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

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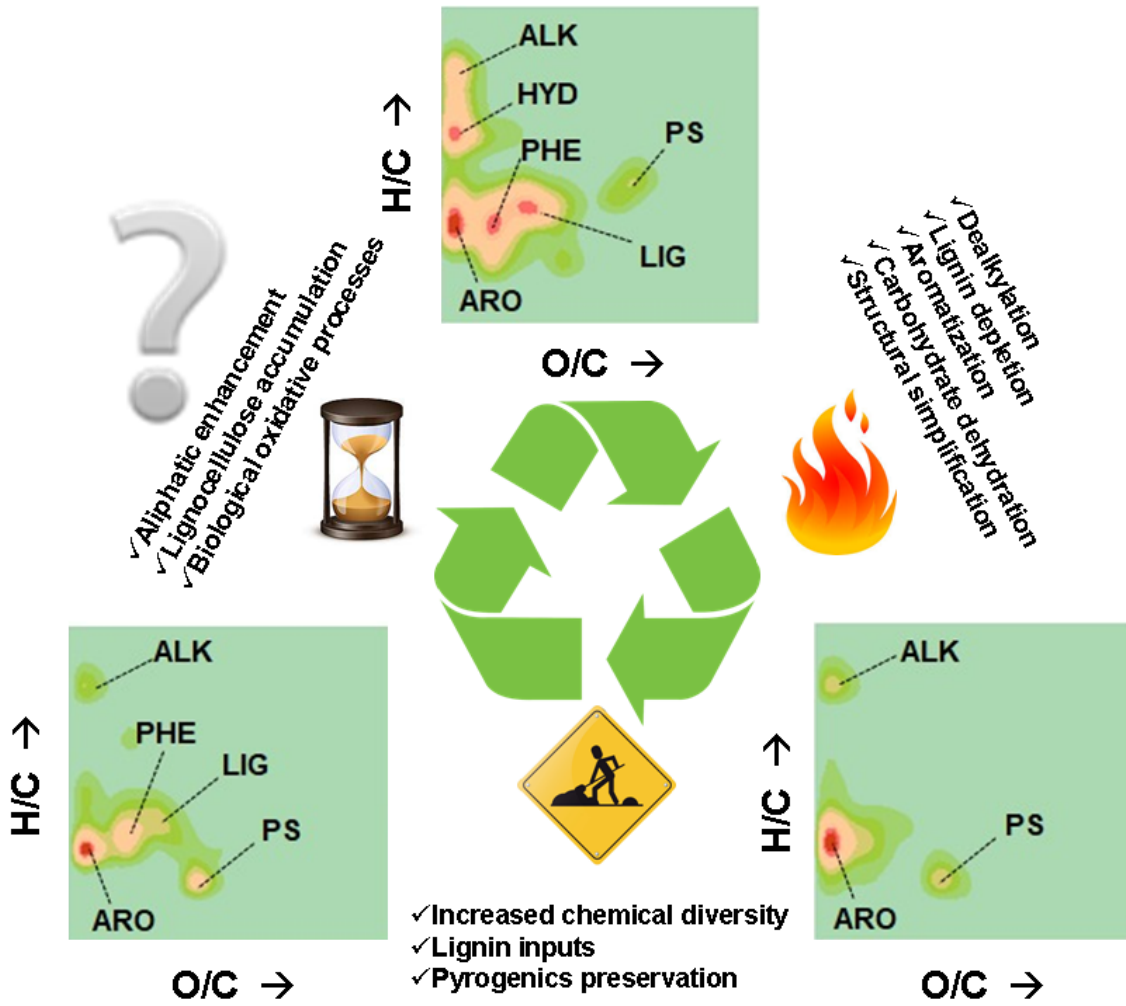
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GRAPHICAL ABSTRACT



