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PII: S0048-9697(20)32232-4

DOI: https://doi.org/10.1016/j.scitotenv.2020.138715

Reference: STOTEN 138715

To appear in: *Science of the Total Environment*

Received date: 12 February 2020

Revised date: 13 April 2020

Accepted date: 13 April 2020

Please cite this article as: N.T. Jiménez-Morillo, G. Almendros, J.M. De la Rosa, et al., Effect of a wildfire and of post-fire restoration actions in the organic matter structure in soil fractions, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.138715

# Effect of a wildfire and of post-fire restoration actions in the organic matter structure in soil fractions

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## Abstract

The impact of wildfires and of restoration actions on soil organic matter (SOM) content and structure was studied in a soil under pine *(Pinus pinea)* from Doñana National Park (SW Spain). Samples were collected from burnt areas before (B) and after post-fire restoration (BR) and compared with an unburnt (UB) site. Analytical pyrolysis (Py-GC/MS) was used to investigate SOM molecular composition in whole soil samples and in coarse (CF) and fine (FF) fractions. The results were interpreted using a van Krevelen graphical-statistical method. Highest total organic carbon (TOC) was found in UB soil and no differences were found between B and BR soils. The CF had the highest TOC values and FF presented differences among the three scenarios. Respect to SOM structure, the B soil was depleted in lignin and enriched in unspecific aromatics and polycyclic aromatic hydrocarbons, and in all scenarios, CF SOM consisted mainly of lignocellulose derived compounds and fatty acids. In general, FF SOM was found more altered than CF. High contribution of unspecific aromatic compounds and polycyclic aromatic hydrocarbons was observed in B-FF whereas BR-FF samples comprised considerable proportions of compounds from labile biomass, possibly due to soil mixing during rehabilitation actions. The fire caused a defunctionalisation of lignin-derived phenolics and the formation of pyrogenic compounds. The van Krevelen diagram was found useful to—at first sight—differentiate between chemical processes caused by fire and of the rehabilitation actions. Fire exerted SOM demethoxylation, dealkylation and dehydration. Our results indicate that soil management actions after the fire lead to an increase in aromaticity corresponding to the accumulation of lignin and polycyclic aromatic compounds. This suggests additional inputs from charred lignocellulosic biomass, including black carbon, that was incorporated into the soil during rehabilitation practices.

**Keywords:** Wildfires, soil organic matter, soil rehabilitation, analytical pyrolysis, chemometrics

## 1. Introduction

Fire is considered one of the main environmental disturbing factors (Neary et al., 2005). In fact, it is estimated that over 8-billion Mg of biomass is burnt globally every year (Levine, 2000). Up to 18% global biomass burning occurs in European forests and mainly in Mediterranean areas where the largest number of fire events (≈50.000 per year) are recorded. Only during 2018, over 7 thousand fire events occurred in Spain that affected more than 29.000 ha of forest (MAPA Spain, 2019). Wildfires may have negative impacts on soil fertility, biodiversity, land resources, global warming and human assets, but also positive environmental effects can occur such as enhanced forest regeneration and nutrient recycling (Stephens et al., 2009). Nonetheless, the positive or negative impact of fire on a particular ecosystem will depend on many factors i.e., fire severity, weather conditions, soil type, topographic constraints vegetation type, fuel characteristics and soil moisture, etc. (Certini et al., 2005; De la Rosa et al., 2008a).

In general, the effect of an average wildfire on the soil profile is restricted to the surface and shallowest layers (< 5 cm depth) (Aznar et al., 2016, Badía et al., 2014). However, is in this uppermost layer where most of the SOM is located and affected to a greater extent by the impact of fire. Therefore, fire may affect primarily topsoil SOM exerting thermal removal (combustion) of all or part of this organic layer, leading to a transformation of the original SOM and the emergence of newly-formed structures, or even in the short time after the fire, a build-up of biogenic partially charred biomass in the form of additions from the fire-affected standing vegetation. So, fire-affected SOM may ultimately consist of a complex mixture of more or less transformed materials with different origin (pyrogenic or biogenic) (González-Pérez et al., 2004, 2008; Jiménez-Morillo et al., 2016a; Miller et al., 2020).

It is known that the effect of fire on SOM chemical composition leads to a loss of lignocellulosic material that dominates in plant biomass, and to a concomitant increase in recalcitrant carbon compounds (De la Rosa et al., 2008b; González-Pérez et al., 2004; Tinoco et al., 2006) made up mainly of condensed structures produced by dehydration and cyclization reactions of raw material (Baldock and Smernik, 2002). Such carbon combustion products, collectively referred to as black carbon, have not a defined structure, ranging from residual charcoal to highly graphitized soot (Goldberd, 1985).

After a wildfire event, Governmental environmental agencies and responsible bodies—in an attempt to revert the effects of fire—invest many resources in rehabilitation actions. Such actions include a wide spectrum of management activities, ultimately motivated by aspects other than environmental health rehabilitation, and that usually include economic, cultural and even aesthetic components (Castro et al., 2010; Lindenmayer and Noss, 2006; McIver and Starr, 2000).

Amongst the most frequently used actions are: i) removing the burnt trees, also known as "salvage logging" (McIver and Starr, 2000); ii) remove and plough the land; and iii) reforestation with native or alien vegetation. Nevertheless, some of these practices may be harmful to soil, sometimes producing more damage than the fire itself. For instance, salvage logging can degrade ecosystem functions and vegetation regeneration, animal and plant diversity, watershed runoff and erosion and nutrient cycling (Castro et al., 2010; Karr et al., 2004; Lindenmayer et al., 2008). For this reason, a body of research has focused in the study of rehabilitation activities, that far from ameliorating post-fire conditions often introduce further disturbances that delay the natural ecosystem recovery (Beschta et al. 2004, Lindenmayer et al. 2008; Pereira et al 2018; Shakesby et al., 1996). By contrast, there is a knowledge gap in the study of both, the direct and indirect effects caused by post-fire rehabilitation activities on the quality of SOM. Furthermore, it is expected that changes produced by rehabilitation activities on the vegetation, soil microbiota and even carbon and nitrogen storage should also play a relevant influence on SOM chemical composition and properties. Analytical pyrolysis (Py-GC/MS) is a fast, direct and reproducible technique increasingly used to explore the chemical composition of complex organic materials and specifically of fire-affected SOM and their fractions (e.g. Almendros et al., 2018; De la Rosa et al, 2018, 2019; Jiménez-González et al., 2016; Jiménez-Morillo et al., 2016a). Pyrolysis is defined as the thermochemical decomposition of organic materials at high temperatures in the absence of oxygen (Irwin, 1982). It is an analytical degradation technique that converts macromolecules into small fragments, which can be further separated and identified by gas chromatography-mass spectrometry (GC/MS). The pyrolytic fragments are considered to be representative of the original larger macromolecules (González-Vila et al., 2009; Leinweber and Schulten, 1993; Martin et al., 1979).

