maciel 2003). Numerous recommendations have been made as to the 'ideal' set-up for analysing soil organic matter (SOM) (Mao *et al.* 2000; Dria *et al.* 2002; Conte *et al.* 2004), but no consensus has yet been reached. However, as discussed by Preston (2001), much of this discussion is moot, because most soil scientists have very limited access to NMR spectrometers, and often lack the resources to implement sophisticated techniques. So even if a consensus could be reached on the ideal field strength, magic angle spinning (MAS) rate, and pulse

sequence, the present situation in which almost all SOM studies use a simple CP sequence and utilise whatever spectrometer is available to them regardless of field strength would likely prevail. In these circumstances, the key question becomes: how comparable are ^{13}C CP NMR spectra acquired on different spectrometers?

Very few direct comparisons of SOM spectra acquired at different fields have been published. Fründ and Lüdemann (1994) reported that ^{13}C CP spectra of 19 soils and 5 humic extracts acquired on a 300 MHz spectrometer at a MAS rate of 15 kHz contained substantially less carboxyl and aryl signal than those acquired on a 100 MHz spectrometer at a MAS rate of 4 kHz. Mao *et al.* (2002) also concluded that the ^{13}C CP NMR spectra of 2 humic acids acquired at different field strength were substantially different. In both cases the differences were attributed to lower CP efficiency at the higher MAS rates required on higher field instruments. On the other hand, Dria *et al.* (2002) reported very similar distributions of C types in spectra of 3 SOM samples acquired on 100 MHz and 300 MHz spectrometers. In a previous study, we reported that ^{13}C CP NMR spectra acquired on 200 MHz and 400 MHz spectrometers differed very little, with just a slightly higher proportion of carboxyl and aromatic C detected at the lower field (Smernik 2005). In that study, as well as comparing CP spectra acquired at different fields, we also tested sensitivity to the Hartman-Hahn matching condition, compared spectra acquired with different MAS rates, spectra acquired using direct polarisation (DP), and gauged the effect of field strength on key relaxation rates.

In this paper, we compare ^{13}C CP NMR spectra acquired on 200 MHz and 400 MHz spectrometers, for 15 SOM samples

collected from an experimental burning site in Germany. The purpose of this paper is not to report the results for this particular set of samples, but rather to gauge the extent to which the differences in organic C chemistry that are evident in the ^{13}C CP spectra are reproducible on different spectrometers.

Materials and methods

Collection and description of soil samples

The samples were collected from an experimental burning site located in south west Germany (Forchtenberg slash-and-burn experiment). The 3.5-ha site is situated in a temperate deciduous forest; the soil is a slightly acidic Haplic Luvisol with partly stagnic properties (Rosch *et al.* 2002). The investigated trial plot (11 by 8 m) was burnt in October 2004; small wood pieces were collected in a row and ignited, and the pile of burning wood was drawn over the ground (Rosch *et al.* 2002).

Soil samples were collected before burning, immediately after burning, and 1 year after burning. For each treatment, 5 samples were analysed (one 0–10 mm, two each of 0–25 and 25–50 mm). The soils were dried at 40°C for 24 h, the aggregates were crushed, and coarse material (roots and charcoal particles) >2 mm was removed by sieving. The organic carbon content of the soil, which did not contain carbonate, was determined by dry combustion (Leco furnace). The nitrogen content of the soil was determined by elemental analysis (Elementar VarioEL). Charcoal carbon concentrations were measured using mid infrared-Fourier transformed infrared spectroscopy (MIR-DRIFT) (Janik *et al.* 2007). Prior to NMR spectroscopy, the soils were treated with 2% HF to remove Fe and concentrate the organic carbon (Skjemstad *et al.* 1994).

NMR spectroscopy

Two spectrometers were used, a Varian Unity 200 spectrometer (henceforth referred to as ‘the 200 MHz spectrometer’) and a Varian Unity INOVA 400 spectrometer (henceforth referred to as ‘the 400 MHz spectrometer’).