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

20 **Abstract**

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

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

46 **1. Introduction**

47 Fire is considered one of the main environmental disturbing factors (Neary et al., 2005). In
48 fact, it is estimated that over 8-billion Mg of biomass is burnt globally every year (Levine,
49 2000). Up to 18% global biomass burning occurs in European forests and mainly in
50 Mediterranean areas where the largest number of fire events (≈ 50.000 per year) are
51 recorded. Only during 2018, over 7 thousand fire events occurred in Spain that affected
52 more than 29.000 ha of forest (MAPA Spain, 2019). Wildfires may have negative impacts
53 on soil fertility, biodiversity, land resources, global warming and human assets, but also
54 positive environmental effects can occur such as enhanced forest regeneration and nutrient
55 recycling (Stephens et al., 2009). Nonetheless, the positive or negative impact of fire on a
56 particular ecosystem will depend on many factors i.e., fire severity, weather conditions, soil
57 type, topographic constraints vegetation type, fuel characteristics and soil moisture, etc.
58 (Certini et al., 2005; De la Rosa et al., 2008a).

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

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

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

82 Amongst the most frequently used actions are: i) removing the burnt trees, also known as
83 “salvage logging” (McIver and Starr, 2000); ii) remove and plough the land; and iii)
84 reforestation with native or alien vegetation. Nevertheless, some of these practices may be
85 harmful to soil, sometimes producing more damage than the fire itself. For instance, salvage
86 logging can degrade ecosystem functions and vegetation regeneration, animal and plant
87 diversity, watershed runoff and erosion and nutrient cycling (Castro et al., 2010; Karr et al.,
88 2004; Lindenmayer et al., 2008). For this reason, a body of research has focused in the study
89 of rehabilitation activities, that far from ameliorating post-fire conditions often introduce
90 further disturbances that delay the natural ecosystem recovery (Beschta et al. 2004,
91 Lindenmayer et al. 2008; Pereira et al 2018; Shakesby et al., 1996). By contrast, there is a
92 knowledge gap in the study of both, the direct and indirect effects caused by post-fire
93 rehabilitation activities on the quality of SOM. Furthermore, it is expected that changes

94 produced by rehabilitation activities on the vegetation, soil microbiota and even carbon and
95 nitrogen storage should also play a relevant influence on SOM chemical composition and
96 properties. Analytical pyrolysis (Py-GC/MS) is a fast, direct and reproducible technique
97 increasingly used to explore the chemical composition of complex organic materials and
98 specifically of fire-affected SOM and their fractions (e.g. Almendros et al., 2018; De la Rosa
99 et al, 2018, 2019; Jiménez-González et al., 2016; Jiménez-Morillo et al., 2016a). Pyrolysis is
100 defined as the thermochemical decomposition of organic materials at high temperatures in
101 the absence of oxygen (Irwin, 1982). It is an analytical degradation technique that converts
102 macromolecules into small fragments, which can be further separated and identified by gas
103 chromatography-mass spectrometry (GC/MS). The pyrolytic fragments are considered to be
104 representative of the original larger macromolecules (González-Vila et al., 2009; Leinweber
105 and Schulten, 1993; Martin et al., 1979).

106 Recently the pyrolysis characteristics of soil humic substances (HS) have been investigated
107 using TG-FTIR-MS and kinetic models and the results effectively associated to the thermal
108 degradation of various functional groups and compounds in HS (Li et al., 2020). The authors
109 found that most of the gas species from HS pyrolysis evolved at a temperature range of 250–
110 500 °C and forecasted that findings for the pyrolysis of soil HS will be critical for predicting
111 changes of the global carbon cycle and soil ecosystems as affected by future climate and fire
112 regimes.

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

119 used to evaluate the chemical alteration produced by a wildfire event on SOM and sieved
120 fractions (Jiménez-Morillo et al., 2016a).