Recently the pyrolysis characteristics of soil humic substances (HS) have been investigated using TG-FTIR-MS and kinetic models and the results effectively associated to the thermal degradation of various functional groups and compounds in HS (Li et al., 2020). The authors found that most of the gas species from HS pyrolysis evolved at a temperature range of 250–500 °C and forecasted that findings for the pyrolysis of soil HS will be critical for predicting changes of the global carbon cycle and soil ecosystems as affected by future climate and fire regimes.

The combination of graphical-statistical methods, such as van Krevelen diagrams (van Krevelen, 1950), with other data i.e. proportions of compounds released by analytical degradation methods, has experienced a noticeable development to monitor chemical changes on SOM produced by natural or anthropogenic impacts (Almendros et al., 2018; Jiménez-Morillo et al., 2018). Recently, the combination between van Krevelen diagrams done from the chemical molecular formulas of Py-GC/MS released compounds has been used to evaluate the chemical alteration produced by a wildfire event on SOM and sieved fractions (Jiménez-Morillo et al., 2016a).

We hypothesize that, after a forest fire in particularly vulnerable ecosystems, restoration rehabilitation management techniques involving mechanical disruption of the topsoil, may cause additional impacts on soils leading to more severe effect than that directly caused by fire. Consequently, this work describes the effects of fire on the chemical composition of SOM and main size fractions, before and after rehabilitation actions. For this purpose, we use a novel perceptual approach combining analytical pyrolysis and a van Krevelen graphical-statistical method, to detect and characterize main chemical changes exerted by a forest fire in SOM from bulk and sieved soil fractions (coarse and fine) under pine (*Pinus pinea*) forest in Doñana National Park (SW Spain).

## 2. Materials and Methods

### *2.1. Sampling area*

A sandy soil classified as Arenosol (FAO, 2015) with a 99.2% of aeolian sand (Holocene) covering gravel and other sandy sediments (Pliocene-Pleistocene), neutral pH (6.8) and C and N contents of 8.52 % and N 0.96 % respectively was chosen for this study. The area under study is located at “Las Madres” site within the Doñana National Park (SW Spain) premises, one of the most important Mediterranean environmental reserve in Europe. The morphology and vegetation cover in the study area have intimately been associated with frequent and recurrent wildfire episodes ranging from low to medium-high severity. The study area is covered with Mediterranean vegetation dominated by pine (*Pinus pinea*) and an understory of bushes of *Halimium halimifolium*, *Daphne gnidium*, *Ulex europaeus*, *Rosmarinus officinalis*, *Lavandula angustifolia*, *Genista pseudopilosa* and *Erica arborea*.

This area is influenced by a Mediterranean climate, where wildfires occur during the warmest, dry season with extreme temperatures. Rainfall is episodic (average 550 mm year$^{-1}$) and highly variable ranging from 200 mm and 1100 mm in a unique rainfall regime and an almost total absence of rain events during the summer (Siljeström and Clemente, 1990).

The sampling area was affected by a wildfire episode in August 2013, burning 80 ha of the pine forest. Two months after the wildfire event, forest managers commenced the restoration actions, which consisted of salvage logging, removing burnt trees, tillage (plough) and reforestation with nursery pine species. The sampling was carried out after the wildfire event and one year after the restoration actions (October 2014). Three composite samples were collected; two in a burnt area, before (Burnt "B": 37° 4'13.27"N, 6°37'18.71"W) and after its restoration (Burnt and restored "BR": 37° 4'11.10"N; 6°37'17.86"W). Also, a control soil sample was collected in a neighbour area not affected by fire (Unburnt "UB": 37° 4'9.00"N; 6°37'16.54"W). All samples were collected in duplicate in nearby points under the same vegetation cover, soil type, physiographic and climatic characteristics. The UB sampling place has a known history of more than 10 years without being affected by fire. Each composite sample was prepared by combining six sub-samples taken within a circular area of *c*. 20 m$^2$ under a well-developed vegetation cover. After the removal of the litter layer, the top 3 cm of soil was sampled and transported to the laboratory in glass containers to avoid contamination by plasticizers and other alien substances. The soil samples were air-dried at laboratory conditions (at 25 °C and approximately 50% relative humidity) during 1 week and sieved (< 2 mm, fine earth) to remove gravel and litter fragments. Each combined fine earth sample (total or whole sample) was further divided by dry sieving into two fractions (1–2 mm "coarse (CF)" and <0.05 mm "fine (FF)").

### *2.2. Total Organic Carbon (TOC)*

Total organic C (TOC), was analysed by dry combustion, both in the bulk samples and its two particle size fractions, using a Flash 2000 HT (C, H, N, O and S) elemental analyser coupled to a thermal conductivity detector (TCD) (Thermo Scientific, Bremen, Germany). Each determination (weight range 1–1.5 mg) was done in triplicate. A calibration curve was made using the recommended standard materials (soil standards series from Elemental Microanalysis, Devon, United Kingdom) also in triplicate.

