Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Mediterranean ecosystems: a solid-state ^{13}C NMR study

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Summary

The variable effect of different types of forest fires on the quantity and quality of soil organic matter (SOM) was analysed by comparing burnt and unburnt soils from six forest ecosystems in central Spain by organic elemental analysis and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Whole soil samples were collected 1 to 2 years after the fires and included one site affected by two fires within 2 years. The fire-affected soils showed no common pattern with respect to the amount of additional carbon (C_{add}) but at all sites, the fire enhanced the aromatic-C content. The weakest fire intensity resulted in the greatest aromatic-C enrichment factor, $EF_{I(aromatic\ C)}$ indicating the greatest local accumulation of char. The respective C_{add} disclosed an $EF_{I(aromatic\ C)}$ to $EF_{I(alkyl\ C)}$ ratio, B_{char}, of $c.1$, which supports a small degree of charring. Extensive combustion and volatilization at stronger fire intensities yielded a decrease of $EF_{I(aromatic\ C)}$ and an increase in B_{char}. These trends are in good agreement with fire intensity and forest fuel combustibility in the various sites and therefore these indices could be used to elucidate the quality and quantity of char input that occurs during and after forest fires. No ^{13}C NMR evidence for substantial inputs from non-charred plant necromass was found for any of the single-burn soils. The large carboxyl-C content of C_{add} is evidence of the occurrence of oxidation reactions very shortly after the fire. In comparing the single and double-burn sites, no additional char input was observed for the double-burn site, possibly because of complete combustion of young shrubs and char remains during the second fire. The large O-alkyl-C portion found in C_{add} of the double-burn soil is best explained by decreased litter degradation.

Introduction

Soil organic matter (SOM) represents an active environmental compartment in which biogeochemical processes have a direct impact on primary production and biodiversity. Both quality and quantity of SOM are expected to be severely affected by forest fires as those occur frequently and recurrently during the hot (up to $c.$ 40°C) and dry summers in Mediterranean ecosystems. Nevertheless, the effects of forest fires could be very variable depending on numerous factors such as fire intensity and duration, but also on the amount and flammability of the vegetation and the litter (Neary *et al.*, 1999). In consequence, the effects of forest fires may range from a dramatic loss of SOM in the topsoil (Rollins *et al.*, 1993; Haslam *et al.*, 1998; Fernández *et al.*, 1999; Neary *et al.*, 1999) to an increase of SOM by accumulation of necromass on the ground that is composed of dry leaves and charred

plant remains (Knicker *et al.*, 2005a). Because charring turns labile organic components such as carbohydrates or amino acids into very recalcitrant aromatic and heteroaromatic forms (Almendros *et al.*, 2003), the incorporation of pyrogenic necromass into the soil is expected to increase the passive SOM pool (Kuhlbusch & Crutzen, 1995; Schmidt & Noack, 2000).

With respect to soil C-sequestration processes, the accumulation of char as a means to alleviate increasing CO_2-concentration in the atmosphere, could be seen as an environmental benefit (Schmidt & Noack, 2000; González-Pérez *et al.*, 2004). On the other hand, heat can also alter SOM and litter towards greater decomposability (Fernández *et al.*, 1997), and fire leads to the release and accumulation of ash especially rich in available nutrients (Kutiel & Inbar, 1993). Both processes were held responsible for the large respiration rates observed during the first weeks after laboratory incubation of fire-affected soils (Almendros *et al.*, 1990; Pietikäinen *et al.*, 2000). After several weeks, however, the respiration rates often decrease below the levels found for the control soils. Heat is also reported to

increase the solubility of SOM (Prieto-Fernández et al., 1998), thus losses of C due to leaching as DOM may have to be considered in fire-affected soils.

An additional intrinsic effect of fire on SOM quantity and quality is the immediate decrease of soil microbial biomass. It has been suggested that most living organisms are killed at temperatures between 50 and 120°C (Neary et al., 1999) and that burning favours bacteria over fungi (Vázquez et al., 1993). In a conifer forest soil, neither the length of fungal hyphae nor the microbial biomass recovered to their control levels even 3 years after a controlled burning (Fritze et al., 1993). Prieto-Fernández et al. (1998) reported that alteration to the soil microbial population by wildfires could last for as long as 4 years. Fernández et al. (1999) observed that changes in soil mineralization indices lasted for at least 2 years after a wildfire and were accompanied by the persistent increase of organic matter stability.

The effects of fire on the SOM concentration and the quantitative importance of charred residues in the whole C-sequestration process is receiving ongoing attention (Kuhlbusch & Crutzen, 1995; Skjemstad et al., 1999; Schmidt & Noack, 2000). Most research on fire-induced alterations of soil molecular constituents has focused mainly on the heat-induced transformations of lignocellulosic material during laboratory-controlled charring experiments (Almendros et al., 1990, 2003; Knicker et al., 1996; Baldock & Smernik, 2002; Czimczik et al., 2002). Reports on SOM alteration due to fire in natural systems are still scarce (Almendros et al., 1988, 1990, 1992; Fernández et al., 1997; Czimczik et al., 2003; Knicker et al., 2005a). They often lead to divergent conclusions depending on local factors, which make it difficult to postulate a generalized model about the lasting effects of fires on SOM. To fill this gap, we compare various fire-affected and control surface soils under oak and pine forests in central Spain by means of elemental analysis and solid-state ^{13}C NMR spectroscopy. The samples were collected approximately 1–2 years after fire events of moderate to great intensity in order to focus on the short-term effects. In addition, a sample set comprising both A and B horizons was analysed to obtain some insights on possible fire-induced chemical alterations of SOM in the subsoil. This set included a site that within 2 years burned twice. With this approach we hoped to extract a common pattern of the compositional changes of SOM due to vegetation fires and to discuss this pattern with regard to SOM stability.

In general, solid-state ^{13}C NMR spectra of SOM are obtained with the cross-polarization magic angle spinning (CPMAS) technique, with which the sensitivity to ^{13}C is increased by polarization transfer from the ^{1}H to the ^{13}C spin system. It is suspected, however, that this obscures the relative intensity distribution in a ^{13}C NMR spectrum of charred material due to inefficient cross-polarization of C in the highly condensed structures that are suggested for such constituents (Smernik et al., 2002). On the other hand, systematic comparisons between the intensity distribution in spectra corresponding to charred SOM, barbecue charcoal and burnt vegetation residues acquired with and without cross-polarization could not confirm intensity loss due to highly condensed (graphitic) aromatic structures (Knicker et al., 2005a,b). Application of special NMR techniques (Czimczik et al., 2003; Knicker et al., 2005b) reinforced this conclusion and showed that in contrast to soot, SOM containing charred necromass should be amenable to quantitative analyses by CPMAS NMR.