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

130

131 **2. Materials and Methods**

132 *2.1. Sampling area*

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

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

147 The sampling area was affected by a wildfire episode in August 2013, burning 80 ha of the
148 pine forest. Two months after the wildfire event, forest managers commenced the restoration
149 actions, which consisted of salvage logging, removing burnt trees, tillage (plough) and
150 reforestation with nursery pine species. The sampling was carried out after the wildfire event
151 and one year after the restoration actions (October 2014). Three composite samples were
152 collected; two in a burnt area, before (Burnt “B”: 37° 4'13.27"N, 6°37'18.71"W) and after its
153 restoration (Burnt and restored “BR”: 37° 4'11.10"N; 6°37'17.86"W). Also, a control soil
154 sample was collected in a neighbour area not affected by fire (Unburnt “UB”: 37° 4'9.00"N;
155 6°37'16.54"W). All samples were collected in duplicate in nearby points under the same
156 vegetation cover, soil type, physiographic and climatic characteristics. The UB sampling
157 place has a known history of more than 10 years without being affected by fire. Each
158 composite sample was prepared by combining six sub-samples taken within a circular area
159 of *c.* 20 m² under a well-developed vegetation cover. After the removal of the litter layer, the
160 top 3 cm of soil was sampled and transported to the laboratory in glass containers to avoid
161 contamination by plasticizers and other alien substances. The soil samples were air-dried at
162 laboratory conditions (at 25 °C and approximately 50% relative humidity) during 1 week
163 and sieved (< 2 mm, fine earth) to remove gravel and litter fragments. Each combined fine
164 earth sample (total or whole sample) was further divided by dry sieving into two fractions
165 (1–2 mm “coarse (CF)” and <0.05 mm “fine (FF)”).

166 2.2. Total Organic Carbon (TOC)

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

173 2.3. Analytical Pyrolysis (Py-GC/MS)

174 Pyrolysis-GC/MS was carried out using a double-shot pyrolyzer (Frontier Laboratories,
175 model 2020i) attached to an Agilent 6890N gas chromatograph. Soil samples (1–2 mg) were
176 placed in small crucible capsules and introduced into a pre-heated furnace at 500 °C for 1
177 min. The pyrolysis evolved gases were then directly introduced for analysis into the GC inlet
178 line heated at 250 °C to prevent condensation. The GC was equipped with a low polarity-
179 fused silica capillary column (J&W Scientific) of 30 m × 250 µm × 0.25 µm film thickness
180 (Ref. DB-5). The oven temperature was held at 50 °C for 1 min and then increased to 100 °C
181 at 30 °C min⁻¹, from 100 °C to 300 °C at 10 °C min⁻¹, and stabilized at 300 °C for 10 min.
182 The transfer line from GC to MSD was set at 280 °C and the carrier gas was helium at a
183 controlled flow of 1 mL min⁻¹. The detector consisted of an Agilent 5973 MSD (mass
184 selective detector), and mass spectra were acquired with a 70 eV ionizing energy. The
185 compound assignment was achieved by monitoring diagnostic ions for the main homologous
186 series, via low-resolution MS and via comparison with published and stored (NIST and
187 Wiley libraries) data. Finally, to summarize the results, the compounds released by Py-
188 GC/MS were categorized into 9 families with known biogenic origin: unspecific aromatic
189 compounds (UAC), polysaccharide-derived (S), protein-derived (P), lignin-derived
190 (methoxyphenols) (Lig), *n*-alkane/alkene pairs (AU+AS), nitrogen compounds (N comp),
191 polycyclic aromatic hydrocarbons (PAH), fatty acids (FA) and others (O). A semi

192 quantification of the products released by analytical pyrolysis was done for each soil sample
193 by converting the peak areas to a percentage of the total chromatographic area. Minor
194 compounds with less than 0.2% of the total chromatographic area were excluded.

195 *2.4. Displaying pyrolytic data as surface density plots*

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

206 *2.5. Statistical analysis*

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

215

216 **3. Results**

217 *3.1. Organic carbon content*

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

224 *3.2. Analytical pyrolysis*

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

228 In the bulk soil samples, UB is found mainly composed by UAC (23%), S (19%), P (18%)
229 and Lig (15%) (Fig. 2A). In contrast, the SOM of B is made up of UAC (>37%), P and S
230 (17% and 16%, respectively). Furthermore, this sample shows a noticeable lignin depletion
231 (< 4%) (Fig. 2B). The BR SOM (Fig. 2C) is composed by UAC (27%), S (19%), P (17%)
232 and Lig (15%). Also, BR SOM has the highest FA relative content (1%).

