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Post-fire recovery of soil organic matter in a Cambisol from typical Mediterranean forest in Southwestern Spain

Marco A. Jiménez-González^a, José María De la Rosa^{b,*}, Nicasio T. Jiménez-Morillo^b, Gonzalo Almendros^a, José Antonio González-Pérez^b, Heike Knicker^b

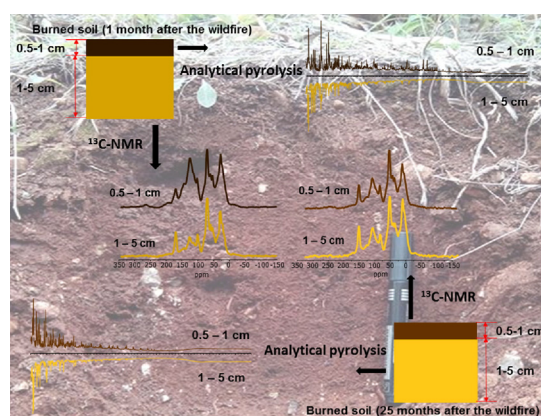
^a Museo Nacional de Ciencias Naturales (MNCN-CSIC), Serrano 115-B, Madrid, Spain

^b Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Av. Reina Mercedes 10, Seville 41012, Spain

HIGHLIGHTS

- Soil organic matter (SOM) as marker of post fire recovery.
- Analytical pyrolysis shows SOM alterations at a molecular level.
- Alteration of SOM quality is due to climate and post fire management activities.
- Major changes exerted by fire on SOM are diluted 2 years later.

GRAPHICAL ABSTRACT



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ABSTRACT

Wildfire is a recurrent phenomenon in Mediterranean ecosystems and contributes to soil degradation and desertification, which are partially caused by alterations to soil organic matter (SOM). The SOM composition from a Cambisol under a Mediterranean forest affected by a wildfire is studied in detail in order to assess soil health status and better understand of soil recovery after the fire event. The soil was sampled one month and twenty-five months after the wildfire. A nearby unburnt site was taken as control soil. Soil rehabilitation actions involving heavy machinery to remove burnt vegetation were conducted sixteen months after the wildfire. Immediately after fire the SOM increased in topsoil due to inputs from charred vegetation, whereas a decrease was observed in the underlying soil layer. Twenty-five months after fire soil-pH increased in fire-affected topsoil due to the presence of ashes, a decrease in SOM content was recorded for the burnt topsoil and similar trend was observed for the water holding capacity. The pyro-chromatograms of burned soils revealed the formation of additional aromatic compounds. The thermal cracking of long-chain *n*-alkanes was also detected. Solid-state ¹³C NMR spectroscopy supported the increase of aromatic compounds in the fire-affected topsoil due to the accumulation of charcoal, whereas the deeper soil sections were not affected by the fire. Two years later, soil parameters for the unburnt and burnt sites showed comparable values. The reduction of the relative intensity in the aromatic C

* Corresponding author.

E-mail address: jmrosa@imase.csic.es (J.M. De la Rosa).

region of the NMR spectra indicated a decrease in the charcoal content of the topsoil. Due to the negligible slope in the sampling site, the loss of charcoal was explained by the post-fire restoration activity, degradation, leaching of pyrogenic SOM into deeper soil horizons or wind erosion. Our results support that in the Mediterranean region, fire-induced alteration of the SOM is not lasting in the long-term.

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1. Introduction

Wildfires cause significant changes in soil physical, chemical and biological properties (González-Pérez et al., 2004; Certini, 2005). Changes in some soil properties such as aggregate stability, cation exchange capacity (Almendros et al., 1984; Badía-Villas et al., 2014), or water repellence (Arcenegui et al., 2007; Jordán et al., 2014), in the soil organic matter (SOM) content are well documented (Certini et al., 2011; Badía-Villas et al., 2014), although the fire-induced alterations of SOM quality and quantity may not last on a long-term scale. Since fire removes the vegetation cover, the risk of soil degradation through soil erosion, leaching of nutrients and SOM loss due to the lack of new litter input increases (De la Rosa et al., 2012; Faria et al., 2015). Desertification risks are of particular importance in Mediterranean ecosystems (Shakesby, 2011) where forest fires are frequent (Rasilla et al., 2010). The periodicity of wildfires has increased dramatically from the 1960s, and consequently the design and application of proper restoration strategies are key issues. Nevertheless, in many occasions the restoration strategies are not the most appropriate for semiarid Mediterranean ecosystems, and lead to irreversible loss of SOM, further degradation and soil losses by erosion.

The SOM is of paramount importance for soil restoration. Several studies have focused on the quantitative analysis of SOM in fire-affected soils, but few works study the SOM quality (Certini et al., 2011; De la Rosa et al., 2012; González-Pérez et al., 2008). After a fire, the amount of SOM may vary largely depending on several factors like the fire intensity and propagation patterns, the combustibility of the vegetation and the accessibility and size of fuel loads (Almendros and González-Vila, 2012). Intense wildfires can destroy most of the SOM whereas it is frequently observed that medium-intensity fires cause an increase of SOM because of inputs of partially burnt plant materials or leaves falling from the post-fire stressed vegetation (Knicker et al., 2006). This fact is important to forecast the erosion risk after a forest fire. In addition to the effect of fire in the total amount of SOM, the fire also produces important changes in SOM quality, exerting alterations in its chemical composition (González-Pérez et al., 2004). The study of fire-mediated SOM alteration and its evolution could provide valuable markers for monitoring the recovery of soils after wildfire, being also informative for decision making and planning environmental restoration actions (González-Pérez et al., 2008).