All solid-state ^{13}C NMR spectra were acquired with MAS and high-power ^1H decoupling. Spectra acquired on the 200 MHz spectrometer were acquired at a ^{13}C frequency of 50.3 MHz and with a MAS rate of 5 kHz, while those acquired on the 400 MHz spectrometer were acquired at a ^{13}C frequency of 100.6 MHz and a MAS rate of 7 kHz. A Doty Scientific high-speed MAS probe was used on the 200 MHz spectrometer and a Doty Scientific supersonic MAS probe was used on the 400 MHz spectrometer. Both probes use 7-mm-diameter cylindrical zirconia rotors and Kel-F end-caps. Free induction decays were acquired with a sweep width of 40 kHz on the 200 MHz spectrometer and 50 kHz on the 400 MHz spectrometer. A total of 1216 data points were collected for all spectra, representing an acquisition time of 15 ms on the 200 MHz spectrometer and 12 ms on the 400 MHz spectrometer. All spectra were zero-filled to 8192 data points and processed with a 50-Hz Lorentzian line broadening and a 0.010-s Gaussian

broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Spectra were acquired on the 200 MHz spectrometer using a standard CP pulse sequence, and on the 400 MHz using a ramped-amplitude CP (CP-ramp) pulse sequence, in which the ^1H spin lock power was varied linearly during the contact time. The ‘width’ of the ramp, which controls the maximum and minimum power levels, was optimised for one of the samples, and this value was used for all of the other samples. CP-ramp was not available on the 200 MHz spectrometer. Spectra represent the accumulation of 4000 scans and were acquired using a 1-ms contact time (Smernik and Oades 2000a, 2000b) and a 1-s recycle delay, which was $>5 \times T_1\text{H}$ determined in preliminary inversion-recovery experiments.

Results and discussion

The ^{13}C CP spectra of the 15 soils acquired on the 200 MHz and 400 MHz spectrometers are shown in Figs 1–3. The soils were sampled from the same field in a slash-and-burn experiment. They vary considerably in C and N content, and also charcoal content, as detailed in Table 1. These

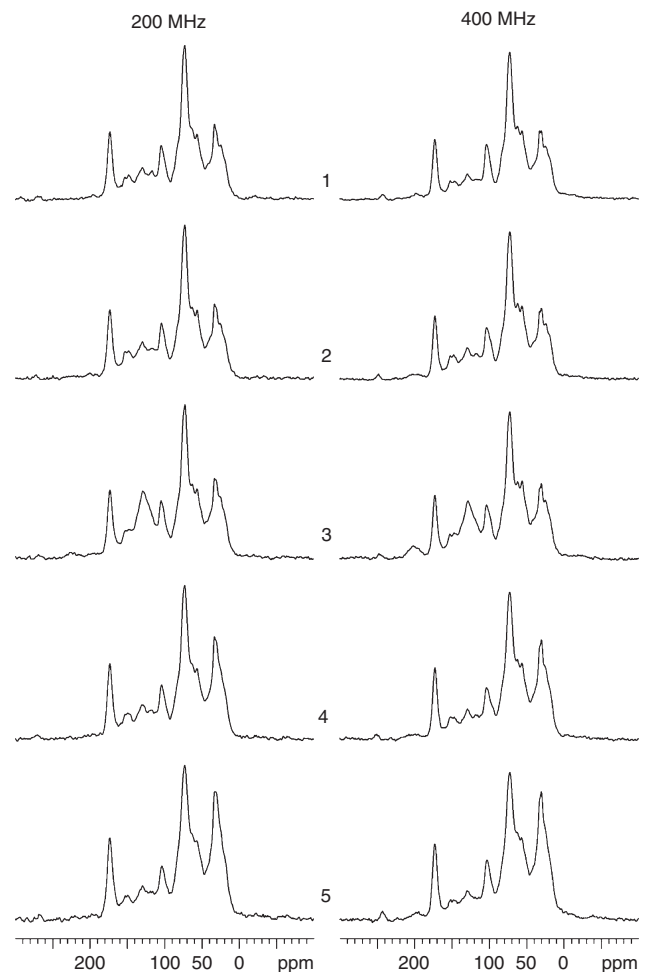


Fig. 1. Solid-state ^{13}C CP NMR spectra of soil samples 1–5.