### *2.3. Analytical Pyrolysis (Py-GC/MS)*

Pyrolysis-GC/MS was carried out using a double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to an Agilent 6890N gas chromatograph. Soil samples (1–2 mg) were placed in small crucible capsules and introduced into a pre-heated furnace at 500 °C for 1 min. The pyrolysis evolved gases were then directly introduced for analysis into the GC inlet line heated at 250 ºC to prevent condensation. The GC was equipped with a low polarity-fused silica capillary column (J&W Scientific) of 30 m × 250 μm × 0.25 μm film thickness (Ref. DB-5). 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. The transfer line from GC to MSD was set at 280 ºC and the carrier gas was helium at a controlled flow of 1 mL min$^{-1}$. The detector consisted of an Agilent 5973 MSD (mass selective detector), and mass spectra were acquired with a 70 eV ionizing energy. The compound assignment was achieved by monitoring diagnostic ions for the main homologous series, via low-resolution MS and via comparison with published and stored (NIST and Wiley libraries) data. Finally, to summarize the results, the compounds released by Py-GC/MS were categorized into 9 families with known biogenic origin: unspecific aromatic compounds (UAC), polysaccharide-derived (S), protein-derived (P), lignin-derived (methoxyphenols) (Lig), *n*-alkane/alkene pairs (AU+AS), nitrogen compounds (N comp), polycyclic aromatic hydrocarbons (PAH), fatty acids (FA) and others (O). A semi quantification of the products released by analytical pyrolysis was done for each soil sample by converting the peak areas to a percentage of the total chromatographic area. Minor compounds with less than 0.2% of the total chromatographic area were excluded.

### *2.4. Displaying pyrolytic data as surface density plots*

Using the structural information provided by the Py-GC/MS analysis it was possible to construct three-dimensional van Krevelen diagrams as described in Almendros et al. (2018). In short, pyrolysis data were represented as density surfaces by plotting the O/C and H/C atomic ratios as inferred from the empirical formulas in the $x$, $y$ plane and pyrolytic yields for individual compounds calculated as abundances as the third dimension in the $z$ axis. These plots are helpful to compare, at first sight, fire-induced reactions that can be inferred from changes in the molecular composition of the SOM viz. decarboxylation, dehydration, demethylation, aromatization and accumulation of newly-formed polycyclic compounds. These are evident from the position and size of the major compound clusters in the diagrams (González-Pérez et al. 2004; Jiménez-Morillo et al. 2016a).

### *2.5. Statistical analysis*

To analyse the main trends in the composition of the SOM in plots affected by fires and further rehabilitation actions, pyrolytic data were also analysed chemometrically using principal components analysis (PCA) performed on the correlation matrix using a varimax rotation. This allowed the reduction of variables to a limited number of comprehensive principal components. The original variables used for PCA were the total abundances of the different families of compound released by pyrolysis of soils in the different scenarios (UB, B and BR). The PCA was performed with the “Statistical Package of Social Sciences” (SPSS) 23.0.

## 3. Results

### 3.1. Organic carbon content

The highest TOC value within bulk soil samples was found for the UB samples, whereas no differences were apparent between the burnt ones (B and BR). Regarding the different particle-size fractions, CF showed the highest TOC value (> 25 %) and a similar TOC decreasing trend than in bulk soil samples (UB>B>BR). The TOC in FF fraction showed differences between sampling scenarios with B-FF sample showing the highest TOC value and BR-FF the lowest (Fig. 1).

### 3.2. Analytical pyrolysis

The cumulative values of the main families of pyrolysis compounds, (Table 1). The surface density plots are depicted in Fig. 2 facilitates the comparison of the chemical structure of the SOM in the different samples.

In the bulk soil samples, UB is found mainly composed by UAC (23%), S (19%), P (18%) and Lig (15%) (Fig. 2A). In contrast, the SOM of B is made up of UAC (>37%), P and S (17% and 16%, respectively). Furthermore, this sample shows a noticeable lignin depletion (< 4%) (Fig. 2B). The BR SOM (Fig. 2C) is composed by UAC (27%), S (19%), P (17%) and Lig (15%). Also, BR SOM has the highest FA relative content (1%).

As regards to the particle size fractions, there are appreciable differences both between the two soil fractions and scenarios. In the UB site, UB-CF fraction (Fig. 2D) shows a high contribution of S and Lig compounds (27% and 19%, respectively), whereas SOM in UB-FF the lipid compounds are the majority (AU+AS, 29%). Furthermore, this fraction displays an almost complete elimination of polysaccharide derived compounds (S) (2%) (Fig. 2G). SOM in B-CF (Fig. 2E) consists mainly of UAC (21%), S (27%), and Lig (21%), whereas the B-FF (Fig. 2H) shows a major contribution of UAC and P compounds (30% and 19%

respectively). In the BR site the BR-CF (Fig. 2F), is mainly composed of Lig and S compounds (32% and 21% respectively). In contrast, the BR-FF SOM (Fig. 2I) is dominated by P, UAC, S and AU+AS (18%, 19%, 16% and 14%, respectively) and displays also the highest relative abundance of FA (10%).

### *3.3. Principal Components Analysis (PCA)*

The results of PCA are represented as a biplot in Fig. 3. In this plot the eigenvectors point to regions with the high loading factors for the variables processed (cumulative percentages of the main groups of pyrolysis compounds), whereas the small squares in the vertices of the triangles indicate soil samples from the three scenarios (UB, B, BR) grouped according to the type of sample, corresponding to bulk soil (B), coarse (CF) and fine (FF) fractions. A high proportion of the total variance (84%) can be explained by the two first components (component 1: 54% and component 2: 30%). The PCA suggested that the samples could be grouped in the above indicated three clusters depicted with triangles, which suggest that most of the variability corresponds to the soil granulometric fraction (bulk, coarse and fine fractions), more than to the impact of fire (UB, B) or rehabilitation practices (BR).

The first cluster, that encompasses the bulk soil samples (B), is mainly influenced by UAC. The second cluster includes coarse fractions of all soil samples. This group is clearly dominated by S, LIG and FA compounds. The third cluster encompasses the fine soil fractions, which shows a dominance of N compounds, PAH and aliphatic compounds (AU+AS).

## **4. Discussion.**

### *4.1. Effect on SOM quantity*

In the soil surface layer, the effect of fire may vary from either an almost elimination of SOM by fire to increases of more than 30% usually due to external additions of charred material from the burnt canopy (Chandler et al., 1983; González-Pérez et al., 2004). This may depend on several factors, both natural i.e., fire type (canopy or aboveground, underground fires “smouldering”), intensity, severity, persistence and even by soil slope (De la Rosa et al., 2008a), and also by anthropogenic interventions, both pre- and post-fire (Francos et al., 2018). One of the most frequent anthropogenic factors is restoration (reforestation, ploughed, salvage logging, etc.).

