



Molecular characterization of wildfire impacts on organic matter in eroded sediments and topsoil in Mediterranean eucalypt stands

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ABSTRACT

Wildfires can increase soil erosion due to the destruction of the vegetation and changes in soil organic matter (SOM) quantity and quality. This fact is especially dramatic in the case of Mediterranean ecosystems. Therefore, the major goal of the present study was to achieve a better understanding of the short-term effects of wildfires on the quantity and quality of organic matter (OM) in the topsoil of burnt Mediterranean eucalyptus plantations in north-central Portugal.

Wildfire had a large impact on slope-scale sediment losses, as they were approximately 30 times higher at the burnt site than at the unburnt site over the first 25 months after the fire. The pH and total nitrogen (TN) content of the burnt topsoil showed a noticeable increase immediately after the wildfire, whereas the total organic carbon (TOC) content revealed the opposite behavior. However, the TOC content showed a partial recovery during the subsequent two years after the fire. The sediments eroded after the fire were consistently more acidic and richer in TOC and TN than the burnt topsoil; they also revealed less pronounced changes with time-since-fire compared with the burnt topsoil.

Analytical pyrolysis analyses indicated that the fire resulted in an enrichment of aromatic compounds, nitrogen (N) constituents, lignin-derived compounds and polysaccharides. The latter is best explained with the input of partially charred OM, ash and decaying parts of plants killed by the fire. The thermal transformation of SOM caused the thermal breakdown and cracking of *n*-alkane compounds, as was revealed by the increase of the ratio of short-to-long chains and the alteration of the typical odd-over-even carbon predominance indexes. The relative abundance of specific biomarkers for vegetation and, in particular for *Eucalyptus globulus*, such as terpenoids eucalyptol and globulol decreased drastically or even disappeared from the pyrolysates of the burnt topsoil. These fire-induced changes in the quality of topsoil OM persisted during the whole post-fire period of 25 months. In general, the Py-GC/MS results pointed out that during the first two years after the fire the recovery of the topsoil OM quality was practically negligible.

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1. Introduction

In Portugal, like in other Mediterranean regions in southern Europe, wildfire frequency and extent have increased dramatically during the last decades (Caon et al., 2014; Marques et al., 2011; Shakesby, 2011) and a substantial reduction of the fire frequency is not expected for the next decades (Pereira et al., 2006). This intensification of the fire regime can be attributed to a combination of socio-economic changes, in particular land abandonment and afforestation with fire-prone tree species such as pine and eucalyptus and an increase in meteorological conditions propitious to wildfires (Llovet et al., 2009; Pereira et al., 2006).

As discussed by Shakesby (2011), wildfires can have important effects on soil geomorphologic and hydrological processes. The commonly observed increases in runoff and soil erosion in recently burnt areas are

typically attributed to the removal of the protective soil cover by vegetation and litter, in combination with heating-induced changes in topsoil properties such as infiltration capacity, aggregate stability and soil water repellency (Badía-Villas et al., 2014a; Granged et al., 2011; Prats et al., 2014; Shakesby and Doerr, 2006; Varela et al., 2010). The combined direct and indirect effects of fires can have important short- to long-term implications for key aspects of soil quality such as the quantity and quality of soil organic matter (SOM), nutrient stocks and pollutants (e.g., polycyclic aromatic compounds), as well as for aquatic habitats receiving sediment- and ash-loaded runoff from upstream burnt areas (Campos et al., 2012; González-Pérez et al., 2004; Smith et al., 2011).

The observed effects of fire on SOM content are highly variable, depending markedly on fire severity, and may range from (almost) complete destruction to increases of up to 30%, especially in topsoil layers as a result of the incorporation of ash and charred material (De la Rosa et al., 2013). The effects of fire on SOM quality continue an important

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research gap, also because recent advances and, in particular, the use of pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), also called analytical pyrolysis, have shown that these effects can be very complex (Aznar et al., 2013; Badía-Villas et al., 2014a; De la Rosa et al., 2008b, 2012; González-Pérez et al., 2004). Analytical pyrolysis provides information concerning the structure of organic molecules, including N species, which cannot be released by hydrolysis. This technique involves thermolytic fractionation of macromolecules into small fragments that are analyzed by gas chromatography–mass spectrometry (GC–MS). Nonetheless, some fire effects on SOM quality are now well-established such as, the increase of aromatic C at the expense of thermo-labile O-alkyl C due to charring as well as the conversion of peptide N into heterocyclic structures (De la Rosa et al., 2008b; González-Pérez et al., 2008; Knicker et al., 2006). Overall, wildfires can lead to a considerable rearrangement of the C forms in SOM and produce a variety of new substances such as water-repellent compounds and a range of pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzofurans and polychlorinated biphenyls, which may have important repercussions for soil health and quality (Arias et al., 2005; González-Pérez et al., 2008, 2014). Among these pollutants, especially PAHs have been identified as an important risk for downstream aquatic habitats (Campos et al., 2012; Gabos et al., 2001).

The present study aimed to determine the short-term effects of wildfires on SOM quality, in particular by comparing burnt and unburnt topsoil of Mediterranean eucalyptus plantations on four occasions, starting immediately after the first post-fire rain till two years later. In addition, this study also aimed to advance the knowledge of the molecular composition of the OM that is being exported by post-fire overland flow following a wildfire. Investigation of the OM composition of transported sediments is of crucial significance for a sophisticated evaluation of wildfire effects on terrestrial ecosystems as well as the aquifer and downstream waters. To do so, this study heavily relies on Py-GC/MS.