Analytical pyrolysis (Py-GC/MS) has been successfully used to describe quantitative changes exerted by fire on SOM molecular composition (De la Rosa et al., 2012). The technique is useful to identify molecular source indicators informing on the origin and transformation of most natural macromolecular substances in SOM. In particular the study of alkyl compounds in SOM (including *n*-alkanes, *n*-alkenes or *n*-fatty acids) have been used to detect alterations produced to SOM through heating (Faria et al., 2015; González-Pérez et al., 2008; Wiesenberg et al., 2009).

Solid-state nuclear magnetic resonance spectrometry (CPMAS ¹³C NMR) is a non-degradative technique which provides valuable quantitative information of the bulk chemical composition of SOM (Wilson et al., 1984). In general, it is considered a powerful technique to assess SOM quality (Preston, 1996) and has also been used to characterize changes in SOM after a fire (Forte et al., 2006; Knicker, 2007).

The objective of the present study was to monitor the effect of a forest fire in general and specific SOM features in a Cambisol from Southwestern Spain, to evaluate post-fire recovery and elucidate how forest rehabilitation management strategies after the fire event affected the

recovery of the soil. In order to achieve that goal a combination of complementary analytical techniques i.e. elemental analysis (EA), solid-state NMR spectroscopy (CPMAS ¹³C NMR) and analytical pyrolysis (Py-GC/MS), has been employed.

2. Material and methods

2.1. Study area and sampling

The study site is located in the “Sierra de San Pablo” close to Montellano municipality in Seville, SW Spain (37° 0.0490' N; 5° 32.8628' W; 510 m a.s.l; slope < 10°) under a typical Mediterranean dry climate, characterized by very dry and hot summers followed by episodes of heavy rain in autumn and winter. In these two years, the average rainfall in the area was 610 mm year⁻¹, reaching temperatures over 40 °C in summer. On 12th August 2012, a wildfire with medium intensity affected an area of ca. 90 ha of this site (Fig. 1). Before the fire, the vegetation was dominated by pine (*Pinus pinaster* and *Pinus halepensis*) and eucalyptus (*Eucalyptus globulus*). As part of the post-fire rehabilitation program, sixteen months after the fire, branches, stems, bushes, trunks of dead trees were removed using heavy machinery. At month 25, the vegetation of the burnt area was composed of just forest understory, which consisted of herbaceous and Mediterranean bush groundcover (mainly *Cistus* sp. and *Halimium* sp., followed by *Rosmarinus officinalis* and *Silybum marianum*) and some small *Pinus halepensis* and *Eucalyptus globulus*. Those species were also present in the unburnt area.

One month after the fire, soil samples from the Calcaric Cambisol (WRB, 2015) were collected from the burnt site (B) and from an unburnt (UB) location with the same physiographic conditions and located nearby, just outside the fire-affected perimeter. The sampling was repeated twenty-five months after the wildfire. In both cases composite samples were prepared from soil material collected in five randomly chosen sections in an area of approximately 100 m². The samples were collected at 0–1 cm, 1–5 cm, 5–10 cm and 10–15 cm soil depths. During the first sampling, and in order to analyse separately the litter layer present, the uppermost soil section (0–1 cm) was divided into two layers; 0–0.5 mm, with macroscopic fragments of leaves and 0.5–1 cm, with incipient macro aggregates. Moreover, samples of charcoal were collected by hand-picking from the surface of the B site. In the laboratory the composite soil samples were oven-dried (40 °C, 48 h) and homogenized by sieving (<2 mm).

2.2. Physical and chemical properties of soil

Soil pH and electrical conductivity was measured in water with a Crison pH-meter BASIC 20 in a soil-water slurry (1:2.5). Water holding capacity (WHC) was determined according to the method described in Guitián and Carballas (1976). Elemental (EA) analysis was carried out by dry combustion in a flash 2000 HT (C, H, S) elemental micro-analyser (Thermo Scientific, Bremen, Germany) at a combustion temperature of 1020 °C. Total nitrogen (N) and carbon (TC) were measured in triplicated and total organic carbon (TOC) was determined after the removal of carbonates by treating the soils samples with 1 M HCl.

2.3. Analytical pyrolysis (Py-GC/MS)

Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) was carried out with a double shot pyrolyser PY2020iD (Frontier Lab Ltd.,



Fig. 1. View of the burned area in Montellano (Seville, SW Spain). (B) Location of the burnt (B) and unburnt sites (UB). Image from Google Earth.

Fukushima, Japan) coupled to a GC/MS system Agilent 6890 using a phenylmethylsiloxane column (Agilent HP-5MS 5%). Pyrolysis was conducted at 600 °C for 1 min. The carrier gas was helium at a flow rate of 1 mL · min⁻¹. The GC oven temperature was held at 50 °C for 1 min, then increased to 100 °C at 30 °C min⁻¹, from 100 °C to 300 °C at 10 °C min⁻¹, and isothermal at 300 °C for 10 min. The detector consisted of an Agilent 5973 mass selective detector, and mass spectra were acquired with a 70 eV ionizing energy. To identify each compound, the results were compared with published and stored (NIST and Wiley libraries).