In this study, the fire produced a SOM loss in the bulk soil samples before and after restoration. Furthermore, there were no differences in TOC between the samples from the burnt soils (B and BR). The same trend appeared in the coarse fraction, but this fraction, as usual in sandy soils, contains more than three times as much organic matter as the bulk soil (Fig. 2). This has been previously observed by several researchers in soils under different canopies (Bird et al., 2000; Nocentini et al., 2010). Jiménez-Morillo et al. (2016a, b, 2017) found that, after the fire, bulk soil samples and its particle size fractions showed increased values of TOC, that was attributed to an additional input of charred biomass. However, here the results showed an opposite trend and a possible interpretation may be linked to the combustion of the old litter layer. This generates the emission of combustion gases ($CO_2$, $NO_x$, etc.), as well as small charred particles to the atmosphere (Willoughby et al., 2016). At the same time, fire may lead to the production of finely-divided charred particles from the pine needles that will eventually add to the fine soil size fractions, thus explaining the TOC increase observed after the wildfire event (Fig. 1). This is in line with previous findings by Skjemstad et al, (1996) that observed an input of small charred particles in fine fractions after a fire which increased the stock of C in the soil. On the other hand, the decrease of TOC content in the BR-FF may be due to a mixing process of shallow (rich in OM) and deep (poor in OM) soil layers during the rehabilitation actions. This may produce a "dilution-effect" between fine fractions present in topsoil and deeper soil layers.

### *4.2. Effects on SOM quality.*

The fire does not only affect the total amount of SOM, but also exerts changes in its chemical composition, either by the incorporation of external material (charred and/or fresh) or by the chemical alteration of the existing SOM (González-Pérez et al., 2004). Recently, van Krevelen diagrams have been implemented to gain information about chemical alterations in SOM exerted by natural and/or anthropogenic factors (Hernández et al., 2018). On the other hand, the combination of this graphical tool and analytical pyrolysis has allowed shedding light on specific chemical fire-induced reactions on SOM (Jiménez-Morillo et al., 2016a, 2018).

In general, SOM in a fire-affected site is characterized by increased aromaticity (Almendros et al., 1988, 1992; Jiménez-Morillo et al., 2018). This may be produced by three processes: i) selective removal thermolabile compounds, mainly carbohydrate and the concomitant concentration of an aromatic residue; ii) newly formed pyrogenic aromatic products; iii) external inputs of charcoal, black-carbon intergrades, from charred plant necromass (Almendros et al., 1997; Miller et al., 2020).

In our case, the results (Table 1 and Fig. 2) showed that, effectively, burnt SOM in the bulk soil samples had a substantial domain of aromatic/condensed compounds with a concomitant depletion of carbohydrates and probably a defunctionalization of lignin-like compounds yielding UAC. The BR SOM in bulk soil sample showed an increase of UAC -which clearly reflect the effect of fire- and a conspicuous decrease of hydroaromatics and unsaturated hydrocarbons. Previous studies have shown that SOM chemical composition of in bulk samples may differ greatly to that in particle size fractions (Jiménez-Morillo et al., 2016a, b, 2017, 2018).

Our results showed that SOM from coarse fractions from unaffected (UB) and fire-affected (B and BR) soils consists of fresh material (i.e., mainly composed of carbohydrates and lignin-like compounds) (Table 1, Figs 2 and 3). Jiménez-Morillo et al. (2018), using ultra-high resolution mass spectrometry, observed this fact in a nearby area but under cork oak canopy. Nevertheless, the fire effect is perceptible in B and BR coarse fractions and reflected in an increase of UAC and a decrease of lignin and alkyl compounds (Fig. 2). This may be caused by two main mechanisms: i) the incorporation of new pyrogenic material characterized by a condensed structure and ii) the chemical alteration of lipid compounds in both charred litter and oldest SOM in the soil surface. In fact, fire may produce either a cycloaddition of alkene compounds by the Diels-Alder pathway (Jiménez-Morillo et al., 2018), followed of an aromatization reaction or as González-Pérez et al. (2008) found, thermal evaporation of free lipids together with a thermal cracking process. This trend is also observed in the case of coarse fractions, in particular the decrease in the content of alkyl products, however the samples retain in all cases an appreciable lignin content, which may correspond to the predominance of partially-decomposed plant remains in the coarse fractions. In the case of the coarse fraction of B and BR soil, a greater similarity is observed concerning the original soil; in fact, a significant proportion of carbohydrate and lignin has been re-established and the loss of aliphatic compounds both alkanes and fatty acids is not noticeable. On the other hand, the BR coarse fraction showed a high relative amount of lignin-like and polysaccharide compounds. This may be due to a further input of wood material during logging activity from the sawed branches and stems, adding an uncommon amount of lignocellulose compounds to the soil.

On the opposing side, SOM in the fine fraction showed a more pronounced humic character, with a remarkably high proportion of UAC, alkyl and protein-like compounds and a low proportion of polysaccharides and lignin-like compounds. This may be attributed to enhanced biological activity. Kellner et al. (2014) observed that some fungal species can defunctionalize lignocellulosic material producing UAC. Concerning the presence of alkyl compounds, lignin oxidation by enzymatic hydroxyl radicals involves ring hydroxylation and ring-opening to produce unsaturated aliphatic compounds (Higuchi, 2004). In this research, it is observed that fire, directly or indirectly, may affect the chemical composition of SOM in soil fine fractions. Recently, Jiménez-Morillo et al. (2018) observed that burnt SOM in fine soil fractions consists of two differentiated C pools; one from the microbial alteration of SOM and other from inputs of pyrogenic material. The van Krevelen density map of B-FF (Fig. 2H), as well as its position in the PCA biplot (Fig. 3), points again to the fact that SOM in this soil shows two well-differentiated C pools. After the wildfire, fine fractions contain a relatively high proportion of lignin-like compounds that suggest additional input of partially charred wood particles. On the other hand, the large proportion of carbohydrate and fatty acids in BR-FF (Fig. 2I) may indicate that restoration activities have produced a mixing of the newer and older SOM.