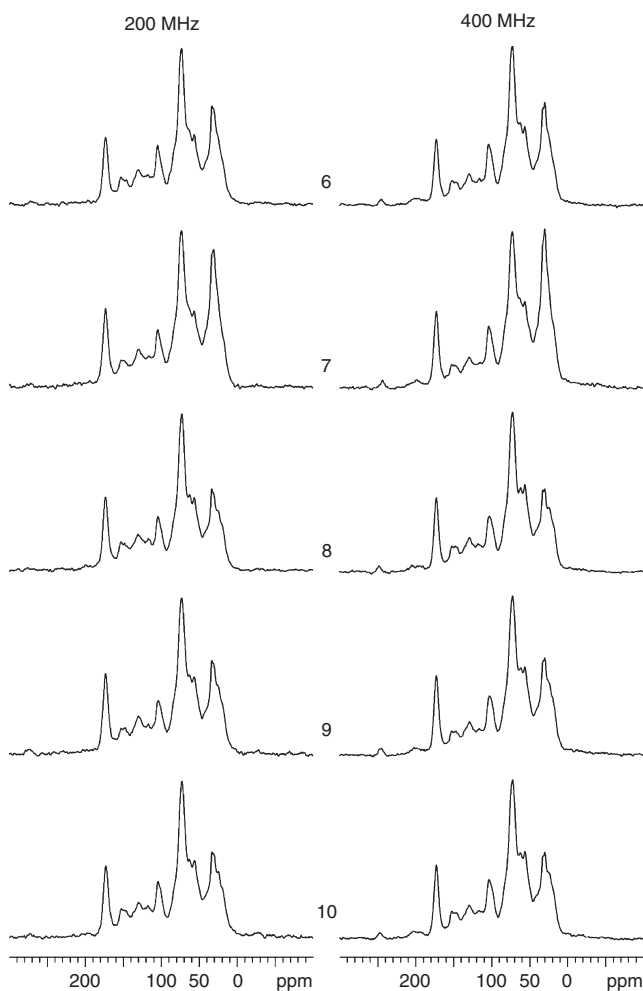


Fig. 2. Solid-state ^{13}C CP NMR spectra of soil samples 6–10.

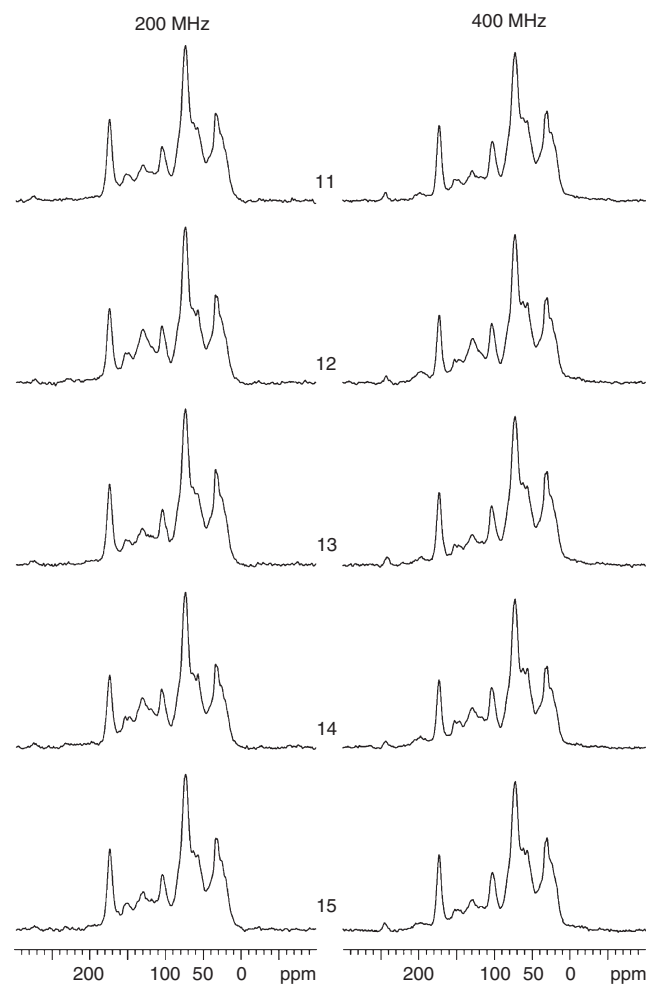


Fig. 3. Solid-state ^{13}C CP NMR spectra of soil samples 11–15.