2.4. Solid state ¹³C nuclear magnetic resonance spectroscopy (CPMAS ¹³C NMR)

The solid-state ¹³C NMR spectra were obtained in a Bruker Avance III HD 400 MHz instrument operating at a frequency of 100.64 MHz and using ZrO₂ rotors of 4 mm OD with Kel-F caps. The cross polarization (CP) technique was used during magic-angle spinning (MAS) of the rotor at 14 kHz. A ramped 1H-pulse was applied during the 1 ms contact time to circumvent Hartmann-Hahn mismatches. Employing a pulse delay of 300 ms, between 10,000 and 40,000 scans were accumulated. A line broadening between 75 and 100 Hz was used. The ¹³C chemical shifts were calibrated relative to tetramethylsilane (0 ppm) with glycine (COOH at 176.08 ppm). The spectra were quantified by subdividing them into the following chemical shift regions as described in Knicker (2011): alkyl C (0–45 ppm); N-alkyl/methoxyl C (45–60 ppm); O-alkyl C (60–110 ppm); aromatic C (110–160 ppm); carbonyl/amide C (160–245 ppm). The ¹³C intensity distribution was determined by integrating signal intensity over the above-mentioned chemical shift regions using the MestreNova 10 software. In order to remove the paramagnetic minerals that may interfere with the NMR signals and to concentrate the SOM, prior NMR analysis the samples were demineralized with 10% (v/v) hydrofluoric acid (HF) (Gonçalves et al., 2003; Knicker, 2011).

3. Results and discussion

3.1. Soil physical, chemical properties and elemental (C, N) composition

One month after the fire a pH increase was observed in the topsoil (0.5–1 cm) samples of burnt (B) site as compared with the UB samples

(7.2 and 6.6 respectively; Table 1), this is attributed to a liming effect caused by the release of bases from the ashes. No remarkable changes were observed at deeper sections. Twenty five months after the wildfire, similar pH values were recorded at both sites (B and UB) probably due to post-fire leaching processes of exchangeable bases. The EC values in the top sections of B soil decreased in comparison with the UB (218 vs. 388 μS · cm⁻¹), as could correspond to fly ash exportation of soluble ions in dust particles. As in the case of pH, the EC of B and UB samples taken 25 months after the wildfire showed similar values. Nevertheless, EC values of soils sampled 25 months after the fire were lower than initially.

After 1 month from the fire there was an increase in WHC in the B topsoil and a decrease in the underlying layer (1–5 cm depth). The WHC decreased sharply in samples collected 24 months later, both in B and UB sites, paralleling the decrease in SOM. This could be due to a loss of humus and litter layer due to the severe dry summer of 2014 and the partial removal of the A-horizon during the post fire rehabilitation activities in site B. Both factors may have contributed to the loss of SOM in the topsoil. The values of total C (%) and TOC (%) shows similar variations (Table 1). After the fire, the TOC of the topsoil (0.5–1 cm) of B sample increased (44%) compared with UB sample (25%) due to the probable input of partially burned biomass from the fire-stressed vegetation. The TOC content decreased in the depth 1–5 cm of burnt soil and no significant differences were found in deeper soil sections. The combustion of SOM during the fire could be in part responsible for the decreased OC content observed at depth 1–5 cm. These results are in agreement with those previously reported from fire-affected Mediterranean soils (Almendros et al., 1988; De la Rosa et al., 2008). Two years after the first sampling the TOC content decreased in the topmost soil layer in B and UB soils. Nevertheless the values were similar in both soils (Table 1).

This result points to the occurrence of enhanced erosive processes or accelerated degradation of SOM, or in combination with a reduction in the inputs from the standing vegetation (Santín et al., 2008). The increase in the C content observed in deep layers in the UB and B soils could be explained by vertical transport of finely divided charred SOM from the topsoil. The N content increased slightly in the topsoil of B site taken one month after the fire. Two years later, the soil affected by the fire and the unburnt area had same N contents. Furthermore, in two years the N content decreased in the topsoil of B site and increased in the underlying layers. These changes in N concentration are closely

Table 1
Values of pH in H₂O; electrical conductivity (EC), water holding capacity (WHC), elemental composition (Total Carbon, total Nitrogen and total organic Carbon) of the burnt and unburnt soil 1 month and 25 months after fire.