Materials and methods

Sample material

The soil samples used in this study were collected from areas close to Madrid (central Spain) under a continental Mediterranean climate with its hot summers and humid winters. All soils were classified according to the ISSS Working Group (1998) World Reference Base. From each site, five soil samples were randomly collected and mixed. A brief description and characteristic soil parameters are given in Tables 1 and 2. The first sample set was obtained from sandy loamy Dystric Cambisols under a *Quercus rotundifolia* forest (Almendros et al., 1990). The control soil area (Q_U) and the burnt site (Q_B) were separated by approximately 25 m and were located in the surroundings of Pantano de San Juan (70 km west of Madrid). A very intense wildfire occurred approximately 15 months before sampling in summer 1989 and removed the herbaceous and brushwood species, but left dead oaks without leaves. From both sites, soil samples were collected from a depth of 10 cm (A horizon). Additionally a sample was taken from a depth of 0–5 cm at site Q_B.

A second sample set was collected from a site close to San Martín de la Vega (30 km south of Madrid) in summer 1997. The materials were derived from the top 5 cm of the A horizon of two Calcaric Cambisols under *Pinus halepensis* that were unaffected ($F1_U$) or affected ($F2_B$) by a very intense fire in June 1996. Additionally, the top 5 cm of the A horizons of a fire-unaffected Umbrihumic Umbrisol ($F3_U$) and an Epidystric Cambisol ($F4_B$) also suffering an intense fire during the summer 1996 were sampled. Here, the charred tree trunks remained but their needles were completely ashed by the fire. Both soils are under *Pinus sylvestris* and are located in Somosierra (100 km north of Madrid). Whereas sites $F1_U$ and $F2_B$ represent young forests, that were reforested 40 years ago, sites F3 and F4 are examples of well-matured forests. The granulometric analysis of all four soils assigns them to silt loam.

The sampling site referred to as P_U–P_B comprises material collected from the top 15 cm (A horizon) of Dystric Cambisols under *Pinus pinea*, also in the surroundings of Pantano de San Juan (80 km west of Madrid) (Almendros et al., 1988). Site P_B was affected by a medium-intensity fire in 1980, 2 years before

Table 1 Origin, parent material, soil type and textural classification of burnt (B) and unburnt (U) soils from the surroundings of Madrid, central Spain

Sample	Location	Vegetation	Fire	Sampling	Parent material	Soil type	Textural classification	Altitude/ m.a.s.l.	Slope/%
Q_U/Q_B	Pantano de San Juan	*Quercus rotundifolia*	Summer 1988. *Very intense*	Summer 1989	Gneiss	Dystric Cambisol	Loamy sand	520	5
$F1_U/F2_B$	San Martín de la Vega	*Pinus halepensis*	Summer 1996. *Very intense*	June 1997	Limestone	Calcaric Cambisol	Silt loam	630/624	0/8
$F3_U/F4_B$	Somosierra	*Pinus sylvestris*	Summer 1996. *Intense*	June 1997	Gneiss	Umbrisol/ Epidystric Cambisol	Silt loam	1580/1615	20/15
P_U/P_B	Pantano de San Juan	*Pinus pinea*	Summer 1980. *Medium*	Spring 1982	Gneis	Dystric Cambisol	Loamy sand	530/532	5/15
$P1_U$	Piedralaves	*Pinus pinaster*	Control	July 1982	Granite	Cambisol	Loamy sand	1040	30
$P2_B$	Piedralaves		Summer 1981. *Intense*	July 1982	Granite	Cambisol	Loamy sand	1040	35
$P3_B$	Piedralaves		1978/1980. *Intense*	July 1982	Granite	Cambisol	Loamy sand	960	30

sampling. The unburnt site P_U is separated from site P_B by a forest road of about 3-m width (Table 1). Sampling took place in spring after removing the litter layer.

In order to elucidate the effect of successive burnings, three additional profiles sampled in July 1982 were included in this study. They were located close to the forest street from Piedralaves to La Adrada (100 km west of Madrid). These sandy Cambisols were vegetated with *P. pinaster* before the fire. Profile $P1_U$ is approximately 80 m from profile $P2_B$ and 500 m from profile $P3_B$. This area is subjected to strong changes in temperature and irregular rainfall of up to 600-mm per year. Soil $P1_U$ suffered no vegetation fire, while $P2_B$ burned in 1981, and $P3_B$ was affected by severe fires in 1978 and 1980. The burnings removed even the trunks and only fragments of charred wood were left on the forest floor. After the latest fire this site was encroached by

Pteridium aquilinum. Samples were taken from the A and B horizons.

Determination of soil characteristics

The pH values were measured in a water suspension (1:2.5; soil:H_2O). The colour was determined from the dried samples with Munsell colour charts. With the exception of sample set F1–F2, total C and total N were measured by dry combustion (975°C; Elementar Vario EL microanalyser, Elementar Analysesysteme GmbH, Hanau, Germany). The detection limits for C and N were 0.4 and 1 µg, respectively. For F1–F2, organic C was determined from the difference in C content before and after heating a sample for 2 h at 450°C (Carmhograph-12 analyser, Bochum, Germany). Their total N content was found with the Kjeldahl method.

Table 2 Analytical characteristics of the burnt (B) and unburnt (U) soils from Central Spain