Table 1. Some properties of the 15 soil samples analysed in this study

Control, samples taken before burning; burnt, samples taken directly after burning; burnt 1 year, samples taken 1 year after burning

Sample	Treatment	Depth (mm)	Organic carbon	Nitrogen (g/kg)	Charcoal carbon	Charcoal carbon (% of SOC)
1	Control	0–10	55.7	4.5	1.6	2.9
2	Burnt	0–10	60.5	4.6	2.4	4.0
3	Burnt 1 year	0–10	24.9	3.9	3.4	13.8
4	Control	0–25	33.3	2.5	1.0	3.0
5	Control	25–50	21.4	1.6	0.5	2.4
6	Control	0–25	44.8	3.2	1.2	2.8
7	Control	25–50	27.5	1.9	0.7	2.6
8	Burnt	0–25	50.4	4.7	1.7	3.3
9	Burnt	25–50	35.5	3.2	1.2	3.1
10	Burnt	0–25	45.3	3.7	1.6	3.5
11	Burnt	25–50	30.0	2.6	0.9	2.8
12	Burnt 1 year	0–25	53.8	3.3	2.8	5.1
13	Burnt 1 year	25–50	39.5	2.3	0.8	2.0
14	Burnt 1 year	0–25	50.2	3.9	2.1	4.2
15	Burnt 1 year	25–50	30.9	2.7	1.0	3.3

differences, as well as the differences in the spectra (Figs 1–3), reflect variations in nature of organic matter with soil depth and the effects of burning.

We (and other researchers in this area) are ultimately interested in using solid-state ^{13}C NMR spectroscopy to understand the effect of management on the nature of SOM.

However, the purpose of this paper is not to report the results for this particular set of samples, but rather to gauge the extent to which the differences in organic C chemistry that are evident in the ^{13}C CP spectra are reproducible on different spectrometers.

Differences between spectra acquired on the 200 MHz and 400 MHz spectrometers were quantified by integrating the spectra over broad chemical shift regions that are assigned to different broad chemical environments. We used a set of 4 integral regions: 185–165 ppm (carboxyl C), 165–110 ppm (aryl C), 110–45 ppm (O-alkyl C), and 45–0 ppm (alkyl C). Signal in spinning sidebands (SSBs) for the carboxyl and aryl resonances was corrected for in the usual way (Schmidt *et al.* 1999), i.e. by adding twice the integrated signal of the low-field SSB to the integrated signal for the central band, and subtracting this signal from the region where the corresponding high-field SSB falls (Tables 2 and 3). SSB correction was complicated by the fact that the ratio of MAS rate to field strength was different for the 2 spectrometers. Therefore, the position and sizes of the SSBs differed. A MAS rate of 5 kHz was used on the 200 MHz spectrometer, resulting in the appearance of

Table 2. Assignment of chemical shift regions for spectra acquired on the 200 MHz spectrometer
CB, Centre band; SSB, spinning sideband

Region	Assignment
A: 285–265 ppm	Carboxyl SSB
B: 265–245 ppm	Aryl SSB
C: 245–210 ppm	Aryl SSB
D: 185–165 ppm	Carboxyl CB
E: 165–110 ppm	Aryl CB
F: 110–45 ppm	O-alkyl + carboxyl SSB + aryl SSB
G: 45–0 ppm	Aliphatic + aryl SSB
Carbon type	Combination of regions
Carboxyl	$D + 2 \times A$
Aryl	$E + 2 \times B + 2 \times C$
O-alkyl	$F - A - B$
Alkyl	$G - C$

Table 3. Assignment of chemical shift regions for spectra acquired on the 400 MHz spectrometer
CB, Centre band; SSB, spinning sideband

Region	Assignment
A: 255–235 ppm	Carboxyl SSB
B: 235–185 ppm	Aryl SSB
C: 185–165 ppm	Carboxyl CB
D: 165–110 ppm	Aryl CB
E: 110–45 ppm	O-alkyl + carboxyl SSB + aryl SSB
F: 45–0 ppm	Alkyl
Carbon type	Combination of regions
Carboxyl	$C + 2 \times A$
Aryl	$D + 2 \times B$
O-alkyl	$E - A - B$
Alkyl	F