### *4.3. Chemical reactions produced by the fire.*

The two-dimension contour van Krevelen plot diagrams obtained by subtracting the compound abundances from pairs of samples corresponding to the different scenarios (Fig. 4) is auto-explicative and summarizes the selective effects of fire and restoration in the soil physical fractions. In these graphs, the proportion of compounds that predominate in the burnt samples with respect to the unburnt or restored presents positive values and are depicted in red colour (it would indicate both, a generation of pyrogenic products or the selective accumulation of heat-resistant structures or both). Conversely, compounds that are more abundant in soils not affected by fire, or in soils subjected to rehabilitation practices present negative values and are shown in blue. Then, positive and negative values (red, blue respectively) illustrate accumulation or depletion of pyrolytic compounds characteristic for each compared scenario, then simplifying the visual identification of the balance between compound groups which reflect with its abundances the impact of fire in the whole soil and its different soil particle fractions.

Therefore, in the whole bulk soil fire produced two different reactions depending on if it was restored or not. A reduction chemical reaction in the B bulk soil sample is evidenced by the elimination of carbohydrates and lignin-like compounds. Within particle size fractions, there were differences between coarse and fine, but there were no major differences between sample before and after restoration. The B and BR coarse fraction suffered an oxidation reaction, which could be well linked with an input of new litter (rich in lignocellulosic compounds). On the other hand, a hydration reaction (rising O/C and H/C) observed in the fine fraction may be attributed to the relative increase of alkyl, carbohydrate and lignin-like compounds. This result is in agreement and confirms previous findings by Jiménez-Morillo et al. (2016a).

## 5. Conclusions

The results obtained suggest that fire and restoration are factors with a significant effect on the quantity and quality of the SOM. The fire leads to a depletion of organic matter in the whole soil and its coarse fraction, resulting from losses of volatile compounds. On the contrary, the concentration of organic matter in the fine soil fraction increased to some extent, at expenses of pyrogenic material from the combustion of the organic matter in coarser fractions. The restoration, produces a general decrease in soil organic matter levels, to a large extent attributed to the mixing and turning of topsoil materials with deeper soil layers, with lower organic carbon content. Concerning SOM quality, the combined use of statistical techniques, such as PCA and the representation of the pyrolytic results as surface density plots in the space defined by the atomic ratios of the pyrolysis compounds, suggested independent changes in SOM either produced by fire or by the subsequent restoration. The non-restored soil samples consist of three different types of organic matter: i) extensively transformed organic matter, with a large influence of alkyl compounds from a possible microbial activity, the same occurs in the unburned sample, ii) organic matter from the partial combustion of plant residues in coarsest particle fractions, mainly thermally altered lignin and iii) heavily condensed, aromatic organic matter of pyrogenic origin. On the opposing side, the organic matter contained in the restored fine fraction shows a remarkable proportion of fresh material (lignin, carbohydrates and fatty acids).

To the best of our knowledge, this is the first attempt to explain the effect of post-fire rehabilitation in SOM composition at a molecular level. A better knowledge of the effect of fire and of rehabilitation practices in SOM and its evolution with time using appropriate and easy to interpret graphical statistical approaches may help decision-makers in choosing the best practices to optimize soil post-fire management and rehabilitation strategies.

## Acknowledgements.

To projects INTERCARBON, CARBOSOIL, and POSTFIRE Projects (CGL2016-78937-R, CGL2013-43845-P and CGL2013-47862-C2-1-R, respectively) funded by the Spanish Ministry for Economy and Competitiveness. The authors also thank project EROFIRE (PCIF/RPG/0079/2018) funded by Fundação para a Ciência e a Tecnologia (FCT, Portugal). N.T. Jiménez-Morillo was funded by an FPI research grant (BES-2013-062573). Alba Carmona Navarro and Desire Monis Carrere are thanked for their technical assistance in Py/GC–MS analysis. Finally, we will like to thank the editor Paulo Pereira and two anonymous reviewers for their thorough, helpful and always constructive comments.

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## Figure captions.

**Fig. 1.** Total organic carbon content (TOC, %) in bulk soil and particle-size soil fractions. Error bars indicate standard deviations between spatial replications.

**Fig. 2.** Surface density plots displaying cumulative abundances of pyrolysis products plotted in the space defined by their atomic H/C and O/C ratios. Labels on the plots indicate major groups of organic compounds: ALK= alkyl compounds (alkanes + alkenes); FA= fatty acids (FA); HYD= hydroaromatics (terpenes, steroids, tetralins…); ARO= unspecific aromatics (alkylbenzenes, naphthalenes, phenanthrenes); PHE= alkylphenols; LIG= lignin-derived; PS= polysaccharide-derived.

**Fig. 3.** Principal Component Analysis of UB, B and BR samples. Labels for the eigenvectors indicate main groups of organic compounds: unspecific aromatic compounds (UAC), lignin-derived (LIG), N-compounds (N comp), *n*-alkanes (AS, alkyl saturated), alkenes (AU, alkyl

unsaturated), fatty acids (FA), polycyclic aromatic hydrocarbons (PAH), polysaccharide-derived (S) and other compounds (O).

**Fig. 4.** Effects of fire and rehabilitation practices on the patterns of pyrolytic products in the different granulometric fractions. Subtraction of density maps showing the percentages of pyrolysis products represented in the space defined by the H/C and O/C atomic ratios of the corresponding compounds. Colour scale of the contour diagrams resulting after the subtraction of compounds abundances indicate the proportions of the compounds that increase in quantity as a result of the effect of fire (negative values) are in red colours), while blue colours indicate compounds that predominate in the unaltered sample, or in the sample subjected to rehabilitation practices.