	Horizon	Depth/cm	Dry colour (Munsell)	pH (H_2O)	$CaCO_3$/mg g^{-1}	C_{org}/mg g^{-1} SE[a]	N/mg g^{-1} SD[a]	C/N
Q_U	A	0–10	10YR 6/4	4.8	0	15.0 ± 0.5	1.2 ± 0.7	12
$Q5_B$	A	0–5	ND	ND	0	60.0 ± 1.5	4.0 ± 0.2	14
Q_B	A	0–10	10YR 3/3	6.2	0	16.4 ± 0.5	1.2 ± 0.5	13
$F1_U$	A	0–5	10YR 3/4	6.9	80	212 ± 3.2	14.7 ± 0.4	15
$F2_B$	A	0–5	10YR 3/1	8.7	280	39 ± 1.5	3.2 ± 0.5	12
$F3_B$	A	0–5	10YR 3/4	4.6	0	60.1 ± 1.2	4.0 ± 0.7	15
F4	A	0–5	10YR 2/1	5.7	0	81.6 ± 1.7	7.3 ± 0.8	11
P_U	O + A	0–15	5YR 6/3	5.7	0	19.0 ± 1.0	1.2 ± 0.2	16
P_B	O + A	0–15	10YR 5/1	6.6	0	40.0 ± 1.0	2.5 ± 0.3	16
$P1A_U$	A	11–25	10 YR 4/2	5.4	0	64.6 ± 1.4	0.28 ± 0.3	23
$P1B_U$	B	25–56	10YR 5/3	5.1	0	14.5 ± 0.5	1.0 ± 0.2	15
$P2A_B$	A	2–35	10YR 3/2	5.8	0	66.1 ± 3.1	3.0 ± 0.4	22
$P2B_B$	B	35–75	10YR 4/3	5.8	0	23.4 ± 0.5	1.1 ± 0.3	22
$P3A_B$	A	2–25	10YR 3/2	6.1	0	81.6 ± 1.5	3.7 ± 0.7	22
$P3B_B$	B	25–60	10YR 4/3	5.9	0	31.7 ± 1.9	1.8 ± 0.3	18

[a]SE, standard error with $n = 4$.

Solid-state ^{13}C NMR spectroscopy

All samples were analysed by solid-state ^{13}C NMR spectroscopy without prior HF-treatment (Bruker DSX 200 NMR spectrometer, Bruker, Karlsruhe, Germany); ^{13}C-resonance frequency = 50.32 (MHz). The cross-polarization magic angle spinning (CPMAS) technique with a spinning speed of 6.8 kHz was applied. A ramped ^1H-pulse starting at 100% to 50% of the initial power was used during a contact time of 1 ms in order to circumvent spin modulation during the Hartmann-Hahn contact. Pulse delays between 200 and 600 ms were used for all spectra. Pre-experiments confirmed that the pulse delays were long enough to avoid saturation. Depending on the C contents of the samples, between 10 000 and 300 000 scans were accumulated. A line broadening between 50 and 100 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 p.p.m.).

The relative contributions of the various C groups were determined by integration of the signal intensity in their respective chemical shift regions according to Knicker *et al.* (2005a). The regions 245–185 p.p.m. and 185–160 p.p.m. are assigned to carbonyl (aldehyde and ketone) and carboxyl/amide C. Olefinic and aromatic C are detected between 160 and 110 p.p.m. O-alkyl and N-alkyl-C signals are found from 110 to 60 p.p.m. and from 60 to 45 p.p.m. Resonances of alkyl C are expected between 45 and 0 p.p.m. Because there is insufficient averaging of the chemical shift anisotropy at a spinning speed of 6.8 kHz, spinning side bands (ssb) of the aromatic-C signals occur at both sides of the central signal (300–275 p.p.m. and 0–50 p.p.m.) at a distance corresponding to the spinning frequency. Their intensities were added to that of the parent signal. To account for the contribution of the ssbs of the carboxyl-C signal, we added twice the intensity of the low-field ssb (325–300 p.p.m.). Because the high-field ssb of the carboxyl-C signal overlaps with the alkyl-C region, the intensity of its low-field ssb had to be subtracted from the intensity in the region between 45 and 0 p.p.m. to obtain the proportion of alkyl C.

For more detailed insights into the alterations of the organic matter due to the fire event, the concentrations of the different C groups were assessed by multiplying the relative intensity of each chemical shift region (unburnt soil, I_{CSU}; burnt soil, I_{CSB}) in the ^{13}C NMR spectrum by the C content of the relevant sample (unburnt soil, C_U; burnt soil, C_B).

From those values, the enrichment factor, EF_I, for each chemical shift region and the difference concentration, D_I, for each C-group were determined according to equations 1 and 2:

$$EF_I = (I_{CSB} \times C_B)/(I_{CSU} \times C_U), \qquad (1)$$

$$D_I = (I_{CSB} \times C_B) - (I_{CSU} \times C_U). \qquad (2)$$

The chemical composition of the additional C (C_{add}) was determined by calculating D_I for each C-group and normalizing the sum to 100%.

Results

Impact of fire on pH and soil colour

The fire-affected soils showed an increase in pH compared with the corresponding unaffected sites (Table 2). This is attributed to combustion of organic matter from the vegetation, litter and soil humus, which results in a nutrient-rich ash layer on the forest floor (liming effect).

In comparison with the controls, the fire-affected soils show lower Munsell values, i.e. are darker (Table 2). In general, decrease in soil lightness is related to an increase in SOM content (Schulze *et al.*, 1993). However, we also found darkening due to fire for sample sets with comparable organic C contents for the control and fire-affected soils (Q_U–Q_B and $P1A_U$–$P2A_B$). In addition, the set $F1_U$–$F2_B$ had a comparable Munsell value, although the fire caused a considerable decrease of organic C. Thus, the compositional properties and the amount of the accumulated char seem to be mainly responsible for the darker soils, which accords with the findings that the extent of soil darkening by SOM is mainly determined by its content of aromatic C (Spielvogel *et al.*, 2004).

Fire-induced changes in the organic matter composition of the single-burn site under oak

With respect to the control soil Q_U under *Quercus rotundifolia*, neither C nor N concentrations of soil Q_B were greatly altered by the very intense fire (Tables 2 and 3) but the latter caused severe alterations of the C composition. Solid-state ^{13}C NMR spectroscopy (Figure 1, Table 4) shows a relative increase of the signal intensity in the chemical shift region assigned to sp^2 C in olefins or aromatic structures (160–140 p.p.m.). Concomitantly, the contribution of O-alkyl C (110–60 p.p.m.) and alkyl C (45–0 p.p.m.) to the total ^{13}C-intensity decreased, whereas the relative intensity between 60 and 45 p.p.m., attributable to methoxyl C or N-alkyl C, remained unchanged. The above alterations are traditionally explained by heat-induced transformations of soil humus during the passage of the fire. In fact, laboratory heating experiments of plant material, peat and humic fractions. (Almendros *et al.*, 1992, 2003; Knicker *et al.*, 1996; Baldock & Smernik, 2002) demonstrated that during charring at moderate intensities, predominantly O-alkyl C and then alkyl C are lost, whereas aromatic C is formed due to dehydration and cyclization of carbohydrates and proteinaceous compounds. Increasing charring intensity leads to a decrease and finally to a complete loss of alkyl C and carboxyl C. However, charring is also connected to C-losses due to volatilization. Thus, the comparable C concentrations in the fire-affected Q_B and control Q_U soils (Table 2) indicate that besides chemical transformations of the native SOM, additional incorporation of necromass during or after the fire had affected the SOM composition at the burnt site.