Sample			Physical & chemical properties			Elemental composition			
			pH	EC ($\mu\text{S cm}^{-1}$)	WHC (%)	TC %	TN %	TOC %	TOC/TN
1 month after fire	Unburnt	Litter				47.3 \pm 0.6	1.1 \pm 0.1	47.3	42.7
		0.5–1 cm	6.6	388 \pm 94	225 \pm 7	25.0 \pm 0.6	1.4 \pm 0.2	23.4	17.2
		1–5 cm	7.4	161 \pm 24	93 \pm 5	9.7 \pm 0.2	0.8 \pm 0.1	8.6	10.5
		5–10 cm	7.5	127 \pm 1	73 \pm 4	5.1 \pm 0.1	0.6 \pm 0.1	4.9	9.2
		10–15 cm	7.7	68 \pm 7	74 \pm 3	4.7 \pm 0.3	0.6 \pm 0.1	4.5	7.5
	Burnt	Litter				51.0 \pm 0.1	1.1 \pm 0.1	51.0	44.8
		0.5–1 cm	7.2	218 \pm 6	392 \pm 8	44.0 \pm 0.4	2.0 \pm 0.2	40.2	20.1
		1–5 cm	7.1	156 \pm 4	68 \pm 3	6.4 \pm 0.2	0.7 \pm 0.1	5.3	8.1
		5–10 cm	7.4	126 \pm 15	72 \pm 4	5.6 \pm 0.4	0.6 \pm 0.1	5.0	8.3
		10–15 cm	7.7	95 \pm 6	65 \pm 3	5.2 \pm 0.1	0.6 \pm 0.1	4.8	8.0
25 months after fire	Unburnt	0–1 cm	7.6	192 \pm 37	78 \pm 5	12.0 \pm 0.2	1.3 \pm 0.1	10.1	7.8
		1–5 cm	7.7	133 \pm 3	61 \pm 3	8.8 \pm 0.4	1.1 \pm 0.1	6.6	5.9
		5–10 cm	7.8	134 \pm 0	60 \pm 3	8.9 \pm 0.1	1.1 \pm 0.1	6.4	5.9
		10–15 cm	7.7	103 \pm 7	61 \pm 4	8.4 \pm 0.1	1.1 \pm 0.1	6.9	6.1
		Ch	7.8	341 \pm 1	104 \pm 5	23.8 \pm 0.1	1.7 \pm 0.1	21.1	12.6
	Burnt	0–1 cm	7.6	202 \pm 14	69 \pm 3	12.0 \pm 1.9	1.3 \pm 0.1	9.0	7.1
		1–5 cm	7.5	132 \pm 11	62 \pm 3	7.7 \pm 0.2	1.1 \pm 0.1	6.6	6.2
		5–10 cm	7.5	135 \pm 0	64 \pm 4	7.8 \pm 0.1	1.1 \pm 0.1	6.8	6.3
		10–15 cm	7.5	84 \pm 3	69 \pm 4	7.1 \pm 0.3	1.0 \pm 0.1	6.2	6.1
		Ch	7.8	341 \pm 1	104 \pm 5	23.8 \pm 0.1	1.7 \pm 0.1	21.1	12.6

Ch: charcoal; standard deviation (S.D) of pH analysis was <0.05; (n = 3).