Table 1: Cumulative abundances (%)* of the main chemical families** released after pyrolysis of bulk soil samples and particle-size soil fractions.

| | UB | | | B | | | BR | | |
|---|---|---|---|---|---|---|---|---|---|
| Family | Bulk | CF | FF | Bulk | CF | FF | Bulk | CF | FF |
| UAC | 22.6 | 16.5 | 15.7 | 37.4 | 21.0 | 29.5 | 27.1 | 18.0 | 19.1 |
| S | 19.2 | 27.3 | 2.4 | 15.9 | 27.2 | 10.0 | 19.3 | 21.4 | 16.2 |
| P | 17.9 | 9.0 | 5.7 | 16.8 | 13.0 | 19.0 | 17.3 | 8.4 | 18.0 |
| Lig | 15.0 | 19.1 | 6.5 | 3.5 | 21.1 | 8.9 | 14.6 | 31.6 | 10.0 |
| AU+AS | 11.6 | 11.6 | 28.9 | 11.9 | 6.4 | 11.8 | 9.2 | 6.8 | 13.5 |
| O | 9.6 | 6.9 | 24.8 | 7.8 | 3.9 | 7.8 | 6.5 | 5.6 | 6.4 |
| N comp | 2.2 | 0.9 | 3.8 | 3.3 | 0.5 | 3.4 | 2.7 | 0.4 | 1.2 |
| PAH | 1.5 | 2.2 | 9.7 | 3.4 | 0.3 | 4.1 | 2.0 | 1.6 | 5.9 |
| FA | 0.3 | 6.5 | 2.5 | 0.1 | 6.5 | 5.4 | 1.1 | 6.2 | 9.7 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

*) Relative to total ion count area. Compounds with peak area > 0.2% of total chromatographic area were not taken into account.

**) Unspecific aromatic compounds (UAC), polysaccharide-derived (S), protein-derived (P), lignin-derived (methoxyphenols) (Lig), *n*-alkane/alkene pairs (AU+AS), nitrogen compounds (N comp), polycyclic aromatic hydrocarbons (PAH), fatty acids (FA) and others (O).

**Author statement file**

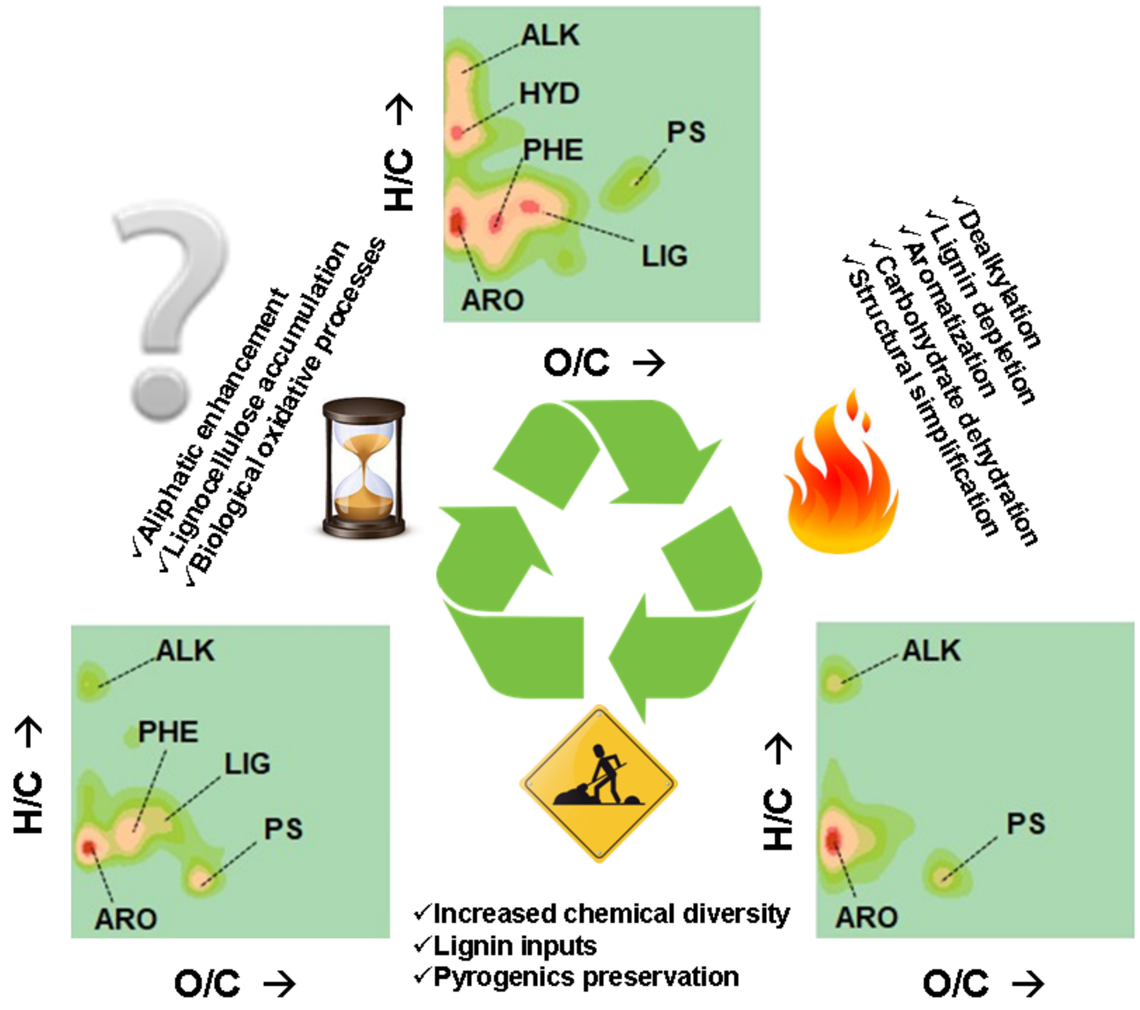
**José A. González-Pérez, Gonzalo Almendros, José M. De la Rosa and Antonio Jordán:** Conceptualization, Methodology, Resources, Funding and Supervision

**All authors** contributed equally to Validation, formal analysis, visualization.

**Nicasio T. Jiménez-Morillo, Lorena M. Zavala, Arturo J.P. Granged:** Investigation (performing the experiments, data/evidence collection)