2. Material and methods

2.1. Study areas and site description

This study was carried out in two eucalyptus plantations (*Eucalyptus globulus* Labill.) located near the Ermida hamlet (40° 08' 46" N; 7° 59' 35" W; 500 m a.s.l.) of the Sever do Vouga municipality, Aveiro District, north-central Portugal (Fig. 1). One of the eucalyptus plantations (EB: eucalyptus burnt) was burnt by a wildfire with moderate severity (Faria et al., 2015; Machado et al., 2015) occurring between the 26th

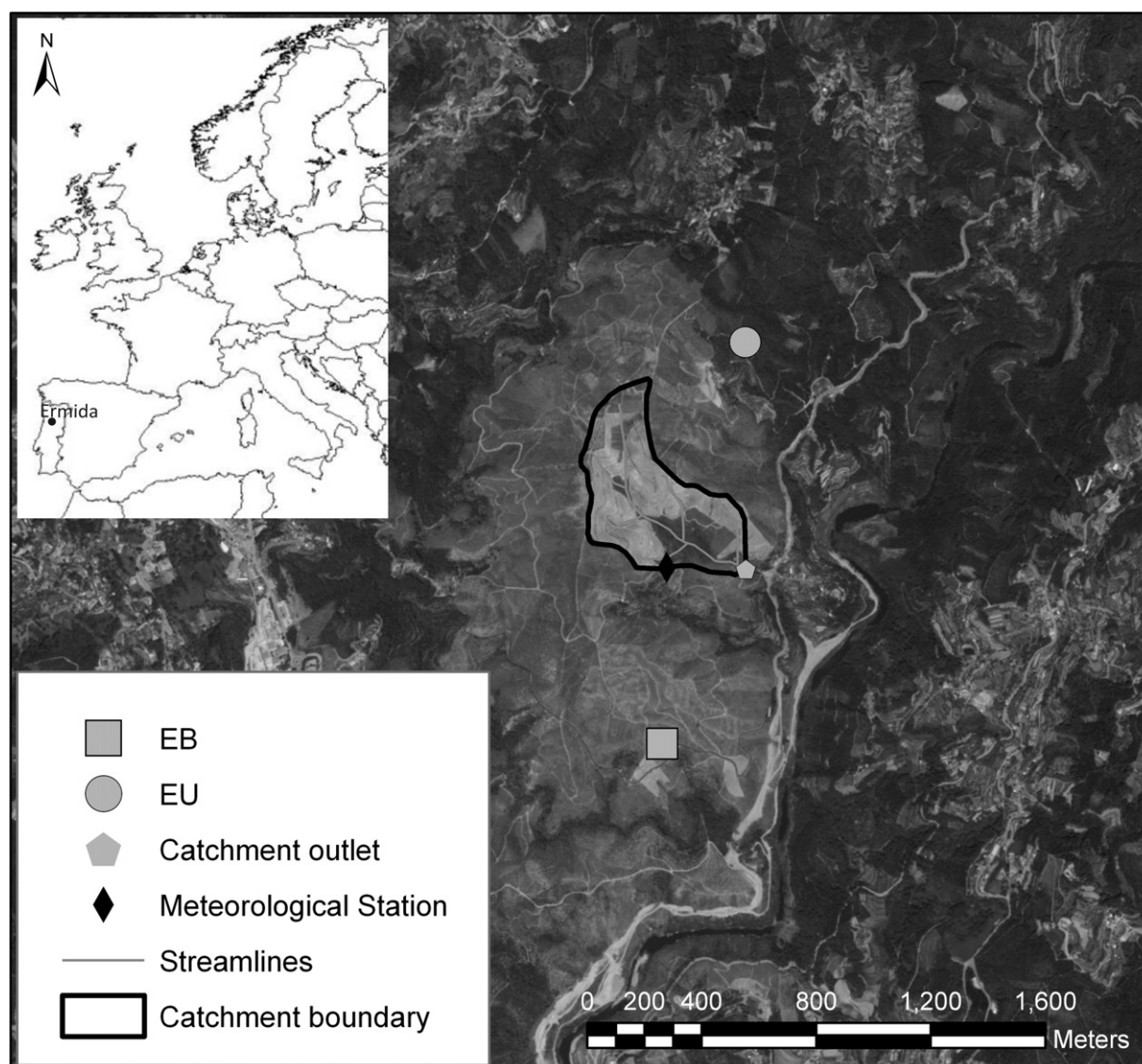


Fig. 1. Location of the Ermida study area and the two study sites, burnt (EB) and unburnt (EU) eucalypt plantations.

and 28th of July 2010. Approximately 300 ha of forested lands was consumed. The other eucalyptus plantation (EU: eucalyptus unburnt) was located just outside the border of the burnt area, with physico-environmental settings comparable to those of the EB site.

The study area has a humid meso-thermal Mediterranean climate (Csb in the Köppen classification), with moderately dry but extended summers (DRA-Centro, 1998). Mean annual temperature at the nearest weather station (Castelo Burgães: 40° 51' 16" N, 8° 22' 55" W at 306 m a.s.l.) was 14.9 °C. Annual rainfall at the nearest rainfall station (Ribeiradio: 40° 44' 39" N, 8° 18' 05" W at 228 m a.s.l.) was, on average, 1609 mm, but varied markedly between 960 and 2530 mm (SNIRH, 2011: 1991–2011). Ermida belongs to the Hesperic Massif, one of the region's major physiographic units, which is mainly composed of pre-Ordovician schists and graywackes, although Hercynian granites do occur at several locations (Ferreira de Brum, 1978). The soils at the two study sites were described in the field and classified as Umbric Cambic Leptosols (Loamic), having shallow A-horizons of 13–20 cm overlying C- or R-horizons consisting of schists (IUSS, 2014).

2.2. Measurement of eroded sediments and collection of sediment and topsoil samples

At the end of August 2010, but before the starting of the rainy season, the two study sites were instrumented with a sediment fence (SF) at the bottom of the slope. The sediment fences or silt fences were made of geotextile fabric and supported by steel rods which were driven vertically into the soil, following the design of Robichaud and Brown (2002). While sediment fences let the overland flow through the mesh, they retain the eroded sediments with an estimated trapping efficiency of 68–93% (Spigel and Robichaud, 2007). The contributing area of the SF was estimated to be 192 m² in the case of the EB site and 89 m² in the case of the EU site.