SSBs 100 ppm from the central band, whereas a MAS rate of 7 kHz was used on the 400 MHz spectrometer, resulting in the appearance of SSBs 70 ppm from the central band. On the 200 MHz spectrometer, the intensity of the high-field SSBs was on average 3% and 4% of those for the centre-bands for the carboxyl and aromatic regions, respectively. On the 400 MHz spectrometer, the intensity of the high-field SSBs was on average 6% and 15% of those for the centre-bands for the carboxyl and aromatic regions, respectively. The choice of MAS rate was governed by several factors. Clearly, it is desirable to spin samples as rapidly as possible in order to decrease the size of SSBs and prevent overlap of SSBs with other resonances. However, rapid spinning may decrease CP efficiency, resulting not only in lower sensitivity, but more importantly in poorer quantitation, as some ^{13}C nuclei, including those without directly attached protons, are more affected (Fründ and Lüdemann 1994; Mao *et al.* 2002; Smernik 2005). Finally, there were hardware restrictions that prevented us spinning faster than 7 kHz on the 400 MHz spectrometer. The treatment of SSB corrections described in Tables 2 and 3 enables the best possible comparison between spectral distributions on the 2 spectrometers in the circumstances. However, this treatment is not perfect for several reasons including:

- (i) In some cases the chemical shift ranges assigned to the central band and sidebands do not differ by exactly 70 ppm for the 400 MHz spectra (Table 3).
- (ii) It is clear from the 200 MHz spectra in Figs 1–3 that there is some signal in the region 185–220 ppm (usually assigned to C in ketones and aldehydes). This signal overlaps with, and is assigned to, the SSB of the aryl signal in the spectra acquired on the 400 MHz spectrometer (Table 3), whereas it is not measured at all in the spectra acquired on the 200 MHz spectrometer. This results in a positive bias in signal assigned to aryl C for the spectra acquired on the 400 MHz spectrometer.
- (iii) The corrections assume equal intensities of high-field and low-field SSBs, which is not always justified (Newman *et al.* 1987). This source of error is potentially larger for the spectra acquired on the 400 MHz spectrometer, since the SSBs are larger.

We could have run the spectra under conditions that gave rise to SSBs of equivalent size and spacing (e.g. by using a MAS rate of 3.5 kHz on the 200 MHz spectrometer). However, the point of this exercise was to not to acquire the most comparable spectra, but rather to choose optimal acquisition conditions for each spectrometer independently and then compare the spectra.

The relative amounts of the 4 C types, determined by integration of the spectra acquired on the 2 spectrometers, are shown in Table 4. These varied from 7.8 to 10.3% for carboxyl C, 14.2 to 27.5% for aryl C, 44.9 to 53.5% for O-alkyl C, and 18.9 to 30.7% for alkyl C (Table 4). These distributions of C types are quite typical for SOM (Mahieu *et al.* 1999).

Figure 4 shows that the amounts of the 4 C types determined from the spectra acquired on the 2 spectrometers are

Table 4. Percentage of total NMR signal assigned to each carbon-type
Determined from spectra acquired on 200 MHz spectrometer (200) and 400 MHz spectrometer (400)

Sample	Carboxyl		Aryl		O-alkyl		Alkyl	
	200	400	200	400	200	400	200	400
1	8.7	8.2	16.8	16.0	53.3	53.5	21.2	22.3
2	9.0	7.8	20.1	18.5	51.1	52.2	19.9	21.6
3	8.1	7.8	26.5	27.5	46.6	44.9	18.9	19.8
4	9.4	8.3	17.4	16.9	49.1	49.7	24.2	25.1
5	8.9	8.5	14.2	14.6	48.5	47.9	28.5	29.0
6	8.3	7.8	17.8	17.3	50.1	50.9	23.8	24.0
7	8.9	8.1	16.9	15.4	46.8	45.9	27.4	30.7
8	9.1	8.3	18.8	18.6	51.0	51.1	21.1	22.0
9	10.1	9.0	18.0	17.6	49.4	49.6	22.5	23.9
10	8.9	8.5	17.5	19.3	50.6	50.0	23.0	22.2
11	10.3	9.5	18.4	17.8	49.8	49.1	21.6	23.5
12	8.8	8.3	22.2	22.5	48.5	47.1	20.4	22.1
13	10.1	9.3	17.1	17.8	50.1	48.9	22.7	24.1
14	9.2	8.6	23.0	23.6	48.3	47.0	19.5	20.8
15	9.8	8.9	17.5	17.5	50.0	49.8	22.7	23.8