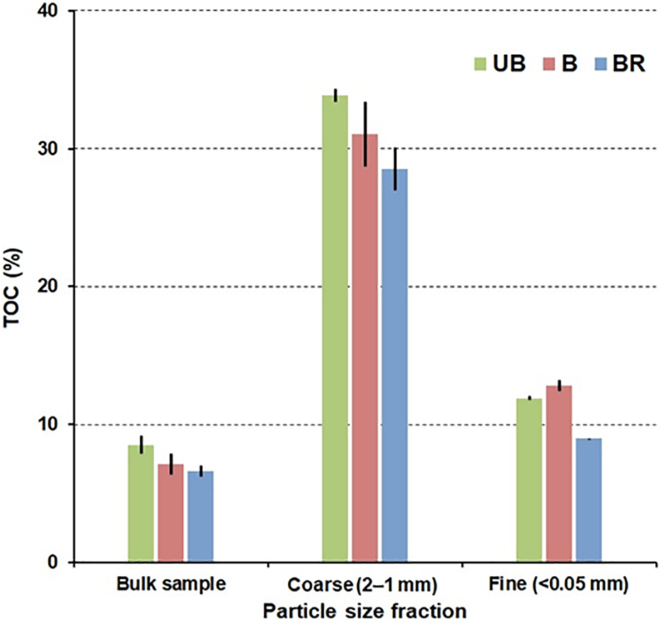
**All authors** contributed equally to writing - review & editing this work

## GRAPHICAL ABSTRACT



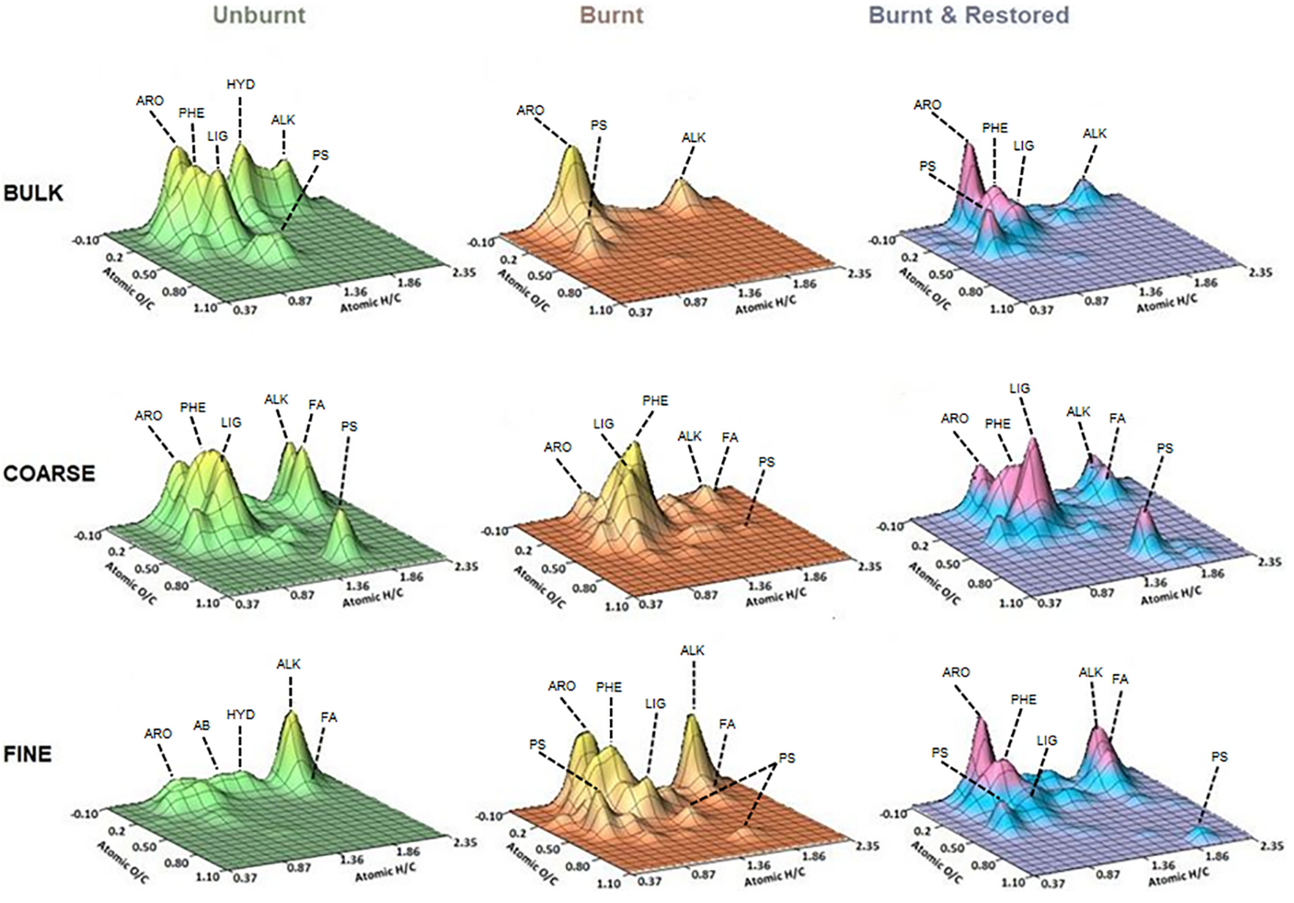
## HIGHLIGHTS

- Analytical pyrolysis revealed differences among burnt, restored and unburnt areas
- The fine fractions were more altered than the coarse and composition differed between scenarios
- Fire induced defunctionalization of lignin phenols and the formation of recalcitrant compounds
- Demethoxylation, dealkylation and dehydration were the main fire-mediated processes in SOM



TOC (%)
0
10
20
30
40
🟩 UB
🟥 B
🟦 BR
Bulk sample
Coarse (2–1 mm)
Fine (<0.05 mm)
Particle size fraction