Between the end of August 2010 and the end of August 2012, the eroded sediments retained by the SF were removed and weighted in the field at a total of 20 occasions. Large intact pieces of litter such as leaves and woody debris were removed. If the retained sediments accounted below <0.5 kg, all of the material was taken to the laboratory; otherwise, one homogenized subsample was collected. These collected samples were analyzed for their moisture content by drying at 105 °C for 24 h to compute sediment yield. The SF samples analyzed in this study were collected during mid-September 2010, immediately after the first significant rainfall events after the fire, as well as 5, 12 and 23 months later (Table 1). Concomitantly, the topsoils (0–2 cm depth) of both study sites were sampled at 5 equidistant points along transects laid out from the bottom to the top of the slopes. The transects were marked to allow shifting their location 1 m across the slope on subsequent sampling occasions and, thereby, to avoid sampling spots disturbed earlier. Litter and, in the case of the EB site, also ashes were carefully removed before soil sample collection. After air-drying at

room temperature, both the SF and the topsoil samples were sieved to the fine-earth fraction (<2 mm), and stored under dark and cool conditions until further analyses (see 2.3). The yield of most SF samples from the unburnt site (SF-EU) was too small (<5 g) to allow the various analyses, so that they were excluded from this study. Composite samples of the topsoil (one per site per sampling occasion) were obtained by thorough mixing of equal-weight sub-samples of the five soil samples collected at each site at each occasion.

2.3. Laboratory analysis of sediment and topsoil samples

Total nitrogen (TN) and total organic carbon (TOC) contents of the samples were determined in triplicates by dry combustion using an elemental analyzer of the PerkinElmer 2400 series and a TOC Analyzer Shimadzu TOC-5050A respectively, whereas the pH values were measured with a glass electrode in the supernatant of a 1:2.5 weight/volume mixture of soil and distilled water in triplicates.

The sediment and composite topsoil samples were analyzed by pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS) using a vertical micro-furnace type double-shot pyrolyzer PY2020iD (Frontier Laboratories Ltd., Fukushima, Japan) attached to a GC/MS system (Agilent 6890 GC and Agilent 5973 MSD). Samples (ca. 1 mg) were introduced in the pre-heated micro-furnace at a pyrolysis temperature of 500 °C for 1 min. The evolved gases from pyrolysis were transferred, through a capillary transfer line interface heated at 350 °C, to the gas chromatograph inlet (splitless mode and 250 °C). The gas chromatograph was equipped with a capillary column (J&W Scientific DB-5 MS) of 30 m × 250 µm × 0.25 µm film thickness. The oven temperature was held at 50 °C for 1 min and then increased to 100 °C at 30 °C min^{−1}, from 100 °C to 300 °C at 10 °C min^{−1}, and stabilized at 300 °C for 10 min using a heating rate of 20 °C min^{−1} in the scan mode. The carrier gas was helium at a controlled flow of 1 mL min^{−1} (De la Rosa et al., 2013). Electron ionization mass spectra were acquired with 70 eV ionizing energy. Identification of the individual compounds was carried out by using the extracted ion chromatograms for different homologous series and comparison with stored data (NIST and Wiley libraries). The peak areas of the different pyrolysis products were calculated as relative abundances based on percent peak areas of the total ion chromatogram trace (total integral of pyrolysis products identified equal to 100).

2.4. Data analyses

Principal component analysis (PCA) was performed by using the software Primer 6 (PRIMER-E Ltd, Plymouth, UK) on the normalized relative abundances of groups of compounds as identified by analytical pyrolysis and grouped according to their structure and origin.

Table 1

Average pH, total organic carbon (TOC), total nitrogen (TN) and ratio TOC/TN of the eroded sediment (SF-EB) samples and of the topsoil (0–2 cm) at a recently burnt (EB) and a long unburnt (EU) eucalypt plantation on four sampling occasions.

Sampling period	Date of sediment collection	Months after fire	Code	pH (in H ₂ O)	TOC (g·kg ^{−1})	TN (g·kg ^{−1})	TOC/N
I	21-Sep-10	2	SF-EB I	6.5	255	17	15
			EB I	6.0	154	14	11
			EU I	3.1	184	8	24
II	16-Feb-11	7	SF-EB II	5.3	255	15	17
			EB II	4.1	96	4	20
			EU II	3.2	127	2	34
III	14-Sep-11	14	SF-EB III	5.0	132	12	11
			EB III	4.2	97	5	17
			EU III	3.4	115	2	37
IV	22-Aug-12	25	SF-EB IV	4.2	312	12	27
			EB IV	4.0	84	3	18
			EU IV	3.5	118	4	25

3. Results and discussion

3.1. General parameters: total organic carbon, total nitrogen and pH

Two months after the wildfire, the EB topsoil still showed a greater pH than the EU topsoil (3.1 vs. 6.0; Table 1), which has been also observed in previous studies (Certini et al., 2011; Granged et al., 2011; Martín et al., 2012; Pereira et al., 2012; Ulery et al., 1993). This fact can be explained by the oxidation of the SOM and the fire-induced, loss of hydroxyl groups and the destruction of organic acids (Dumontet et al., 1996). In addition, the release of basic ions formerly bound in the litter contributed to liming effect of fires. Ulery et al. (1993) found a similar increase in topsoil pH of three units, immediately after burning. In laboratory experiments, Terefe et al. (2008) found that the pH increased significantly in soils with high soil organic matter contents and low clay contents following exposure to temperatures of 200–500 °C. Such, soil burning experiments under laboratory conditions, however, merely show the temperature on soil and do not include the liming effect of ashes. However, five months later, the pH of the EB topsoil dropped markedly (4.1) and remained practically constant until the end of the study although it was still higher than the pH of the EU topsoil. Arocena and Opio (2003) found that fire-induced differences in pH values continued to exist three years after a wildfire. In contrast, Granged et al. (2011) found that the pH returned to pre-fire values between 3 and 6 months after a prescribed fire in a eucalyptus forest. The EU topsoil revealed a slight increase in pH throughout this study, possibly due to the deposition of ashes blown in from the burnt area.