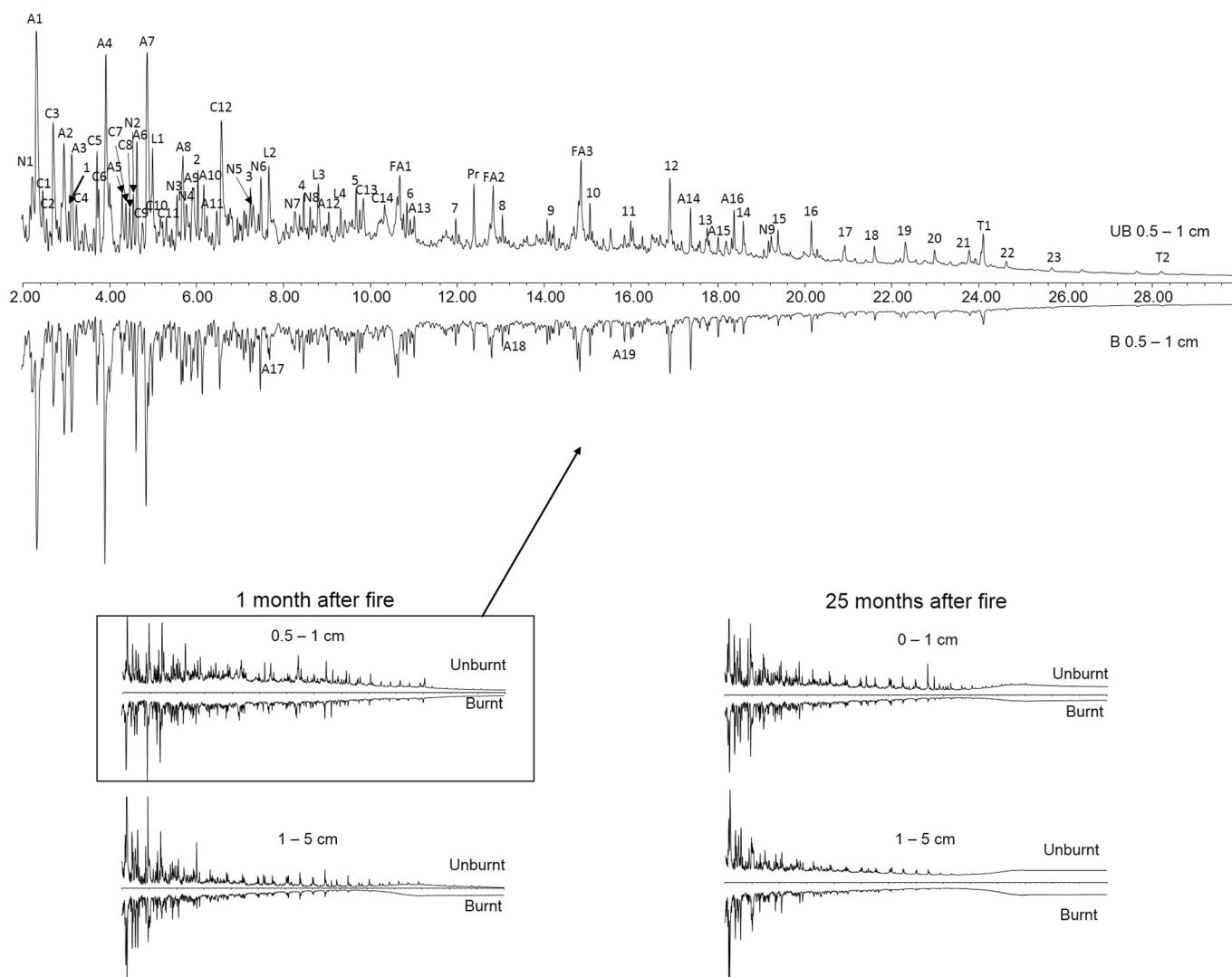


Fig. 2. Pyro-chromatograms of the samples taken 1 month after the fire at 0.5–1 and 1–5 cm depths and of the samples taken 25 months after the fire at depths 0–1 and 1–5 cm for the burnt (B) and unburnt (UB) sites.

associated with the observed SOM variations. After the fire, the re-establishment of the plant-soil trophic system promoted the increase of N. Two years later these N is transported to deeper layers and the N content increased with depth. The ratio TOC/N did not show noticeable changes between both soils after the fire. The TOC/N ratios of recently burned soils are usually lower than those of the original soils (Almendros et al., 1984; González-Pérez et al., 2008). At our site, this effect can be seen in samples taken one month after the fire for depths 1–5 cm and 5–10 cm. Two years later, the ratios TOC/N were similar in B and UB and lower in comparison with the samples taken 1 month after the fire. Different authors reported similar trends for burnt soils under pine forest (De la Rosa et al., 2008; Francioso et al., 2011; Mastrolonardo et al., 2015), which was related with the specific preservation of *N*-aromatic structures (called *black nitrogen*) produced by thermal alteration of SOM during the fire (De la Rosa et al., 2008).

3.2. Analytical pyrolysis (Py-GC/MS)

Fig. 2 depicts the chromatograms of compounds released by direct pyrolysis from the UB and B soils. The major compounds identified are listed in Table 2. In general, the compounds present in both soils were similar. However, a higher abundance of aromatic compounds (mainly polycyclic aromatic compounds-PAHs) was identified in the B samples.

Specifically, these consisted of naphthalene, 2-methyl (A17), anthracene (A18) and phenanthrene, 1,7-dimethyl- (A18). Fig. 3 shows the relative abundances of the different component classes, which was calculated by adding the peak area of the compounds forming each series. The relative amounts of carbohydrate and lignin-derived compounds decreased in the B soil in comparison with UB. In contrast, the relative amounts of nitrogen-containing and aromatic compounds increased. These differences are evident at the topsoil (depths 0.5–1 cm and 1–5 cm) and are still present 25 months after the fire. The increase in the relative abundance of aromatic compounds after the fire is mainly due to cyclization reactions during the combustion of the SOM and the incorporation of charred SOM (González-Pérez et al., 2008). Carbohydrates are thermo-labile compounds, thus its depletion in B sites was expected. The relative abundance of lignin-derived compounds and fatty acids in the topsoil of UB site decreased substantially two years later. This result, combined with the changes observed in the elemental composition (TOC and TN), points to decreased inputs of biomass. Aromatic compounds including polycyclic aromatic hydrocarbons (PAHs) increased their relative abundance in B samples as regards UB site. Furthermore, several PAHs occurred exclusively in the chromatogram of B samples. The accumulation of PAHs is frequently observed in burnt SOM, as correspond to its origin as pyrogenic compounds from condensation/aromatization reactions (De la Rosa et al., 2008).

Table 2

Peak identification of pyrolysis gas chromatography–mass spectrometry by component classes.