Table 3 C and N enrichment factors (EF) in soils from central Spain induced by fire

Sample set		C_{org}/mg g^{-1}	N/mg g^{-1}
Q_U/Q_B	Difference	1	0
	EF	1.1	1
$F1_U/F2_B$	Difference	−173	−11.5
	EF	0.18	0.22
$F3_U/F4_B$	Difference	22	3.3
	EF	1.4	1.8
P_U/P_B	Difference	21	0.6
	EF	2.1	1.3
$P1A_U/P2A_B$	Difference	1	0.2
	EF	1.0	1.1
$P2A_B/P3A_B$	Difference	16	0.7
	EF	1.2	1.2
$P1A_U/P3A_B$	Difference	17	0.9
	EF	1.3	1.3
$P1B_U/P2B_B$	Difference	9	0.2
	EF	1.6	1.2
$P2B_B/P3B_B$	Difference	8	0.7
	EF	1.3	1.5
$P1B_U/P3B_B$	Difference	17	0.9
	EF	2.2	1.8

The poor auto-combustibility of oak biomass may have been responsible for large inputs of litter after the death of the oaks caused by the high temperature generated during the burning of sclerophyllic brushwood (Almendros *et al.*, 1990). Disintegration and slow incorporation of unburnt remains from dead roots represent an additional potential C source. In order to elucidate the impact of this additional organic carbon (C_{add}) on SOM composition, we calculated the enrichment factors (EF_I) of the different C-groups according to equation (1) (Table 5). They confirm a net increase of aromatic C ($EF_I = 1.6$). The small net decrease of O-alkyl and alkyl C ($EF_I = 0.9$) further discloses that fresh litter and dead roots with their large contents of O-alkyl C had only a minor impact on the fast recovery of the quantity of SOM. The additional contribution of aromatic C is even more obvious in the soil material obtained from the top 5 cm ($Q5_B$). Because of the water content and poor thermal conductivity of mineral soils, the temperature decreases quickly with soil depth during a fire (Campbell *et al.*, 1995). Therefore litter and above-ground vegetation are mainly affected by the heat. Because of this and the fact that incorporation of charred necromass will first occur into the first few centimetres of the topsoils, their humic material will be more affected than the SOM in deeper soil.

A further interesting feature is the slightly increased intensity in the carboxyl/amide C (185–160 p.p.m.) and aldehyde/ketone C (245–185 p.p.m.) regions in the spectrum of the burnt soil from 10-cm depth with respect to that of the control soil. This points to a greater degree of oxidation of the post-fire humic material and reveals that already within 15 months after the fire, a considerable part of the charred residues were transformed to carboxylate.

Fire-induced changes in the organic matter composition of the single-burn sites under pine

The ^{13}C NMR spectrum of the top 5 cm of soil $F1_U$ under a young forest of *P. halepensis* shows the typical distribution pattern of poorly humified material. It is dominated by the O-alkyl C signal followed by a resonance line assigned to alkyl C. The large organic C concentration of 212 mg g^{-1} is consistent with a considerable contribution of only partly degraded litter. At this location, the intense fire resulted in a great reduction of the organic C content to 39 mg g^{-1} in the post-fire soil $F2_B$, possibly due to the great combustibility of the resinous plant cover. The fire resulted in complete destruction of the forest and the litter layer and also affected the humic material in the topsoil. Although the total N content was decreased by the fire, the smaller C/N ratio of the $F2_B$ soil compared with $F1_U$ indicates a relative enrichment of N-compounds.

The solid-state ^{13}C NMR spectrum of soil BF2 shows the typical pattern expected for heavily charred organic matter (Figure 1, Table 4). The O-alkyl C comprised only 11% of the total ^{13}C-intensity, whereas aromatic C amounts to 60%. Calculating EF_I for the different chemical shift regions showed a fire-induced decrease of all C-groups with the exception of aromatic C, possibly due to chemical transformation of native SOM during charring. Some heavily charred necromass, which remained on the forest floor after the fire, represents an additional source of increasing aromaticity of the SOM. The extremely small proportion of O-alkyl C in the $F2_U$ soil reveals further that fresh litter material was not produced or at least did not accumulate to a noticeable extent during the post-fire period of 1 year.

The pattern of heavily charred organic material is also identified in the ^{13}C NMR spectrum of sample $F4_B$ (Figure 1, Table 4) but, with respect to the control soil $F3_B$, the C- and N-concentrations increased by an EF of 1.7 and 1.4, respectively (Table 3). This suggests that more charred necromass was incorporated during the post-fire stage than humic material was lost by combustion. The char input and heat-induced chemical transformations of native humus enhanced the aromatic-C content by $EF_I = 2.5$ (Table 5). Compared with $F3_B$ the O-alkyl C and N-alkyl C contributions were reduced by approximately 40%, whereas the proportion of alkyl C was only lowered by 15%. In spite of an expected decline of carboxyl C after the fire due to decarboxylation during combustion, a relatively large $EF_I = 1.65$ was calculated for this C-group. Thus, oxidation of charred residues during the post-fire stage could also be deduced for this pine forest site.