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

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

244 *3.3. Principal Components Analysis (PCA)*

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

255 The first cluster, that encompasses the bulk soil samples (B), is mainly influenced by UAC.

256 The second cluster includes coarse fractions of all soil samples. This group is clearly
257 dominated by S, LIG and FA compounds. The third cluster encompasses the fine soil
258 fractions, which shows a dominance of N compounds, PAH and aliphatic compounds
259 (AU+AS).

260

261 **4. Discussion.**

262 *4.1. Effect on SOM quantity*

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

271 In this study, the fire produced a SOM loss in the bulk soil samples before and after
272 restoration. Furthermore, there were no differences in TOC between the samples from the
273 burnt soils (B and BR). The same trend appeared in the coarse fraction, but this fraction, as
274 usual in sandy soils, contains more than three times as much organic matter as the bulk soil
275 (Fig. 2). This has been previously observed by several researchers in soils under different
276 canopies (Bird et al., 2000; Nocentini et al., 2010). Jiménez-Morillo et al. (2016a, b, 2017)
277 found that, after the fire, bulk soil samples and its particle size fractions showed increased
278 values of TOC, that was attributed to an additional input of charred biomass. However, here
279 the results showed an opposite trend and a possible interpretation may be linked to the
280 combustion of the old litter layer. This generates the emission of combustion gases (CO₂,
281 NO_x, etc.), as well as small charred particles to the atmosphere (Willoughby et al., 2016). At
282 the same time, fire may lead to the production of finely-divided charred particles from the
283 pine needles that will eventually add to the fine soil size fractions, thus explaining the TOC
284 increase observed after the wildfire event (Fig. 1). This is in line with previous findings by
285 Skjemstad et al, (1996) that observed an input of small charred particles in fine fractions
286 after a fire which increased the stock of C in the soil. On the other hand, the decrease of
287 TOC content in the BR-FF may be due to a mixing process of shallow (rich in OM) and

288 deep (poor in OM) soil layers during the rehabilitation actions. This may produce a
289 “dilution-effect” between fine fractions present in topsoil and deeper soil layers.

290 *4.2. Effects on SOM quality.*

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

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

305 In our case, the results (Table 1 and Fig. 2) showed that, effectively, burnt SOM in the bulk
306 soil samples had a substantial domain of aromatic/condensed compounds with a concomitant
307 depletion of carbohydrates and probably a defunctionalization of lignin-like compounds
308 yielding UAC. The BR SOM in bulk soil sample showed an increase of UAC -which clearly
309 reflect the effect of fire- and a conspicuous decrease of hydroaromatics and unsaturated
310 hydrocarbons. Previous studies have shown that SOM chemical composition of in bulk
311 samples may differ greatly to that in particle size fractions (Jiménez-Morillo et al., 2016a, b,
312 2017, 2018).

313 Our results showed that SOM from coarse fractions from unaffected (UB) and fire-affected
314 (B and BR) soils consists of fresh material (i.e., mainly composed of carbohydrates and
315 lignin-like compounds) (Table 1, Figs 2 and 3). Jiménez-Morillo et al. (2018), using ultra-
316 high resolution mass spectrometry, observed this fact in a nearby area but under cork oak
317 canopy. Nevertheless, the fire effect is perceptible in B and BR coarse fractions and
318 reflected in an increase of UAC and a decrease of lignin and alkyl compounds (Fig. 2). This
319 may be caused by two main mechanisms: i) the incorporation of new pyrogenic material
320 characterized by a condensed structure and ii) the chemical alteration of lipid compounds in
321 both charred litter and oldest SOM in the soil surface. In fact, fire may produce either a
322 cycloaddition of alkene compounds by the Diels-Alder pathway (Jiménez-Morillo et al.,
323 2018), followed of an aromatization reaction or as González-Pérez et al. (2008) found,
324 thermal evaporation of free lipids together with a thermal cracking process. This trend is
325 also observed in the case of coarse fractions, in particular the decrease in the content of alkyl
326 products, however the samples retain in all cases an appreciable lignin content, which may
327 correspond to the predominance of partially-decomposed plant remains in the coarse
328 fractions. In the case of the coarse fraction of B and BR soil, a greater similarity is observed
329 concerning the original soil; in fact, a significant proportion of carbohydrate and lignin has
330 been re-established and the loss of aliphatic compounds both alkanes and fatty acids is not
331 noticeable. On the other hand, the BR coarse fraction showed a high relative amount of
332 lignin-like and polysaccharide compounds. This may be due to a further input of wood
333 material during logging activity from the sawed branches and stems, adding an uncommon
334 amount of lignocellulose compounds to the soil.