Alkanes and alkenes	Peak label	Fatty acids compound	Peak label
Nonane/ene pair	1	Dodecanoic acid	FA1
Dodecane/ene pair	2	Tetradecanoic acid	FA2
Tridecane/ene pair	3	Hexadecanoic acid	FA3
Tetradecane/ene pair	4	Lignin derived structures	
Pentadecane/ene pair	5	Phenol, 2-methoxy-	L1
Hexadecane/ene pair	6	2-Methoxy-4-vinylphenol	L2
Heptadecane/ene pair	7	Vanillin	L3
Pristane	Pr	Phenol, 2-methoxy-4-(1-propenyl)-	L4
Octadecane/ene pair	8	Nitrogen compounds	
Nonadecane/ene pair	9	Pyridine	N1
Eicosane/ene pair	10	Indene	N2
Heneicosane/ene pair	11	Benzyl nitrile	N3
Docosane/ene pair	12	2-Methylindene	N4
Tricosane/ene pair	13	1H-Inden-1-one, 2,3-dihydro-	N5
Tetracosane/ene pair	14	Indole	N6
Pentacosane/ene pair	15	1H-Indeno	N7
Hexacosane/ene pair	16	1H-Indole, 7-methyl	N8
Heptacosane/ene pair	17	3,4-Dihydro-3-methyl-1-phenylquinolin-2(1H)-one	N9
Octacosane/ene pair	18	Polysaccharides (carbohydrates)	
Nonacosane/ene pair	19	Cyclopentanone 2-(1-methylpropyl)	C1
Triacontane/ene pair	20	Furfural	C2
Henetriacontane/ene pair	21	Furan, 2,5-dimethyl	C3
Dotriacontane/ene pair	22	2-Cyclopenten-1-one, 2-methyl	C4
Tritriacontane/ene pair	23	Methyl furfural	C5
Aromatic compounds (including PAHs)		2-Cyclopenten-1-one, 3-methyl	C6
Toluene	A1	2-Cyclopenten-1-one,2-hydroxy-3-methyl-	C7
Xyleno	A2	2-Cyclopenten-1-one,2,3-dimethyl-	C8
Styrene	A3	Acetophenone	C9
Phenol	A4	Benzofuran, 2-methyl-	C10
Benzene, 1,2,4-trimethyl	A5	Maltol	C11
Phenol, 2-methyl-	A6	Benzofuran 2,3-dihydro-	C12
Phenol, 4-methyl-	A7	Ethanone, 1-(3-hydroxy-4-methoxyphenyl)-	C13
Phenol, 2,4-dimethyl-	A8	d-Allose	C14
Phenol, 3-ethyl-	A9	Others structures (steroids)	
Naphthalene	A10	Stigmastan-3,5-diene	T1
Phenol, 3,4-dimethyl-	A11	Stigmast-4-en-3-one	T2
Naphthalene, 2,6-dimethyl-	A12		
Naphthalene,1,4,5-trimethyl-	A13		
Phenanthrene, 1-methyl-7-(1-methylethyl)-	A14		
1-Methyl-4- <i>p</i> -tolyl-naphthalene	A15		
1-Phenanthrenecarboxylic acid	A16		
Naphthalene, 2-methyl	A17		
Anthracene	A18		
Phenanthrene, 1,7-dimethyl-	A19		

PAHs: polycyclic aromatic hydrocarbons.

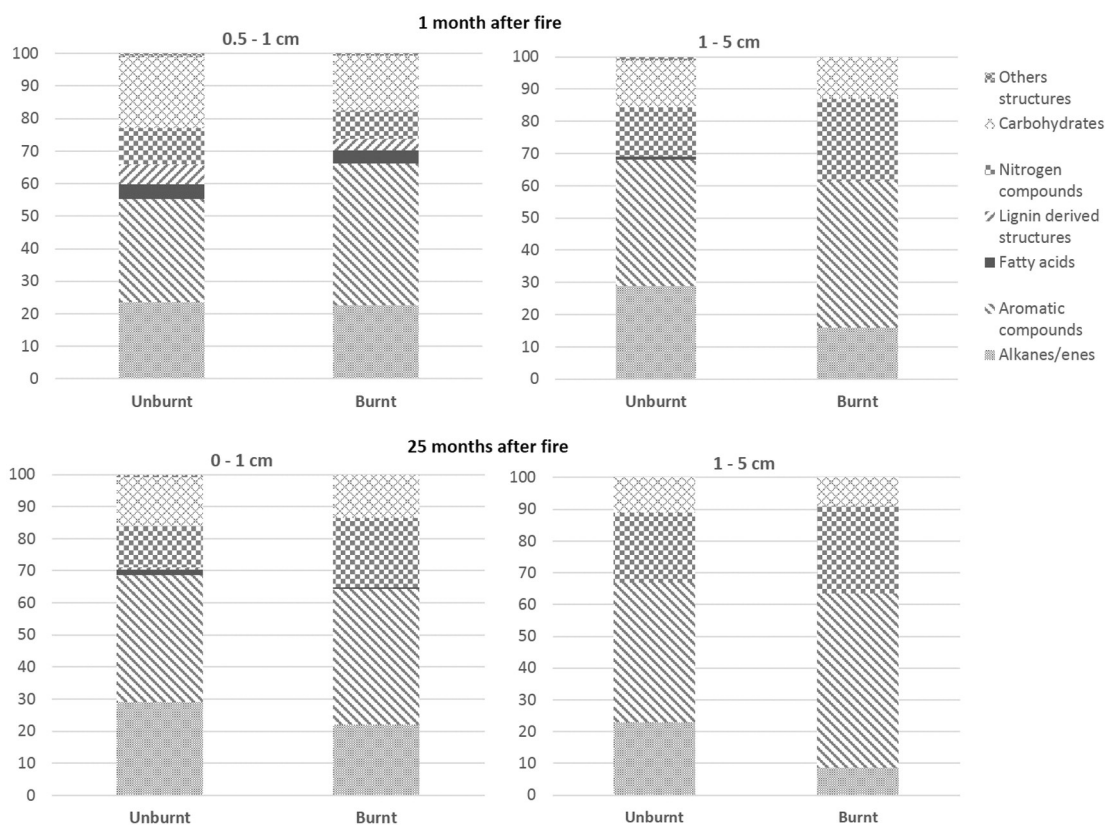


Fig. 3. Relative abundance of the different component classes obtained by the integration of the peaks area from the pyro-chromatograms.