The pH of the SF–EB after the fire decreased more gradually with time-since-fire than the pH of the EB topsoil but was consistently higher than for the EB topsoil at all four sampling periods. This is best explained by the admixture of ashes *s.l.* (sensu lato, i.e., including charcoal and partially charred plant and litter material) in the SF–EB. Shakesby et al. (2013) reported higher pH values in the sediments that had eroded four months following a prescribed fire in a shrub-dominated catchment in central Portugal than in the sediments that had eroded prior to the fire. The pH of these post-fire sediments, however, did not differ in a consistent manner from the pH of topsoil.

Two months after the wildfire, the TOC content of the topsoil from the burnt area were markedly lower than of the EU soils (154 vs. 184 g kg^{−1} respectively). Such a fire-induced decrease in TOC content (of approx. 16%) is in agreement with the findings of previous studies of Mediterranean soils (Badía-Villas et al., 2014b; Certini et al., 2011; Gimeno-García et al., 2000; Granged et al., 2011; Mataix-Solera et al., 2002) and indicates that charcoal production did not compensate for the OM loss due to combustion (Knicker et al., 2006). The temporal pattern of the TOC contents at the EB site was similar to that of the pH values, reflecting a clear decrease (−38%) by mid-February 2011 and then remaining basically unchanged until the end of the study. However, one has to bear in mind, that a similar tendency was also observed for the EU site which may indicate that this pattern is unrelated to the wildfire. While the post-fire losses in OC may, at least in part, have resulted from the removal of the protective litter and vegetation cover, the changes in TOC content at the EU site are probably related to inter-annual and variations in climatic conditions during the study period. Thus, the considerably dry summer of 2008 the lead to a reduced biomass production and, thus, to a lower input of fresh OM into the soil.

The TOC contents at the EB sites were in accordance with previous studies by Campo et al. (2008), who attributed it to post-fire soil losses and slow vegetation recovery. Martins et al. (2013) and Prats et al. (2014) reported considerable erosion rates as well as reduced recovery of the ground vegetation for other recently burnt eucalyptus plantations in the Ermida study area.

The SF–EB showed consistently higher TOC contents than the EB topsoil which was most likely related to the preferential transport of ashes *s.l.* by post-fire overland flow. The underlying assumption that the TOC content of the ashes and charcoal was higher than that of the

topsoil is sustained by the findings of various studies (Bodí et al., 2014; De la Rosa et al., 2008a; Santín et al., 2012). With cumulative erosion and hence with increasing time-since-fire, it may be expected that the contribution of ash decreases due to a selective transport of ashes which leads to its exhaustion. Such a scenario, however, is not supported by the present results, since the highest TOC contents were determined for the SF–EB collected during the last sampling occasion. The exceptional high TOC contents of the SF–EB obtained from the last sampling event is best explained by a highly erosive event, which mobilized more sediments per mm of rainfall than any of the preceding events. Nonetheless, Malvar et al. (2013) also did not find clear evidence that OM losses in nearby eucalyptus plantations decreased noticeably with time-since-fire during the first two years after fire.

On the first sampling occasion, the EB topsoil showed a 1.7-fold increase of TN as a result of the fire indicating that N-rich charcoal in which N is mostly bound in N-heterocyclic structures accumulated on the soil (De la Rosa et al., 2008b; Knicker et al., 2005). The temporal pattern of the topsoil TN contents at the two study sites were comparable but seem unrelated to the occurrence of the wildfire.

Comparable to the TOC, the TN content of the SF–EB was higher than that of the EB topsoil on all four sampling occasions, suggesting the same causes as underpin the fire-induced increases in topsoil TN contents. Unlike the TOC contents, however, the TN contents of the SF–EB did suggest a gradual decrease with time-since-fire.

The TOC/TN ratio diverged conspicuously between the EB and the EU site on the first sampling occasion (11 vs. 24) and was maintained throughout the entire study period. Such a fire-induced decrease in the C/N ratio has been observed in various studies (De la Rosa et al., 2008b; Fernández et al., 1999; González-Pérez et al., 2004) and could be due to the accumulation of newly-formed heterocyclic N forms.

3.2. Sediment losses

Cumulative sediment losses over the first two years after the wildfire were roughly 30 times lower at the EU site than at the EB site (Table 2). At the latter, the bulk of these losses (80%) occurred during the first seven months were produced by 44% of the cumulative rainfall.

The cumulative sediment losses at the EB plantation over the first post-fire year amounted to 1.1 Mg ha^{−1} y^{−1} (Table 2), closely matching the threshold value for tolerable soil losses of 1 Mg ha^{−1} y^{−1} proposed by Verheijen et al. (2009, 2012). The marked decrease in sediment losses over the second year agreed well with the commonly observed decrease in erosion response with time-since-fire (e.g., Shakesby and Doerr, 2006; Shakesby et al., 2013). These sediment losses during the first study year were higher than those reported by the majority of plot-scale erosion studies in the Mediterranean after moderate severity fires, as reviewed by Shakesby (2011). The four samples of SF–EB analyzed in this study were produced by the first rainfalls after the wildfire, (amounting to 25 mm), by 108 mm of rainfall between mid-January and mid-February 2011, by 65 mm of rainfall between mid-August and mid-September 2011, and by 42 mm of rainfall between mid-June and mid-August 2012 (Fig. 2). In the case of the EU plantation, the amount of

Table 2

Cumulative sediment losses and cumulative rainfall amounts of the topsoil (0–2 cm) at a recently burnt (EB) and a long unburnt (EU) eucalypt plantation on four sampling occasions.