At a further pine forest site, 2 years after medium intensity fire, increases of the C- and N-concentrations by EF of 2.2 and 2.1 were detected in the A horizon of the burnt site (P_B)
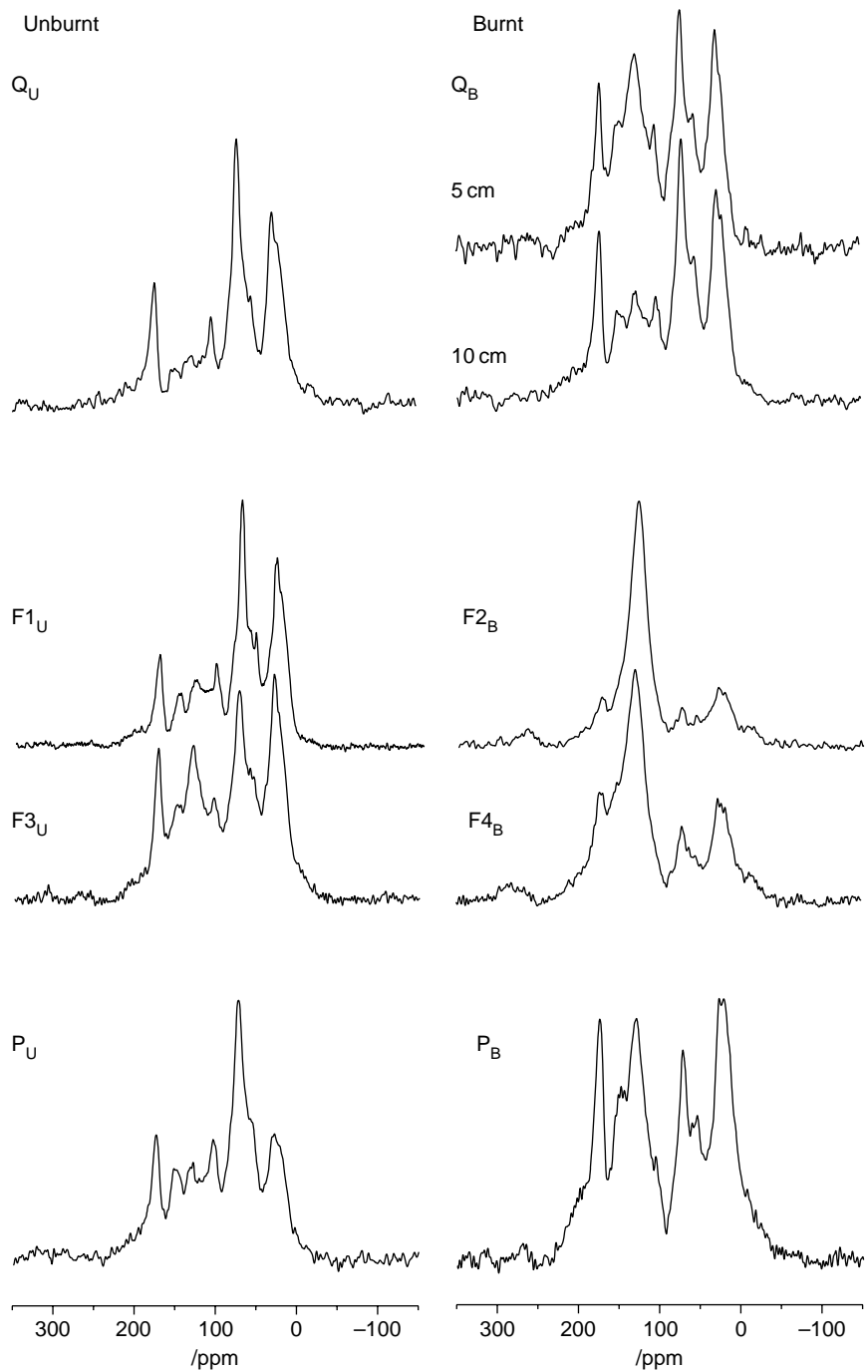
Figure 1 Solid-state ^{13}C NMR spectra of burnt and control soils from forest stands in the area around Madrid (central Spain).

compared with the control soil (P_U) (Table 3). According to the NMR spectra (Figure 1), C_{add} derived mainly from aromatic C, alkyl C and carbonyl C (EF_I around 3) (Table 5). The minor contributions of O- and N-alkyl C to C_{add} underline the small importance of fresh litter inputs during the post-fire stage. Therefore, the considerable amount of C_{add} is best assigned to charred necromass. The noticeable alkyl-C content

of C_{add} may be caused by the lesser charring intensity of this medium-intensity fire. It may also be related to the enhancement of the lipid content at the post-fire site (Almendros et al., 1988), which possibly corresponds not only to dry thermal distillation and further fixation of pine resins but also to the release of large amounts of alkanes and fatty acids from the burned necromass.

Table 4 Intensity distribution in the solid-state ^{13}C NMR spectra (%) of unburnt soil (U) and burnt (B) soils from central Spain (Madrid). The data from the samples from Piedralaves are shown in Table 6

| | Carbonyl 245–185 | Carboxyl/Amide 185–160 | Aromatics 160–110 | O-Alkyl 110–60 | N-Alkyl/Methoxyl 60–45 | Alkyl 45–0 | |
			p.p.m.				P^a
Q_U	4	10	15	34	8	28	1.3
Q_B	6	12	23	28	8	24	1.2
$Q5_B$	3	12	32	26	7	21	0.9
$F1_U$	3	9	19	34	8	27	1.2
$F2_B$	3	8	61	12	3	14	0.3
$F3_U$	3	11	27	27	7	25	0.9
$F4_B$	5	14	50	13	3	16	0.5
P_U	5	12	23	35	9	18	1.4
P_B	6	13	33	17	6	25	0.7

^{a}Polarity index P = (carbonyl/carboxyl/amide C + O/N − alkyl C)/(aromatic C + alkyl C).

Fire-induced changes in the organic matter composition at the double-burn pine forest site

The soil from the A horizon of the single-burn site $P2_B$ showed comparable C and N concentrations with the control sample $P1A_U$, but increases in EF of 1.3 (C) and 1.4 (N) were determined for the A horizon of the double-burn site ($P3A_B$) (Table 3). The solid-state ^{13}C NMR spectrum of $P1A_U$ shows the same intensity distribution as the unburnt sample $F1_U$, whereas the spectra of $P2A_B$ and $P3A_B$ confirm the presence of charred residues by the relative increase of intensity in the aromatic C and carboxylic C regions (Figure 2). However, with respect to $P2A_B$, $P3A_B$ shows a smaller amount of aromatic C (Table 6), and concomitantly more O-alkyl C. This demonstrates that, in spite of double burning, which was expected to increase the char content, the input of fresh litter material exceeded that of pyromorphic necromass.

Comparable EF_I of approximately 2 were obtained for aromatic C and carboxylic C in the sample set $P1A_U$–$P2A_B$ and $P1A_U$–$P3A_B$, whereas the EF_I of these C groups was 1 for the set $P2A_B$–$P3A_B$. This confirms that double burning did not enhance the contribution of char (Table 7). Whereas at site $P2A_B$, the input of uncharred necromass could not compensate for O/N-alkyl C and alkyl C losses during combustion in the A horizon ($EF_I < 1$), the conditions at $P3A_B$ allowed litter production that was large enough to recover the O/N-alkyl C and alkyl C concentrations to values found for $P1A_U$ ($EF_I = 1$).