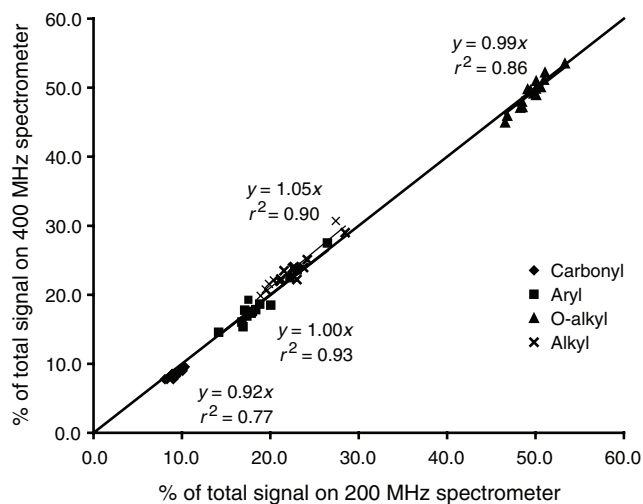


Fig. 4. Comparison of percentage signal assigned to different C types derived from spectra acquired on the 2 spectrometers. A 1 : 1 line is included to aid comparison.

very similar. Correlations between corresponding values are strongest for aryl C ($r^2=0.93$), followed by alkyl C ($r^2=0.90$), O-alkyl C ($r^2=0.86$), and carboxyl C ($r^2=0.77$), reflecting the order of decreasing variation of these parameters (i.e. the proportion of aryl C varied the most between samples and the proportion of carboxyl C content varied the least). The strength of the correlations is consistent with estimated uncertainty in each measurement of around 2% (Baldock and Smernik 2002; Smernik *et al.* 2006). There is no apparent bias for aryl or O-alkyl C, as the slopes of the correlation curves are within 1% of the 1:1 line. On the other hand, a slight bias is apparent for carboxyl C, the values of which were, on average, 8% lower when determined on the 400 MHz spectrometer. There is also a slight bias apparent for alkyl C, the values of which were, on average, 5% higher when determined on the 400 MHz spectrometer.

The negative bias against carboxyl C at the higher field (and more crucially higher MAS rate) is consistent with previous findings by ourselves (Smernik 2005) and others (Fründ and Lüdemann 1994; Mao *et al.* 2002). However, in these previous studies, there was also a bias against aryl C, which we do not see here. This may be due to our treatment of SSBs. As discussed above, the small amount of signal in the region 185–210 ppm due to ketone and aldehyde C is disregarded in the integration scheme of the spectra acquired on the 200 MHz spectrometer, but falls within the aryl SSB, and hence is counted as aryl C in the integration scheme of the spectra acquired on the 400 MHz spectrometer. This may cancel out the expected negative bias for aryl C at the higher field. The negative bias against carboxyl C must be counteracted by a relative increase in signal elsewhere. We see this in the alkyl C region, but not in the O-alkyl region. This may be a further effect of the inflated aryl SSB intensity, since this signal is subtracted from the region assigned to O-alkyl C in the integration scheme of the spectra acquired on the 400 MHz spectrometer.

Conclusions

These results provide some reassurance as to the validity of the large number of SOM studies that utilise ^{13}C CP NMR characterisation. Firstly, the strong correlations between distributions of C types derived from ^{13}C CP NMR spectra acquired on 2 different NMR spectrometers ensure that differences between the soils identified in the NMR spectra are independent of which spectrometer the spectra were acquired on. This is the most important point for most SOM studies. Secondly, the correlations lie close to the 1:1 line, i.e. the actual distributions are fairly independent of the spectrometer, notwithstanding the slight biases in carboxyl C (on average 8% lower on 400 MHz spectrometer) and alkyl C (on average 5% higher on 400 MHz spectrometer). This means that comparisons between distributions of C types derived from spectra

acquired on these 2 spectrometers would only be affected by fairly small biases. By extension, provided sample preparation and acquisition conditions are appropriate, there is no reason why SOM samples should not be characterised using field strengths up to 400 MHz. However, it should also be remembered that all ^{13}C CP spectra of SOM are subject to potential biases associated with remote protonation, highly mobile domains, and paramagnetic relaxation. In other words, the differences between ^{13}C CP spectra acquired on different spectrometers are likely to be smaller than differences between ^{13}C CP spectra and ^{13}C DP (direct polarisation) spectra. It remains, as ever, prudent to gauge the potential for quantitation problems by spin counting (Smernik and Oades 2000a, 2000b; Keeler and Maciel 2003) and to implement less sensitive or more sophisticated techniques (Mao *et al.* 2000; Smernik and Oades 2000a, 2000b, 2003; Mao *et al.* 2002) to obtain better quantitation when required.

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