335 On the opposing side, SOM in the fine fraction showed a more pronounced humic character,
336 with a remarkably high proportion of UAC, alkyl and protein-like compounds and a low
337 proportion of polysaccharides and lignin-like compounds. This may be attributed to
338 enhanced biological activity. Kellner et al. (2014) observed that some fungal species can

339 defunctionalize lignocellulosic material producing UAC. Concerning the presence of alkyl
340 compounds, lignin oxidation by enzymatic hydroxyl radicals involves ring hydroxylation
341 and ring-opening to produce unsaturated aliphatic compounds (Higuchi, 2004). In this
342 research, it is observed that fire, directly or indirectly, may affect the chemical composition
343 of SOM in soil fine fractions. Recently, Jiménez-Morillo et al. (2018) observed that burnt
344 SOM in fine soil fractions consists of two differentiated C pools; one from the microbial
345 alteration of SOM and other from inputs of pyrogenic material. The van Krevelen density
346 map of B-FF (Fig. 2H), as well as its position in the PCA biplot (Fig. 3), points again to the
347 fact that SOM in this soil shows two well-differentiated C pools. After the wildfire, fine
348 fractions contain a relatively high proportion of lignin-like compounds that suggest
349 additional input of partially charred wood particles. On the other hand, the large proportion
350 of carbohydrate and fatty acids in BR-FF (Fig. 2I) may indicate that restoration activities
351 have produced a mixing of the newer and older SOM.

352 *4.3. Chemical reactions produced by the fire.*

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

364 compound groups which reflect with its abundances the impact of fire in the whole soil and
365 its different soil particle fractions.

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

376

377 **5. Conclusions**

378 The results obtained suggest that fire and restoration are factors with a significant effect on
379 the quantity and quality of the SOM. The fire leads to a depletion of organic matter in the
380 whole soil and its coarse fraction, resulting from losses of volatile compounds. On the
381 contrary, the concentration of organic matter in the fine soil fraction increased to some
382 extent, at expenses of pyrogenic material from the combustion of the organic matter in
383 coarser fractions. The restoration, produces a general decrease in soil organic matter levels,
384 to a large extent attributed to the mixing and turning of topsoil materials with deeper soil
385 layers, with lower organic carbon content. Concerning SOM quality, the combined use of
386 statistical techniques, such as PCA and the representation of the pyrolytic results as surface
387 density plots in the space defined by the atomic ratios of the pyrolysis compounds,
388 suggested independent changes in SOM either produced by fire or by the subsequent

389 restoration. The non-restored soil samples consist of three different types of organic matter:
390 i) extensively transformed organic matter, with a large influence of alkyl compounds from a
391 possible microbial activity, the same occurs in the unburned sample, ii) organic matter from
392 the partial combustion of plant residues in coarsest particle fractions, mainly thermally
393 altered lignin and iii) heavily condensed, aromatic organic matter of pyrogenic origin. On
394 the opposing side, the organic matter contained in the restored fine fraction shows a
395 remarkable proportion of fresh material (lignin, carbohydrates and fatty acids).

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

401

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411

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586

587 **Figure captions.**

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

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

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

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

601 **Fig. 4.** Effects of fire and rehabilitation practices on the patterns of pyrolytic products in the
602 different granulometric fractions. Subtraction of density maps showing the percentages of
603 pyrolysis products represented in the space defined by the H/C and O/C atomic ratios of the
604 corresponding compounds. Colour scale of the contour diagrams resulting after the
605 subtraction of compounds abundances indicate the proportions of the compounds that
606 increase in quantity as a result of the effect of fire (negative values) are in red colours),
607 while blue colours indicate compounds that predominate in the unaltered sample, or in the
608 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.