Table 3 shows the values of average chain length (ACL) in *n*-alkanes and *n*-alkenes and the ratio short/long-chains. The fire induced a decrease in the ACL of *n*-alkanes and *n*-alkenes, and this difference remained in SOM two years after the fire. The ACL decrease is accompanied by an increase in the ratio of short-to-long *n*-alkanes after the fire. The *n*-alkenes presented similar changes after the fire. This is a well-known effect; fire systematically causes an increase of low molecular weight alkyl compounds from thermal cracking of plant waxes and other biopolymers (Almendros et al., 1988; De la Rosa et al., 2012). For this reason, the alkyl homologues could be suitable surrogates for the impact of wildfires in the SOM and its further evolution with the time after fire.

As regards post-fire recovery, conspicuous differences between the pyro-chromatograms of B and UB suggest that the topsoil composition at a molecular level was not completely restored after more than two years (25 months) from the passage of fire.

3.3. ¹³C solid state nuclear magnetic resonance spectroscopy

With the exception of the topsoil from the B site, the ¹³C NMR spectra of HF-treated soils are dominated by the signal assigned to carbohydrates in the *O*-alkyl C region (60–110 ppm) (Fig. 4). The alkyl/*O*-alkyl C ratio has been proposed as an index of SOM decomposition in forest soils (Baldock and Preston, 1995) and this increased in the UB soils from the humus soil layer (0.5–1 cm) to the mineral horizons. Within the mineral horizon no major alteration is observed. The signal intensity in the *O*-alkyl C region (60–110 ppm) decreased in the topsoil due to fire, from 40.7 to 26.7% for UB and B samples respectively. This result may be explained in terms of the loss of vegetation during the fire, and the destruction of thermolabile carbohydrate-derived structures (González-Pérez et al., 2004). The topsoil of B, sampled one month after the fire, showed clear evidence for the accumulation of charcoal indicated by the high content of aromatic C (32.5%; Table 4). However, no

Table 3
Comparison of parameters calculated from *n*-alkanes and *n*-alkenes released by analytical pyrolysis at 600 °C.

Sample	Depth	<i>n</i> -Alkanes		<i>n</i> -Alkenes		
		ACL	$\frac{\sum C_9-C_{23}}{\sum C_{24}-C_{33}}$ Short/long	ACL	$\frac{\sum C_9-C_{23}}{\sum C_{24}-C_{33}}$ Short/long	
1 month after fire	Unburnt	0.5–1 cm	19.1	2.5	16.4	3.1
		1–5 cm	17.8	2.9	15.5	4.4
	Burnt	0.5–1 cm	17.0	4.9	15.1	5.1
		1–5 cm	15.5	3.7	14.0	4.0
25 months after fire	Unburnt	0–1 cm	16.6	3.1	15.3	3.8
		1–5 cm	15.6	5.5	13.5	3.4
	Burnt	0–1 cm	16.1	5.7	14.1	4.0
		1–5 cm	14.7	3.4	11.9	4.2

Average chain length (ACL): $(\sum Z_n \times n) / \sum Z_n$, with Z_n as relative amount of *n*-alkanes with *n* carbons.