Monitoring period	Date of sediment collection	Cumulative sediment losses (kg·ha ^{−1})		Cumulative rainfall (mm) Burnt (EB)
		Burnt (SF–EB)	Unburnt (SF–EU)	
I	21-Sep-10	9	0.3	25
II	16-Feb-11	1048	13	1119
III	14-Sep-11	1100	28	1472
IV	22-Aug-12	1306	46	2550

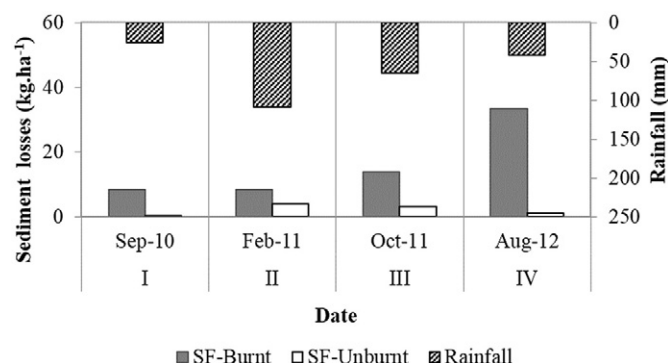


Fig. 2. 1 to 2-monthly sediment losses (SF) and corresponding rainfall amounts at a recently burnt (EB) and a long unburnt (EU) eucalypt plantation on four sampling occasions.

eroded sediments increased monotonically with increasing rainfall amount; in the case of the EB plantation, however, there was no obvious relationship between the amounts of eroded sediments and rainfall. Specific sediment losses at the EB were comparatively low for the winter-2011 sampling period and comparatively high for the summer-2012 sampling period (0.08/0.80 vs. 0.22–0.33 kg ha⁻¹ mm⁻¹ rainfall). Even so, the specific sediment losses at the EB site were at least twice as high as those at the EU site (0.01–0.05 kg ha⁻¹ mm⁻¹ rainfall) on all four sampling occasions.

3.3. Organic matter composition in topsoil and eroded sediments

The pyrolysis products identified in the total ion current chromatograms (TIC) and their relative abundances for each of the individual samples are presented in Appendix A. The identified compounds were grouped according to their structure and origin into the following nine main groups: terpenoids; hydroaromatic steroids; *n*-alkanes/enes; *n*-

fatty acid methyl esters (FAMES); lignin-derived compounds; aromatic non-specific compounds; nitrogenated (N) compounds; polysaccharide-derived compounds and other compounds of unknown origin (unspecific).

The scatter plot of the first two principal components (PCs; Fig. 3), resumes the similarities in OM composition between the eroded sediments and (un-) burnt topsoil samples, and simultaneously shows the main groups of compounds responsible for these similarities. Together, the first two PC's accounted for 84% of the variability with the first PC (PC1) explaining 62% and the second PC (PC2) explaining 22%. The scatter plot allowed a good separation of the samples into three different sets. One set included the eroded sediments the first sampling period (SF-EB I), which showed a relatively strong affinity with aromatic non-specific compounds. The second set included the eroded sediments of the three following sampling occasions (SF-EB II, III and IV) as well as all burnt topsoil samples (EB I, II, III and IV), which had a similar composition in terms of N-compounds, *n*-alkanes/enes and polysaccharide-derived compounds. These results suggested that, seven months after the fire, the SF-EB had a similar composition as the EB topsoil. The third set include all unburnt topsoil samples (EU I, II, III and IV), which distinguished itself from the other samples through the presence of terpenoids and hydroaromatic steroids. Overall, PC1 was related to compounds such as *n*-FAMES, polysaccharide-derived compounds, lignin-derived compounds, terpenoids and hydroaromatic steroids, while PC2 was associated with aromatic non-specific compounds, N-compounds and *n*-alkanes/enes, and polysaccharide-derived compounds.

The relative abundances of the above-mentioned nine main groups of identified compounds are presented in Fig. 4. The aromatic non-specific compounds were among the most abundant compounds in all samples. Their relative abundance was lower in the EU than EB topsoil and lower in the SF-EB samples, amounting to 29–33%, 40–52% and 44–69%, respectively. As it is shown by the PCA diagram, the detected aromatic compounds were mainly composed of alkyl benzenes (e.g., toluene, xylenes), polycyclic aromatic hydrocarbons (PAHs: indene, naphthalene, phenanthrene, anthracene and biphenyl), and (methyl-) phenols. Previous studies (e.g., González-Pérez et al., 2014) suggested that such compounds can be formed by incomplete combustion during wildfires and are indicative for the presence of charcoal. Accordingly, the PAHs were more abundant, as well as, more diverse in the EB and SF-EB samples than in the EU samples (Appendix A). These differences

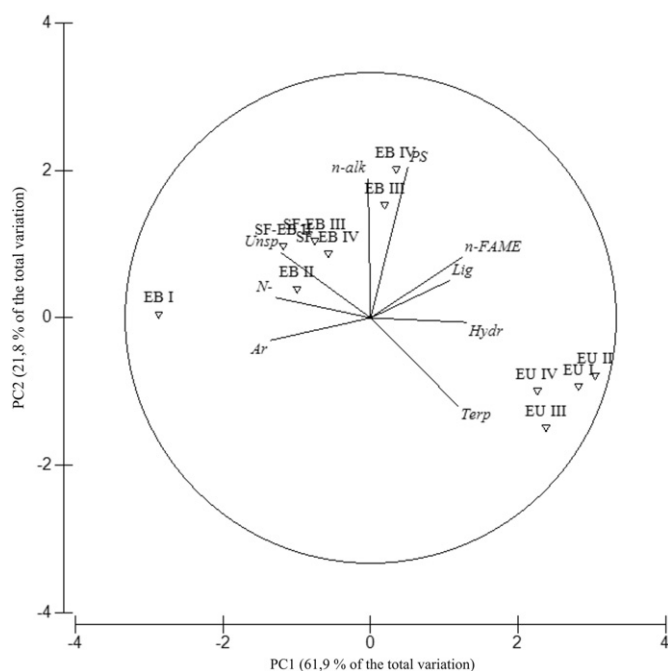


Fig. 3. Principal component analysis (PCA) of similarities in organic matter composition between the eroded sediments (SF-EB), burnt (EB) and unburnt topsoils (EU) and the main groups of compounds identified in Py-GC/MS. Terpenoids (terp); hydroaromatic steroids (Hydr); *n*-alkanes/enes (*n*-alk); *n*-fatty acid methyl esters (*n*-FAMES); lignin-derived compounds (Lig); aromatic non-specific compounds (Ar); nitrogenated compounds (N); polysaccharide-derived compounds (PS) and other compounds of unknown origin (Unsp).