Family	UB			B			BR		
	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).

Figure 1

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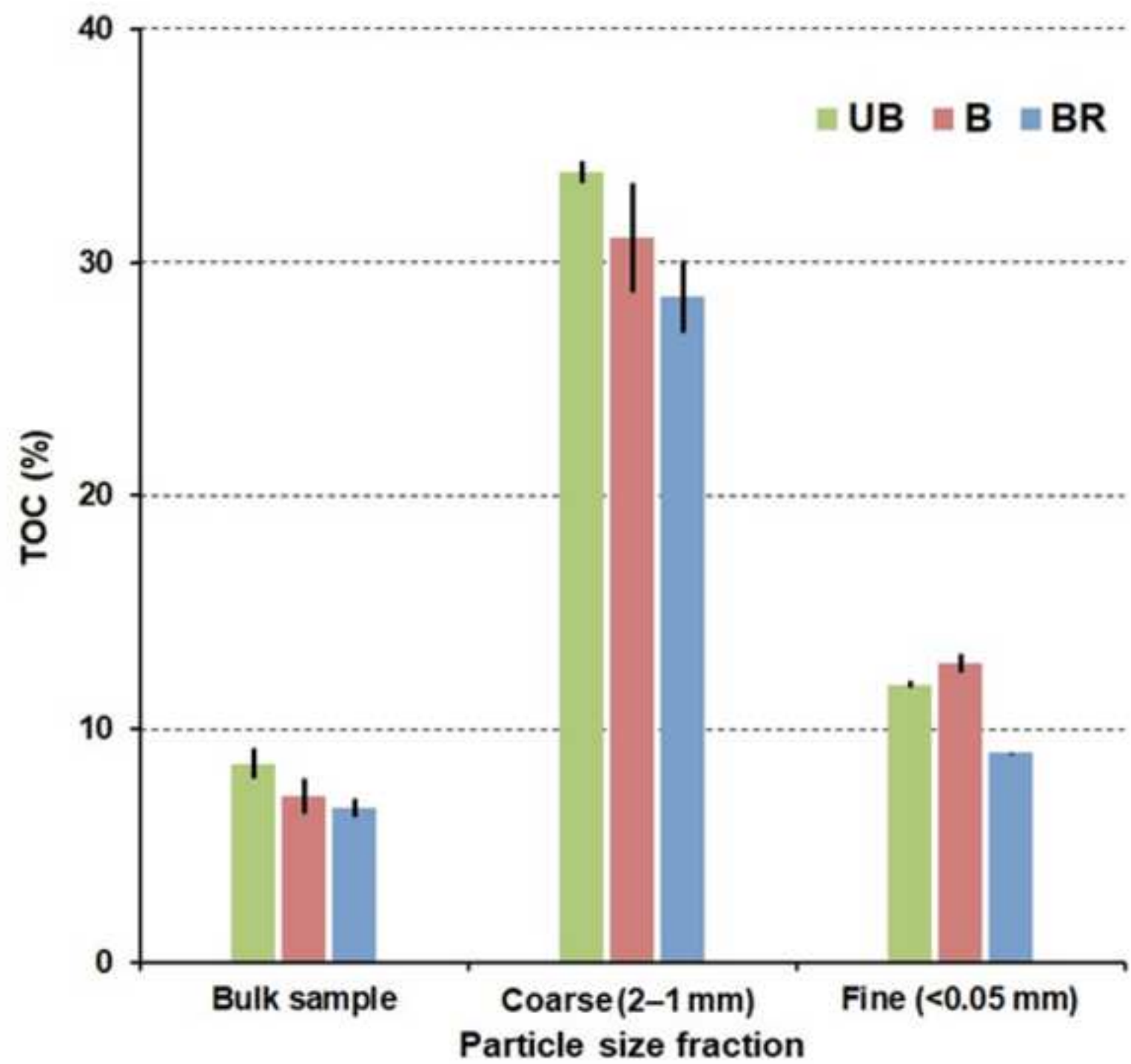