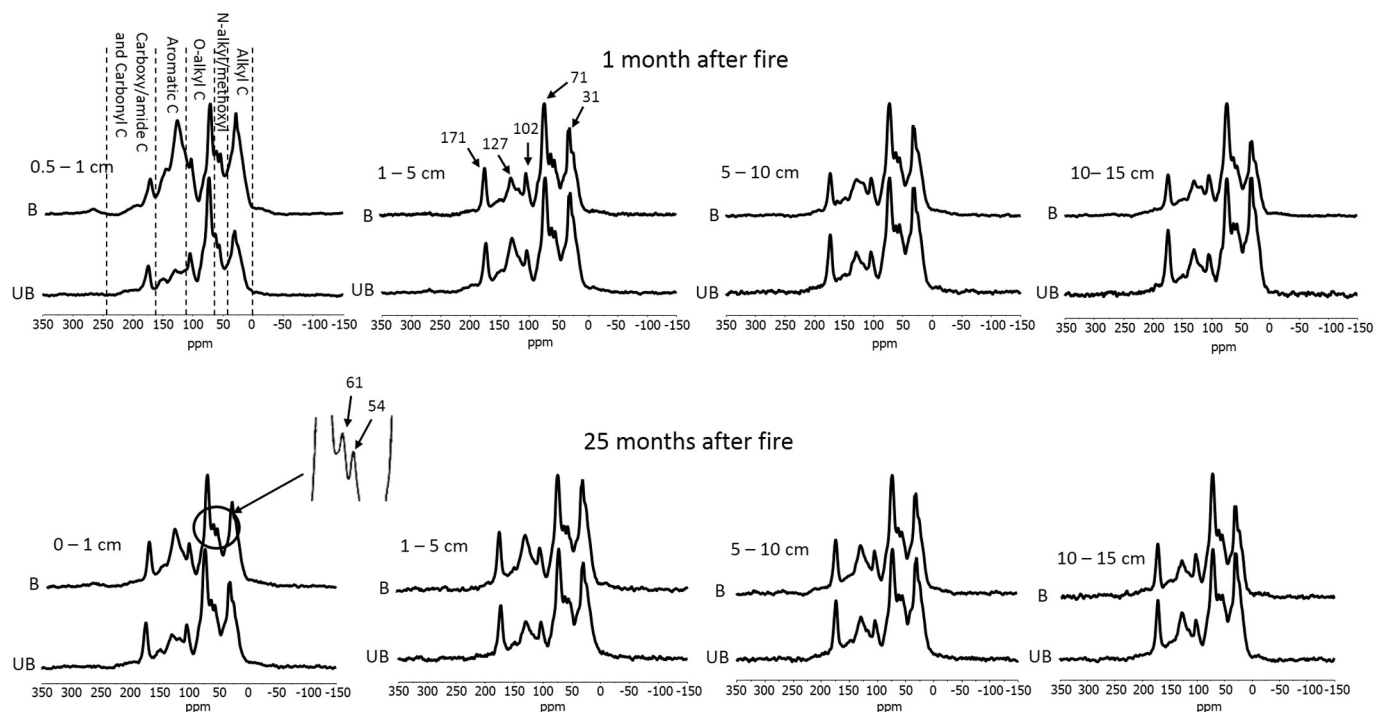


Fig. 4. Solid-state ^{13}C NMR spectra of HF-treated soil samples from the different depths of the burnt (B) and unburnt (UB) sites taken one month and 25 months after fire, respectively.

major difference is observed with respect to the SOM, even for samples taken 25 months after the fire event, whereas the carbohydrate content of the topsoil of UB was slightly lower in 2014 than in 2012. Note that in the topsoil of B site, the relative contribution of aromatic C decreased from 32.5 to 24.3% of the TOC after 25 months from the fire, which is consistent with a decrease of the proportion of charred residues. Because of the low slope of the chosen sites it seems unlikely that this loss was mainly induced by erosion of the topsoil. In addition to wind transport, the partially degraded pyrogenic SOM may have leached into the subsoils as it had been previously observed in umbric Ferralsols (Velasco-Molina et al., 2016). In the soils studied, 25 months after the fire, a slight increase of the aromaticity of the B subsoil sections 1–5 cm and 5–10 cm was observed. In contrast to the expected long term occurrence of charcoal (Egli et al., 2012), the observed loss of charcoal may indicate, in addition to leaching/migration of pyrogenic condensed materials, the occurrence of biochemical degradation during the more than 2 years of recovery time.

4. Conclusions

In general differences between the SOM characteristics of the fire-affected and unburnt soils were essentially found in topsoil samples and tended to disappear with time. In particular the aromatic-rich SOM structures produced during a vegetation fire in the Mediterranean areas may not accumulate systematically in the course of time. The low stability of charred residues may explain why, in spite of the high fire frequency, the pattern of burnt residues is rarely seen in SOM of forest soils in this region. Nevertheless, molecular-level analyses based on pyrolysis data showed clear alterations that were not recovered during the two years comprised in this study. The comparison of the pyrograms shows a fire-induced increase in aromatic compounds and a concomitant decrease in other constituents, such as carbohydrates, fatty acids, lignin-derived compounds or alkyl products. Two years after the wildfire, part of the changes exerted by fire in the molecular composition and properties of the burnt soil were still present. Anyway, the

Table 4

Assessment (%) of the different C types as seen by ^{13}C NMR integration regions.

Sample	Depth (cm)	245–160	160–110	110–60	60–45	45–0	Alkyl C/O-alkyl C	
1 month after fire	Unburnt	0.5–1 cm	9.6	16.7	40.7	9.4	23.6	0.6
		1–5 cm	11.0	22.2	31.0	9.3	26.5	0.8
		5–10 cm	10.9	17.7	32.0	10.8	28.6	0.9
		10–15 cm	11.5	16.3	31.3	11.0	29.9	1.0
	Burnt	0.5–1 cm	8.9	32.5	26.7	7.6	24.3	0.9
		1–5 cm	9.2	18.5	35.1	10.1	27.1	0.8
		5–10 cm	9.1	20.2	33.5	10.0	27.2	0.8
		10–15 cm	11.0	18.5	37.2	9.4	23.9	0.6
25 months after fire	Unburnt	0–1 cm	9.2	17.7	35.9	10.6	26.6	0.7
		1–5 cm	10.0	17.5	32.0	10.9	29.6	0.9
		5–10 cm	10.6	18.5	31.6	10.6	28.7	0.9
		10–15 cm	11.1	18.4	31.0	11.1	28.4	0.9
	Burnt	0–1 cm	9.6	24.3	31.6	9.3	25.2	0.8
		1–5 cm	10.1	21.5	30.3	9.8	28.3	0.9
		5–10 cm	10.6	19.7	32.5	10.0	27.2	0.8
		10–15 cm	12.4	16.7	35.4	10.3	25.2	0.7

C region values are given in ppm.

alteration in the SOM quality of samples taken in 2014 is notable in both B and UB sites, thus in addition to post fire management activities, climatic conditions probably also played a significant role.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:<http://dx.doi.org/10.1016/j.scitotenv.2016.02.134>. These data include the Google map of the most important areas described in this article.

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