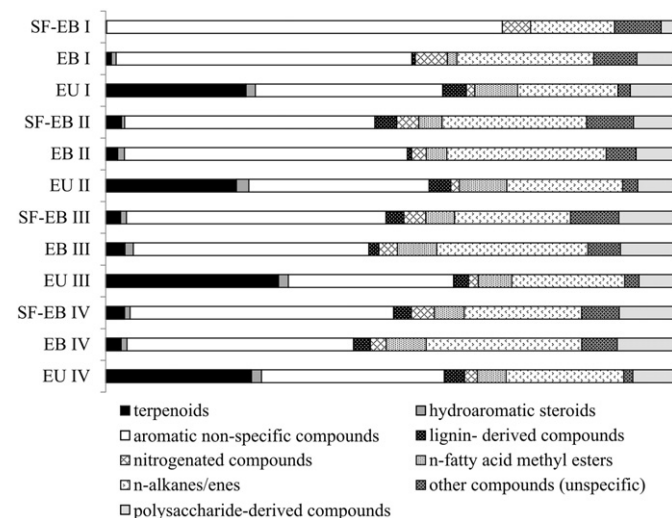


Fig. 4. Cumulative relative abundance of the major types of pyrolysis products identified in eroded sediments (SF-EB), burnt (EB) and unburnt topsoils (EU) under eucalypt on the four periods in study. Period I: 2 months after fire; Period II: 7 months after fire; Period III: 14 months after fire and Period IV: 25 months after fire.

are most probably due to the presence of chars derived from biomass (Badía-Villas et al., 2014b; Campo et al., 2011; De la Rosa et al., 2012; Tinoco et al., 2006). It has been postulated that black carbon – i.e., carbonized substances produced during vegetation fires may be a major precursor of the aromatic substances present in burnt soils (Schmidt and Noack, 2000). The hydrophobic nature of charcoal residues might have contributed to the comparatively high erosion rates at the EB site (Malvar et al., 2013; Prats et al., 2014; Shakesby and Doerr, 2006). Not only long unburnt but also recently burnt eucalyptus plantations in the study region have been found to exhibit extreme topsoil water repellency, especially during dry antecedent weather conditions (Keizer et al., 2005, 2008). Phenols and alkylphenols were found in all samples, probably originating from phenolic precursors compounds such as lignin, tannin, proteinaceous biomass, and carbohydrates (Tegelaar et al., 1995) or derived from the heat-transformed products of such constituents (Knicker et al., 2008).

Lignin-derived compounds were identified in all samples, except for the SF-EB samples collected at the first sampling occasion following the first post-fire rains of September 2010. The relative abundance of these lignin-derived compounds tended to be slightly lower in the EB samples (1–3%) than in SF-EB samples (3–4%), whereas that of EU samples was maintained constant (4%) during the study period. Among these compounds, the most abundant were 2-methoxy-4-vinylphenol, vanillin, vanillic acid methyl ester and acetovanillone, which probably derived from plants (Simoneit, 2002). In addition, the presence of 4-Allyl-2-methoxyphenol (eugenol) was especially noteworthy as it is characteristic for woody materials (Sharma et al., 2004). Eugenol was identified in the Py-GC/MS chromatograms of earlier studies of Mediterranean forest soils (De la Rosa et al., 2008b, 2012; Knicker et al., 2013). In the present study, eugenol was detected in the EU samples but not in the EB, so that it could be a valid marker of fire occurrence in eucalyptus plantations.

The principal forms of N-compounds identified in this study were hydrazine 1,1-dimethyl; pyridine and benzonitriles. The N-compounds tended to occur with a lower relative abundance in the EU samples (1–2%) than in the EB (3–6%) as well as SF-EB samples (4–5%). This behavior was consistent with that observed for the TN contents. Furthermore, it was in accordance with the increases in heterocyclic N-compounds that were associated with the alteration of SOM by fire (De la Rosa et al., 2008b; Knicker, 2010).

Polysaccharide-derived compounds were present in all pyrolysates of the soil and sediment samples collected in this study. They are considered to originate from plant, fungal and/or microbial materials. They consist of furans, lactones (furanones), cyclic ketones (cyclopentanones) and anhydrosugars (Gregorich et al., 1996; Yassir and Buurman, 2012). The most abundant polysaccharide-derived compounds in the studied samples were furans (furan, 3-methyl-; benzofuran; 2-furancarboxaldehyde, 5-methyl-; furan, 2-(1-pentenyl)-; 1H-Inden-1-one, 2,3-dihydrotetramethyl-), anhydrosugars (D-allose) and furfural. The relative abundance of the polysaccharide-derived compounds attained its lowest value in the eroded sediments (SF-EB: 3–10% vs. EU: 7–8% and EB: 7–10%). The compound D-allose (corresponding to peak 140, Appendix A) probably originated to a large extent from polysaccharides that have been thermally altered (Poirier et al., 2005). Its presence solely in the EU could indicate that the wildfire-induced soil heating transformation of some polysaccharidic compounds.

Terpenoids – which are commonly used as plant biomarkers – occurred with higher relative abundance in the EU samples (23–30%) than in both the EB (1–3%) and SF-EB samples (<1–3%), as it is also shown by the PCA diagram (Fig. 3). This suggested that the wildfire had a drastic impact on plant cover, and produced a noticeable change in the SOM molecular composition. Eucalyptol and globulol – which are indicators for the presence of *E. globulus* (de Blas et al., 2013; Song et al., 2009) – attained relative abundances of 2% and 1%, respectively, in EU samples, but occurred less frequently and with a lower

contribution in both the EB and SF-EB samples. Only the EB sample taken mid-September 2011 contained very low amounts of eucalyptol and globulol (0.3%). None of the SF-EB samples revealed globulol, but several contained eucalyptol from mid-February 2011 onwards, albeit with low relative abundances which decreased with time-since-fire from 0.5 to 0.3%. The appearance of globulol in the SF-EB, some six months after the fire and its subsequent decrease in relative abundance with time-since-fire suggested input from litter fall from scorched eucalyptus crowns and/or from post-fire logging rather than input from litter fall from resprouting eucalyptus.