Figure 1


Unburnt
Burnt
Burnt & Restored
BULK
ARO
PHE
LIG
HYD
ALK
PS
-0.10
0.2
0.50
0.80
1.10
Atomic O/C
0.37
0.87
1.36
1.86
2.35
Atomic H/C
ARO
PS
ALK
ARO
PS
PHE
LIG
ALK
COARSE
ARO
PHE
LIG
ALK
FA
PS
ARO
LIG
PHE
ALK
FA
PS
ARO
PHE
LIG
ALK
FA
PS
FINE
ARO
AB
HYD
ALK
FA
ARO
PHE
PS
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ALK
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PS
ARO
PS
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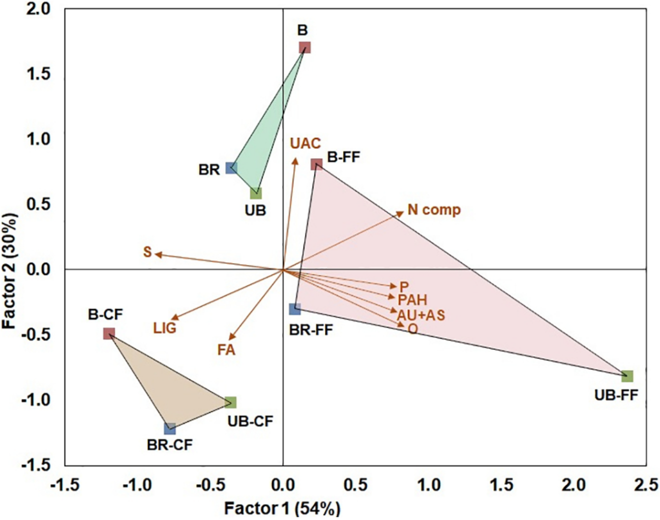
LIG
ALK
FA
PS

Figure 2



2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
Factor 2 (30%)
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
Factor 1 (54%)
B
BR
UB
B-FF
BR-FF
UB-FF
B-CF
BR-CF
UB-CF
UAC
N comp
S
LIG
FA
P
PAH
AU+AS
O

Figure 3

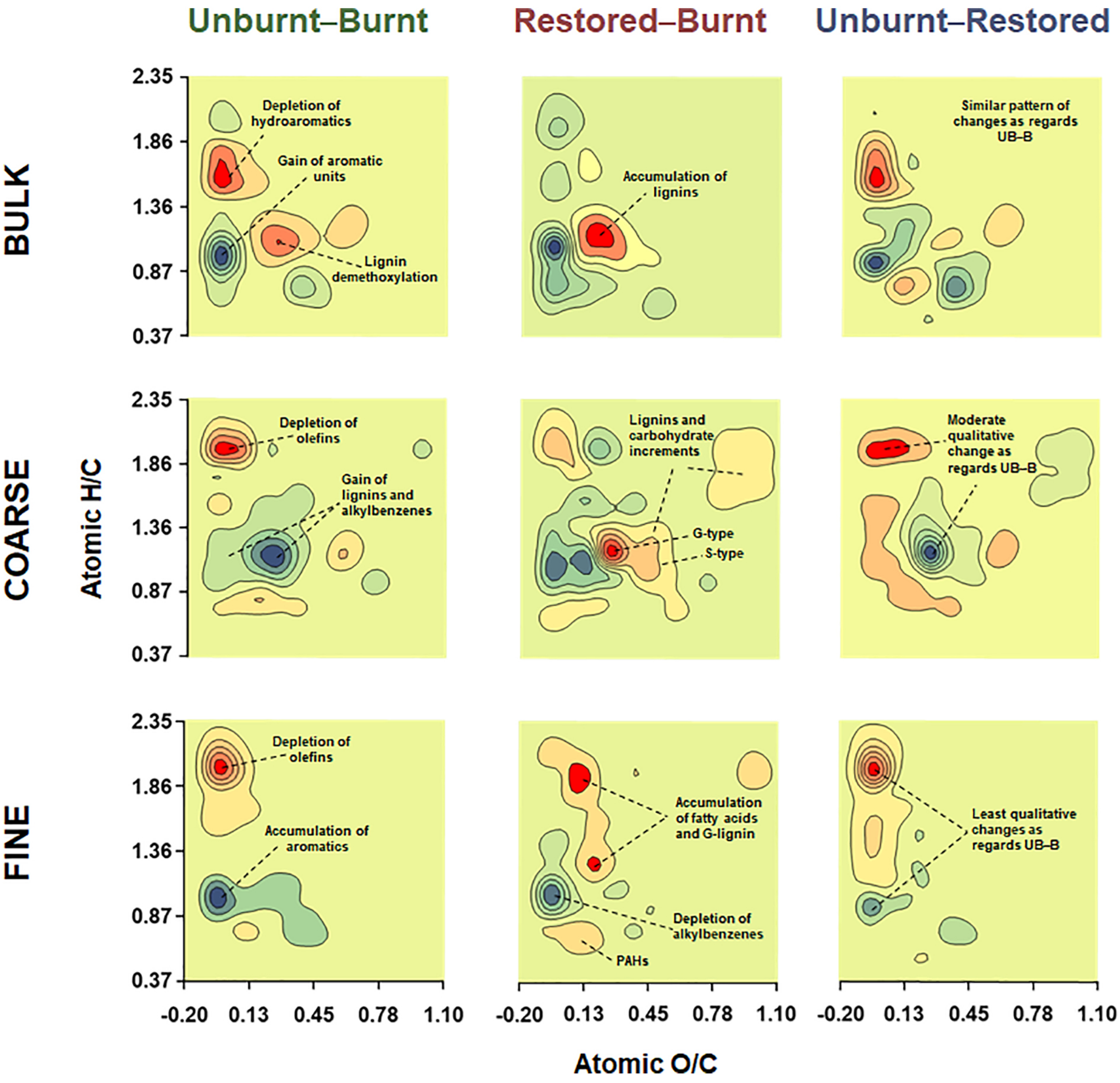

Unburnt–Burnt
Restored–Burnt
Unburnt–Restored
BULK
COARSE
FINE
Atomic H/C
Atomic O/C
2.35
1.86
1.36
0.87
0.37
-0.20
0.13
0.45
0.78
1.10
Depletion of hydroaromatics
Gain of aromatic units
Lignin demethoxylation
Accumulation of lignins
Similar pattern of changes as regards UB–B
Depletion of olefins
Gain of lignins and alkylbenzenes
Lignins and carbohydrate increments
G-type
S-type
Moderate qualitative change as regards UB–B
Depletion of olefins
Accumulation of aromatics
Accumulation of fatty acids and G-lignin
Depletion of alkylbenzenes
PAHs
Least qualitative changes as regards UB–B

Figure 4