Table 5 Content of various C groups (mg g^{-1} soil) in the unburnt (U) and burnt (B) soils from central Spain (Madrid) and their enrichment factors (EF_I) in the fire-affected soils. D_I gives the difference between the content of the single C-group in the burnt and control sample. B_{char} is the ratio $EF_{I(aromatic\ C)}/EF_{I(alkyl\ C)}$ and is regarded as an index for the degree of charring of C_{add}. The data from the samples from Piedralaves are shown in Table 7

| | Carbonyl 245–185 | Carboxyl/Amide 185–160 | Aromatics 160–110 | O-Alkyl 110–60 | N-Alkyl/Methoxyl 60–45 | Alkyl 45–0 | |
			p.p.m.				B_{char}
Q_U	0.06	0.15	0.23	0.52	0.12	0.42	
Q_B	0.10	0.19	0.36	0.46	0.12	0.38	
D_I	0.04	0.04	0.13	−0.06	0.00	−0.04	
EF_I	1.60	1.24	1.55	0.88	1.01	0.90	1.7
$F1_U$	0.72	1.83	3.92	7.22	1.75	5.82	
$F2_B$	0.25	0.69	5.30	1.00	0.26	1.20	
D_I	−0.47	−1.14	1.38	−6.22	−1.49	−4.62	
EF_I	0.35	0.38	1.35	0.14	0.15	0.21	6.4
$F3_U$	0.16	0.67	1.61	1.62	0.44	1.50	
$F4_B$	0.41	1.11	4.08	1.03	0.28	1.30	
D_I	0.25	0.45	2.47	−0.59	−0.17	−0.20	
EF_I	2.51	1.67	2.54	0.63	0.63	0.86	3.0
P_U	0.08	0.21	0.42	0.62	0.15	0.32	
P_B	0.25	0.50	1.29	0.65	0.23	0.97	
D_I	0.17	0.29	0.87	0.03	0.08	0.66	
EF_I	3.10	2.41	3.08	1.04	1.51	3.08	1.0
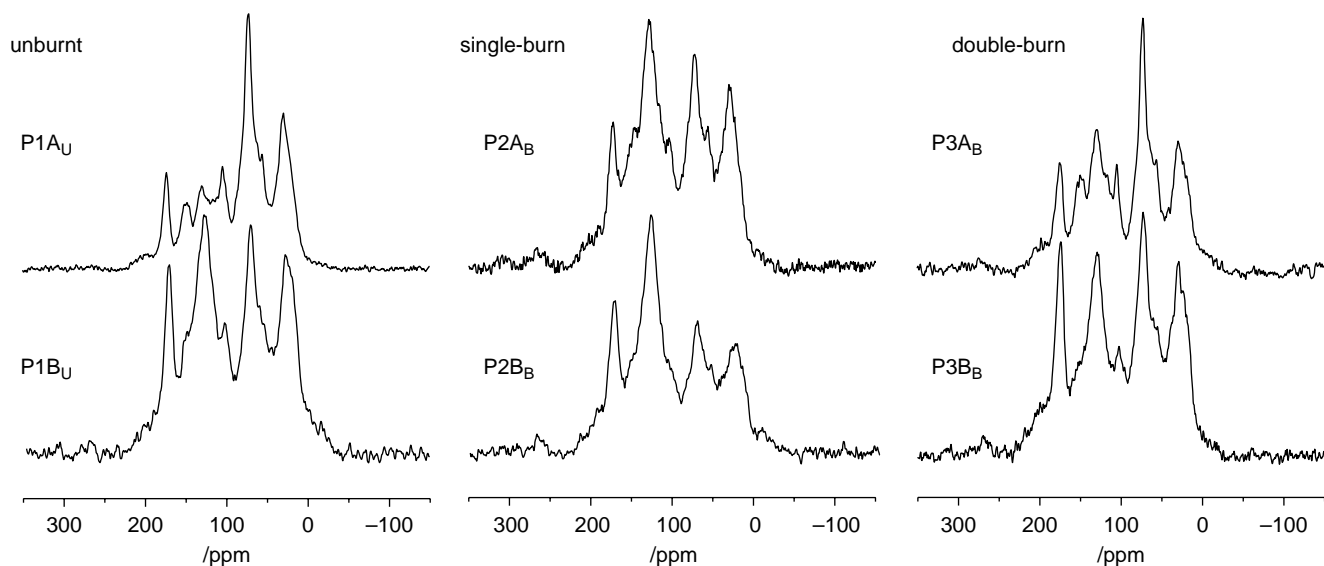
Figure 2 Solid-state ^{13}C NMR spectra of the A and B horizons from an unburnt (P1), single-burn (P2) und a double-burn (3) pine forest site.

For the B horizons, the single burning resulted in the enhancement of the organic C and N concentrations ($EF_C = 1.6$, $EF_N = 1.2$) in P2B$_B$ relative to the control site (P1B$_U$) (Table 3). Possibly, this was caused by an increased contribution of decaying roots in the soil after combustion of the above-ground vegetation. However, compared with the ^{13}C NMR spectrum of P1B$_U$, a relative increase in aromatic C is unveiled, which indicates that fresh plant remains were not the sole source of C_{add} (Figure 2, Table 5).

Calculation of EF_I for the different chemical-shift regions confirms an enrichment of O/N-alkyl C and alkyl C (EF_I: 1.2–1.4) in the B horizon (Table 7), which could support the idea of the leaching of soluble carbohydrate or proteinaceous fractions from decaying litter or root exudates. On the other hand, the aromatic and carboxylic-C contents showed greater increases ($EF_I = 2$), which may be explained by input of oxidized structures leached from charred residues that had accumulated in the topsoil.

In spite of the double burning, the contribution of aromatic C to the total organic C in soil P3B$_B$ is considerably smaller (28%) than the value (39%) determined for soil P2B$_B$ (Table

6). Relative to P1B$_U$, the $EF_I = 1.9$ of aromatic C for P3B$_B$ is comparable with that of the sample set P1B$_U$–P2B$_B$ ($EF_I = 2$). This discloses that, as in the topsoil, double burning did not increase the char content in the subsoil compared with single burning (Table 7). However, P3B$_B$ contains twice the amount of O/N-alkyl and alkyl C identified for the single-burn site.