Hydroaromatic steroids were found in the pyrochromatograms of all topsoil samples but with lower relative abundances in SF-EB and EB than in EU (c. 1 vs. 2%). Furthermore, they occurred with similar relative abundances in the pyrograms of SF-EB and of EB ($\approx 1\%$), except of those from the first sampling. In contrast, β -sitosterol occurred with higher relative abundances in SF-EB and EB than EU (0.1–0.3% vs. 0.1%). This compound is indicative for plant residues since it is one of the most common steroids in the wax and gums of higher plants (Baker, 1982).

The doublets of *n*-alkanes/*n*-alkenes series represented an important fraction of the pyrolysis products, ranging from 15 to 27% of the total integrated area of the pyrochromatogram (Fig. 4). Their C numbers varied from C₉ to C₃₁, and showed bimodal distributions whose maxima partially overlapped for the different types of samples (Fig. 5). These overlapping maxima coincided with the ranges of C₁₃ to C₁₅ (EU: C₁₅; EB: C₁₃–C₁₅; SF-EB: C₁₃, C₁₅) and C₂₁ to C₂₂ (EU: C₂₁, C₂₂; EB: C₂₂; SF-EB: C₂₁). In addition, the pyrogram of EU showed a third maximum at C₂₉.

The typical molecular ratios for the *n*-alkanes are given in Table 3. Compared to OM of the EU samples, that of the EB samples lose the odd-over-even predominance (Carbon Preference Indexes – CPI), a reduction in the average chain length (ACL), and an increase in the ratio of short-to-long *n*-alkanes ($\sum C_9\text{--}C_{22}/\sum C_{23}\text{--}C_{31}$). The OM of the SF-EB samples showed the same differences in comparison with the EB samples. These differences are well-known to indicate heating-induced cracking of long chain homologous molecules in burnt forest soils. Therefore, they have been suggested as surrogate biomarkers for assessing the direct effects of wildfires on SOM as well as its subsequent recovery with time-since-fire (De la Rosa et al., 2012, 2013; González-Pérez et al., 2008). In fact, these markers are more and more applied in studies of ancient soils as indicators for biomass burning (Eckmeier and Wiesenberger, 2009) and subsequent incorporation of charred biomass (Knicker et al., 2013; Wiesenberger et al., 2009). The differences in *n*-alkanes molecular ratios between the SF-EB and EB samples were most pronounced for the samples of the first sampling occasion, for which an ACL of 14.7 and 17.2 and a short-to-long ratio of 8.8 and 6.9 were determined. The difference of both indicators was smaller for the material collected at the next two sampling occasions but then increased again for that of the last sampling occasion. The latter reflected first and foremost a change in the properties of the burnt topsoil. By mid-August 2012, two years after the fire, the ACL and short-to-long ratio of the EB closely approximated the values of the EU, thus suggesting a perceptible recovery from the direct fire effects.

Fatty acids (FAs) were found with rather low relative abundances in the majority of samples, typically ranging from 2 and 8%. Furthermore, they were absent in all SF-EB samples. However, analytical pyrolysis is expected to underestimate FA detection due to incompatibility of FA with non-polar columns used in GC as well as due to their decarboxylation at elevated temperatures (Bahri et al., 2006).

4. Conclusions

Two years after the fire partial recovery of the soil properties were indicated. The eroded sediments after the fire were consistently more acidic and richer in TOC and TN than the burnt topsoil, and also revealed less pronounced changes with time-since-fire, which confirmed that