Discussion

Alteration pattern of SOM as induced by vegetation fires

One goal of the present study was to extract a common pattern of the impact of vegetation fires on the quality and quantity of SOM in post-fire soils. However, with respect to organic matter accumulation, no consistent behaviour could be found at first sight. For instance, when comparing the pine stands F1$_U$–F2$_B$ the intense fire led to a decrease, and at the sites P$_U$–P$_B$, F3$_U$–F4$_B$ and P1$_U$–2$_B$–3$_B$ resulted in an increase of the C and N contents. The C and N concentrations in the top 10 cm of the site under oak (Q$_U$–Q$_B$) showed only minor alterations. On the other hand, a common pattern for all

Table 6 Intensity distribution (%) in the solid-state ^{13}C NMR spectra of the sample set P1-P3 from Piedralaves

	Carbonyl 245–185	Carboxyl/Amide 185–160	Aromatics 160–110	O-Alkyl 110–60	N-Alkyl/Methoxyl 60–45	Alkyl 45–0	
			p.p.m.				P[a]
P1A$_U$	2.2	8.1	21.3	36.9	8.4	23.0	1.3
P1B$_U$	3.4	11.5	32.9	24.8	6.6	20.9	0.9
P2A$_B$	3.5	10.8	35.1	25.8	6.8	17.9	0.9
P2B$_B$	4.7	13.7	39.4	21.0	5.5	15.8	0.8
P3A$_B$	3.9	10.1	30.6	29.8	7.0	18.6	1.0
P3B$_B$	6.0	13.6	27.9	26.2	6.7	19.7	1.1

[a]Polarity index P = (carbonyl/carboxyl/amide C + O/N – alkyl C)/(aromatic C + alkyl C)

Table 7 Content of various C groups (mg g^{-1} soil) in the unburnt (U) and burnt (B) soils from Piedralaves, central Spain (Madrid) and their enrichment factors (EF$_I$) in the burnt soils. D$_I$ gives the difference between the content of the single C-group in the burnt and control sample. B_{char} is the ratio EF$_{I(aromatic\ C)}$/EF$_{I(alkyl\ C)}$ and is regarded as an index for the degree of charring of C_{add}

| | Carbonyl 245–185 | Carboxyl/Amide 185–160 | Aromatics 160–110 | O-Alkyl 110–60 | N-Alkyl/Methoxyl 60–45 | Alkyl 45–0 | |
			p.p.m.				B_{char}
P1A$_U$	0.14	0.53	1.39	2.40	0.55	1.50	
P2A$_B$	0.23	0.71	2.32	1.71	0.45	1.18	
D$_I$	0.1	0.2	0.9	−0.7	−0.1	−0.3	
EF$_I$	1.6	1.4	1.7	0.7	0.8	0.8	2.1
P1A$_U$	0.14	0.53	1.39	2.40	0.55	1.50	
P3A$_B$	0.32	0.83	2.51	2.44	0.58	1.52	
D$_I$	0.2	0.3	1.1	0.0	0.0	0.0	
EF$_I$	2.2	1.6	1.8	1.0	1.0	1.0	1.8
P2A$_B$	0.23	0.71	2.32	1.71	0.45	1.18	
P3A$_B$	0.32	0.83	2.51	2.44	0.58	1.52	
D$_I$	0.1	0.1	0.2	0.7	0.1	0.3	
EF$_I$	1.4	1.2	1.1	1.4	1.3	1.3	0.8
P1B$_U$	0.05	0.17	0.49	0.37	0.10	0.31	
P2B$_B$	0.11	0.32	0.91	0.48	0.13	0.36	
D$_I$	0.1	0.1	0.4	0.1	0.0	0.0	
EF$_I$	2.1	1.8	1.8	1.3	1.3	1.2	1.5
P1B$_U$	0.05	0.17	0.49	0.37	0.10	0.31	
P3B$_B$	0.19	0.43	0.89	0.84	0.21	0.63	
D$_I$	0.1	0.3	0.4	0.5	0.1	0.3	
EF$_I$	3.8	2.5	1.8	2.3	2.2	2.0	0.9
P2B$_B$	0.11	0.32	0.91	0.48	0.13	0.36	
P3B$_B$	0.19	0.43	0.89	0.84	0.21	0.63	
D$_I$	0.1	0.1	0.0	0.3	0.1	0.3	
EF$_I$	1.8	1.4	1.0	1.7	1.7	1.7	0.6

single-burn samples was still recognizable. It includes a relative but also an absolute increase of aromatic-C structures in the fire-affected soils with respect to the corresponding control sites (Table 5). This is connected to a decrease in the polarity of the samples as indicated by the polarity index P (Tables 4 and 6) that could explain in part the remarkable water repellency observed in post-fire soils. We can use the extent of the enrichment of aromatic structures as an indicator of char accumulation. The large EF$_I$ = 3.1 for aromatic C identifies site P$_B$ as that with the largest char production relative to the pre-fire C_{org} content, although the burnt soil had experienced only a medium-intensity fire. A more complete volatilization during intense fires may be a reason for the smaller EF$_I$ values of the aromatic structures at F2$_B$ and F4$_B$. The greater combustibility of relatively recent litter compared with more humified material was previously observed for grass material with respect to peat (Almendros et al., 1990, 2003; Knicker et al., 1996) and may also explain the differences observed between the sites F2$_B$ and F4$_B$.

Further, increased heat treatment results in a continuing loss of O-alkyl and alkyl C with a concomitant enrichment of aromatic C. The rate at which this process occurs, however, depends on the stability of the burnt litter or SOM (Almendros et al., 1990; Knicker et al., 1996). Therefore, the aromatic C/alkyl C

ratio could be an index to describe the degree of charring of vegetation residues and SOM. For our samples, B_{char} was calculated for C_{add} from the ratio EF$_{I(aromatic\ C)}$/EF$_{I(alkyl\ C)}$ to determine the degree of charring of the organic C introduced to the soil during and after the fire. The ratios range from 1 for the samples P$_U$–P$_B$ to 2 and 3 for P1A$_U$–P2A$_B$ and F3$_U$–F4$_B$, respectively, and to 6.5 for F1$_U$–F2$_B$. The observed trend is in accordance with the increasing fire intensity and fuel combustibility reported for the various sites. Thus, this ratio may indeed represent a reasonable index for elucidating the degree of charring of the necromass produced and accumulated during and after a vegetation fire.

Impact of recovery time after a fire on SOM composition

None of the topsoils showed an EF$_I$ > 1 for the O-alkyl C content after a single burn. Therefore, we can assume minor or no net input of fresh or only slightly charred necromass within 1 to 2 years after the fire. Greater inputs of root residues remaining after burning of the above-ground vegetation can also be excluded as a source of additional SOM input, at least for our single-burn sites. This finding is in contrast to previous results obtained after comparing the SOM of a fire-affected

and unaffected soil in southern Spain, sampled 5 years after a fire (Knicker et al., 2005a). Here, a considerable part of C_{add} was attributable to fire-unaffected organic sources. Because that fire was also classified as intense and left only a few tree stems after its passage, the observed differences between the present and recent studies are not sufficiently explained by variation in the charring intensity. This is supported by the fact that, in spite of only a medium-intensity fire, the C_{add} of P_U showed negligible O-alkyl C contributions.

However, the time factor has also to be considered. It seems that at the sites in central Spain, 1–2 years of recovery was too short for sufficient production of biomass and litter to develop a substantial amount of new and uncharred SOM. At the stand in southern Spain, on the other hand, the longer recovery time of 5 years may well be enough to restore soil resilience, thus allowing the recovery of the original properties. A new vegetation cover of shrubs and herbs was built up, which resulted in biomass and litter production that was large enough to explain the doubling of the C-concentration in the fire-affected topsoil. Also, decreased microbial activity may have contributed to the accumulation of organic material in the soil.

Carboxyl content

With the exception of the burnt soil at $F2_B$, the C_{add} of the remaining burnt soils contains a large proportion of carboxyl C. It seems that oxidation of char started very shortly after the fire event. Irrespective of whether this oxidation was induced by microbial activity or caused by abiotic reactions, the resulting chemical alterations are likely to increase char availability for microbial attack and thus decrease its refractory nature. The suspicion that black carbon exhibits less recalcitrance than commonly assumed has already been published (Bird et al., 1999). Previous studies demonstrated CO_2 production during microbial degradation of char (Hamer et al., 2004). Addition of glucose resulted in a priming effect and increased mineralization. On the other hand, the formation of polar, carboxyl-C structures could also have increased the stability of charred residues by enhancing adsorption to the mineral phase in particular to metal oxides (Lehmann et al., 2005). However, concomitantly, greater carboxylation of charred residues can increase the water solubility of the originally apolar remains. Continuous leaching of DOM into deeper horizons may thus be responsible for an ongoing decrease of pyrogenic SOM in the topsoil. Such a scenario could also explain the relatively large aromatic-C proportion of the SOM in the single-burn B horizon of site $P2_B$ and the observation that in spite of great fire activity in ancient times, only weak indications for greater char accumulation could be found in many topsoils.

Double burning

In comparison with the single-burn site $P2_B$, our analysis revealed no additional input of charred material into the

SOM from the A and B horizons of $P3_B$, although the two fires were severe enough to completely destroy the vegetation. On the other hand, the great intensity of the fire may be the variable responsible for this unexpected finding. The first fire destroyed the ground vegetation together with the litter layer and killed most of the trees. Charred necromass was seen to have accumulated. A possible scenario may have been that the new vegetation cover of shrubs and herbs together with the decaying char remains represented an improved fuel that suffered complete combustion without leaving considerable amounts of black carbon. After the second fire, vegetation consisting mainly of Pteridium aquilinum developed. A former study showed reduced biological activity at the double-burn site with respect to $P1_U$ and $P2_B$ (Velasco et al., 1986). According to this study, the humus form evolved from moder at sites $P1_U$ and $P2_B$ to mor at site $P3_B$, which indicates that reduced microbial activity may be responsible for a slowdown of the degradation of newly produced litter. The distribution of the different C groups, with the large proportion of O-alkyl C (50%) calculated for C_{add} for $P2A_B$–$P3A_B$, supports the idea that this material was mainly responsible for the increase of SOM in the A horizon after the second fire (Figure 3).

Such partly degraded material fosters considerable amounts of dissolved organic matter, which may have leached after autumn, winter and spring rainfalls. Dissolved organic matter may have accumulated in the deeper horizons, resulting in a small increase in the organic C from 23 mg g^{-1} soil at site $P2_B$ to 32 mg g^{-1} at site $P3_B$. Accordingly, calculation of the C distribution in C_{add} shows large contributions of O-alkyl C
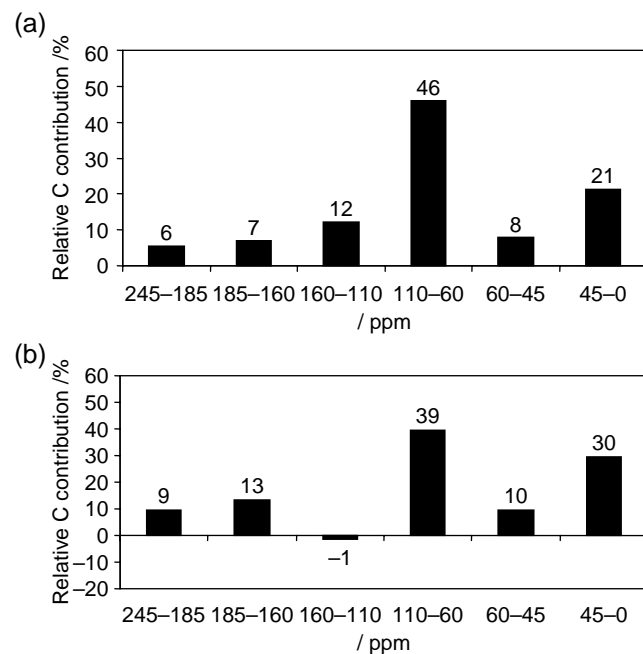
Figure 3 Relative C distribution in C_{add} accumulated in the double-burn soil P3 relative to the single-burn soil P2 calculated for (a) the A horizon and (b) the B horizon.

and alkyl C. Alternatively, the observed organic matter composition of C_{add} may have been caused by root exudates and root residues of decaying fire-affected vegetation.

Conclusions

Solid-state CPMAS ^{13}C NMR spectroscopic comparison of soils from Mediterranean pine and oak forests affected or not by forest fires showed great diversity in the fire-induced transformation patterns of SOM. However, calculation of the enrichment factors of total organic carbon and of the individual C groups together with the charring index B_{char} allowed us to extract a relationship between organic matter transformation and the intensity and type of fire. Increasing fire intensity was accompanied by a decrease of soil organic matter accumulation and the percentage of charred residues produced relative to the C_{org} of the control soil. This is in accordance with a greater C loss due to more efficient combustion. The respective pyrogenic remains, however, showed greater aromaticity with greater fire intensity. Although indications were found that, irrespective of the fire type, oxidation of char occurred very early during the post-fire period, the difference in aromaticity is expected to affect recalcitrance and degradability of the charred residues. Consequently, after incorporation into the soil, the long-term impact of the pyrogenic necromass on the chemical composition and stability of SOM is also expected to vary with respect to type and intensity of the forest fire. Because char in soil is commonly considered as an efficient C-sink, potential variation in its recalcitrance may be an important consideration if the role of black carbon in C-sequestration in soils is to be elucidated.

Acknowledgements

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