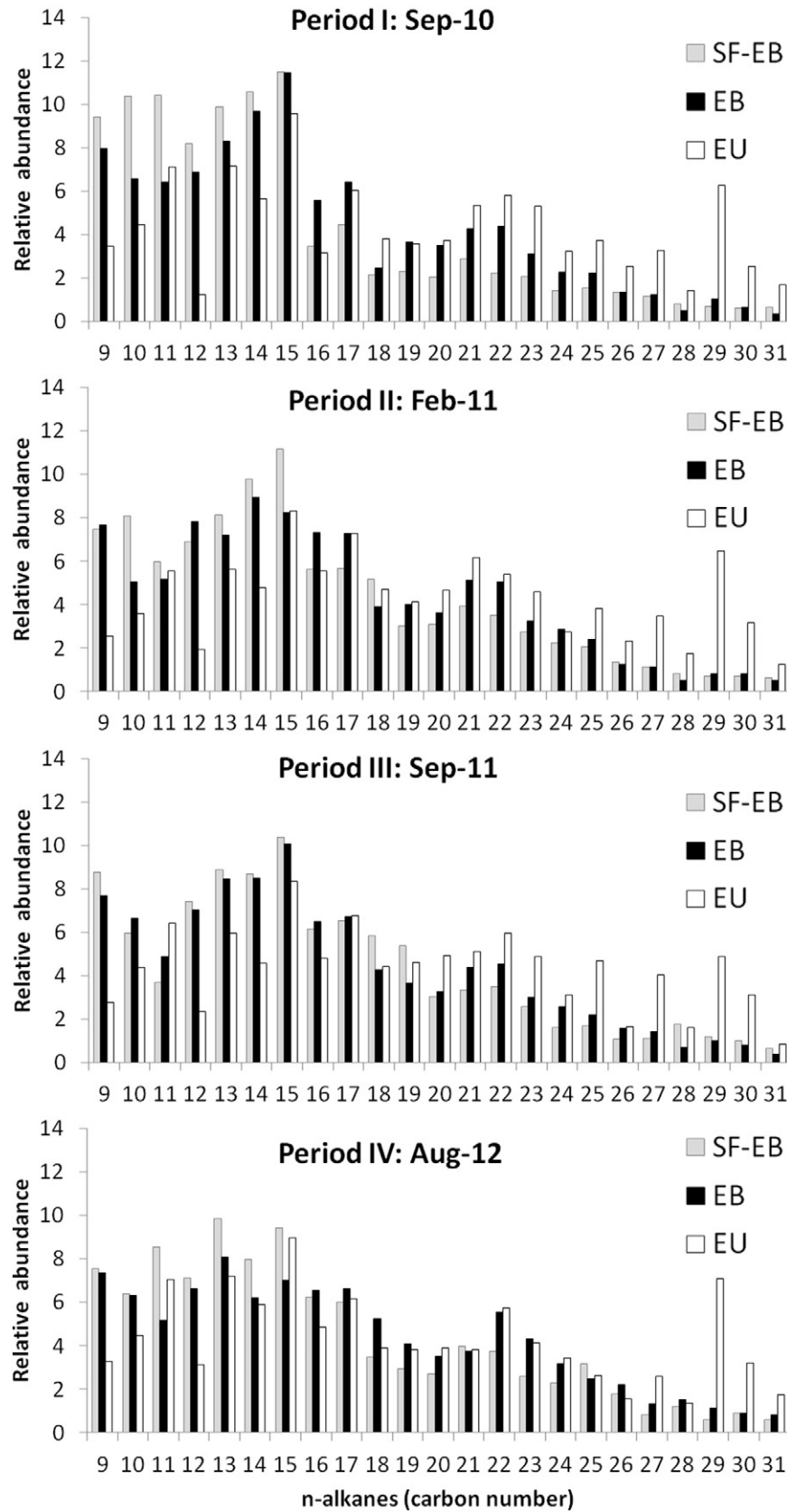


Fig. 5. Relative abundance of *n*-alkanes/enes in the eroded sediments (SF-EB), burnt (EB) and unburnt (EU) topsoils under eucalypt plantation on four sampling occasions. *Period I*: 2 months after fire; *Period II*: 7 months after fire; *Period III*: 14 months after fire and *Period IV*: 25 months after fire.

Table 3Molecular ratios for *n*-alkanes in the eroded sediments (SF-EB), burnt (EB) and unburnt (EU) topsoils under eucalypt plantation on four sample occasions.

Periods	$\sum C_9-C_{22} / \sum C_{23}-C_{31}$ short/long			Diff.		CPI (odd/even)			Diff.		CPI short			Diff.		CPI long			Diff.		ACL			Diff.	
	SF-EB	EB	EU	SF	EB	SF-EB	EB	EU	SF	EB	SF-EB	EB	EU	SF	EB	SF-EB	EB	EU	SF	EB	SF-EB	EB	EU	SF	EB
				vs. EB	vs. EU				vs. EB	vs. EU				vs. EB	vs. EU				vs. EB	vs. EU				vs. EB	vs. EU
I	8.8	6.9	2.3	1.8	4.6	1.3	1.3	1.7	0	−0.4	1.3	1.2	1.5	0.1	−0.3	1.5	1.7	2.1	−0.2	−0.4	14.7	17.2	18.6	−2.5	−1.4
II	7.1	6.4	2.4	0.7	4.0	1.1	1.1	1.5	0	−0.4	1.1	1.1	1.3	0	−0.2	1.4	1.5	2.0	−0.1	−0.5	16.0	16.3	19.1	−0.3	−2.8
III	6.9	6.4	2.5	0.5	3.9	1.2	1.2	1.5	0	−0.3	1.2	1.1	1.3	0.1	−0.2	1.3	1.4	2.0	−0.1	−0.6	16.0	16.1	18.7	−0.1	−2.5
IV	6.2	4.6	2.6	1.6	2.0	1.3	1.1	1.4	0.2	−0.3	1.3	1.1	1.3	0.2	−0.2	1.2	1.3	1.9	−0.1	−0.6	15.9	16.9	18.5	−1.0	−1.5

Average chain length = $(\sum Z_n \times n) / \sum Z_n$, with Z_n as relative amount of *n*-alkanes with *n* carbons.Carbon preference index of *n*-alkanes = $(\sum C_{9-31\text{odd}} / \sum C_{10-30\text{even}})$.Carbon preference index of short chain *n*-alkanes = $(\sum C_{9-21\text{odd}} / \sum C_{22-30\text{even}})$.Carbon preference index of long chain *n*-alkanes = $(\sum C_{9-31\text{odd}} / \sum C_{22-30\text{even}})$.

Diff. = difference between sediment–burnt (SF vs. EB) and burnt–unburnt topsoil (EB vs. EU).

the loss of SOM in quality and quantity occurred during the two years monitored.

Analytical pyrolysis of topsoil and sediment samples exposed that fire effects at the burnt site involved:

- a comparative enrichment of the topsoil in aromatic compounds and especially, PAHs derived from charcoal and partially charred OM as well as an additional enrichment of the eroded sediments, which should be duly considered due to its abundance of persistent organic pollutants.
- increases in heterocyclic N together with an increase in the short-to-long ratio of *n*-alkanes, and reduction in average chain length, which all indicated thermal transformation of the fire affected SOM.
- a decrease of biomarkers of *E. globulus* as well as in other terpenoids used as specific biomarkers of vegetation which is consistent with noticeable fire-induced changes in vegetation cover.

In addition, the Py–GC/MS results indicated that the recovery of the topsoil SOM quality from the immediate fire effects was partial during the two years covered by this study.

Finally, the present study showed that moderate-severity wildfire considerably increased the sediment losses during the first year after the wildfire such that they exceeded the well-established threshold for tolerable soil losses of $1 \text{ Mg ha}^{-1} \text{ y}^{-1}$. Therefore, the long-term effects of fire and post-fire erosion on SOM quality would deserve further research attention, especially through a chrono-sequence of time-since-fire. The long-term recovery of SOM is particularly relevant from a management point-of-view, given the crucial role of SOM in the key ecosystem services provided by eucalyptus plantations such as biomass production and carbon sequestration as well as the widespread occurrence of eucalyptus plantations in Portugal and across the globe.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catena.2015.07.007>.

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