Figure 2

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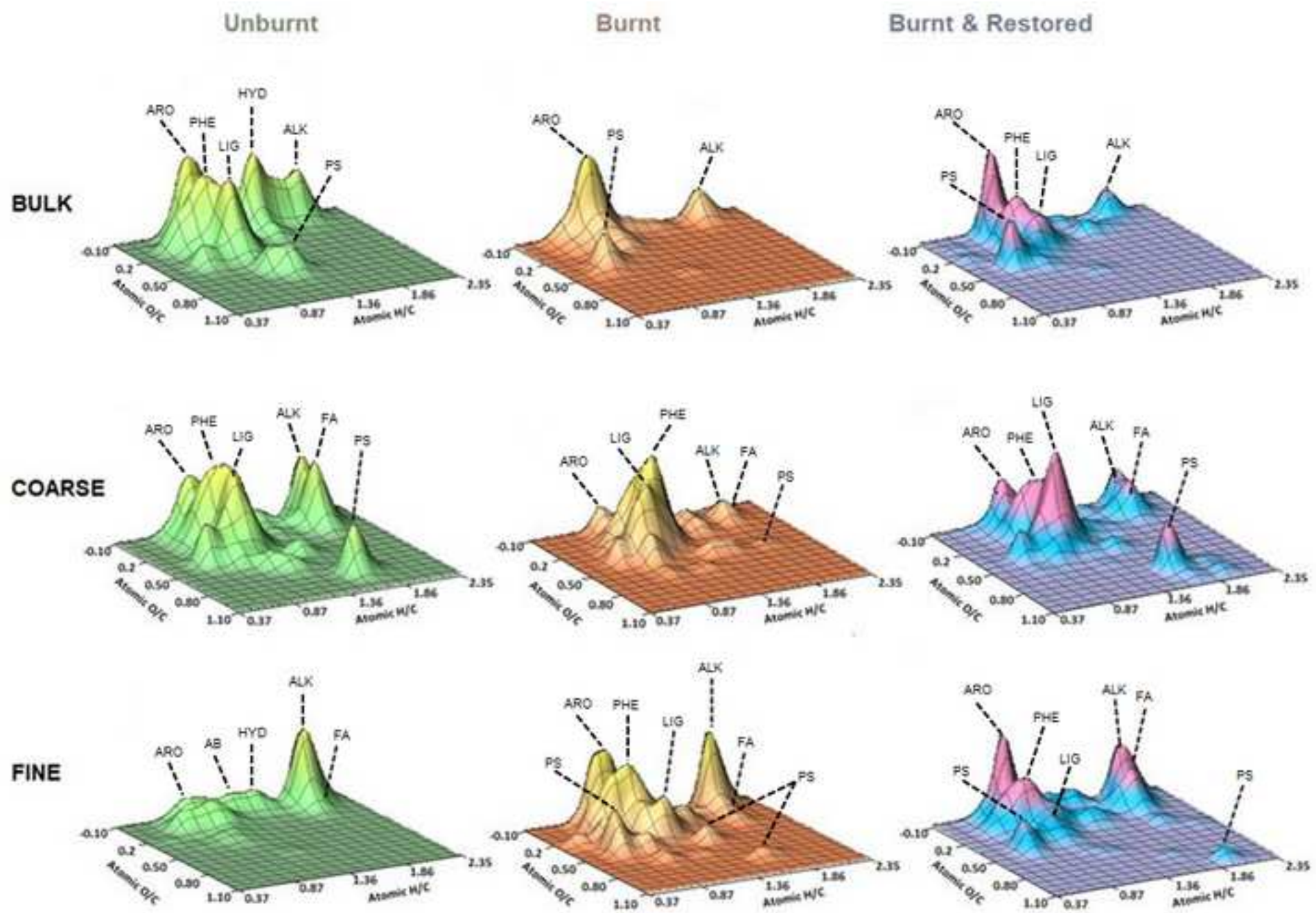


Figure 3

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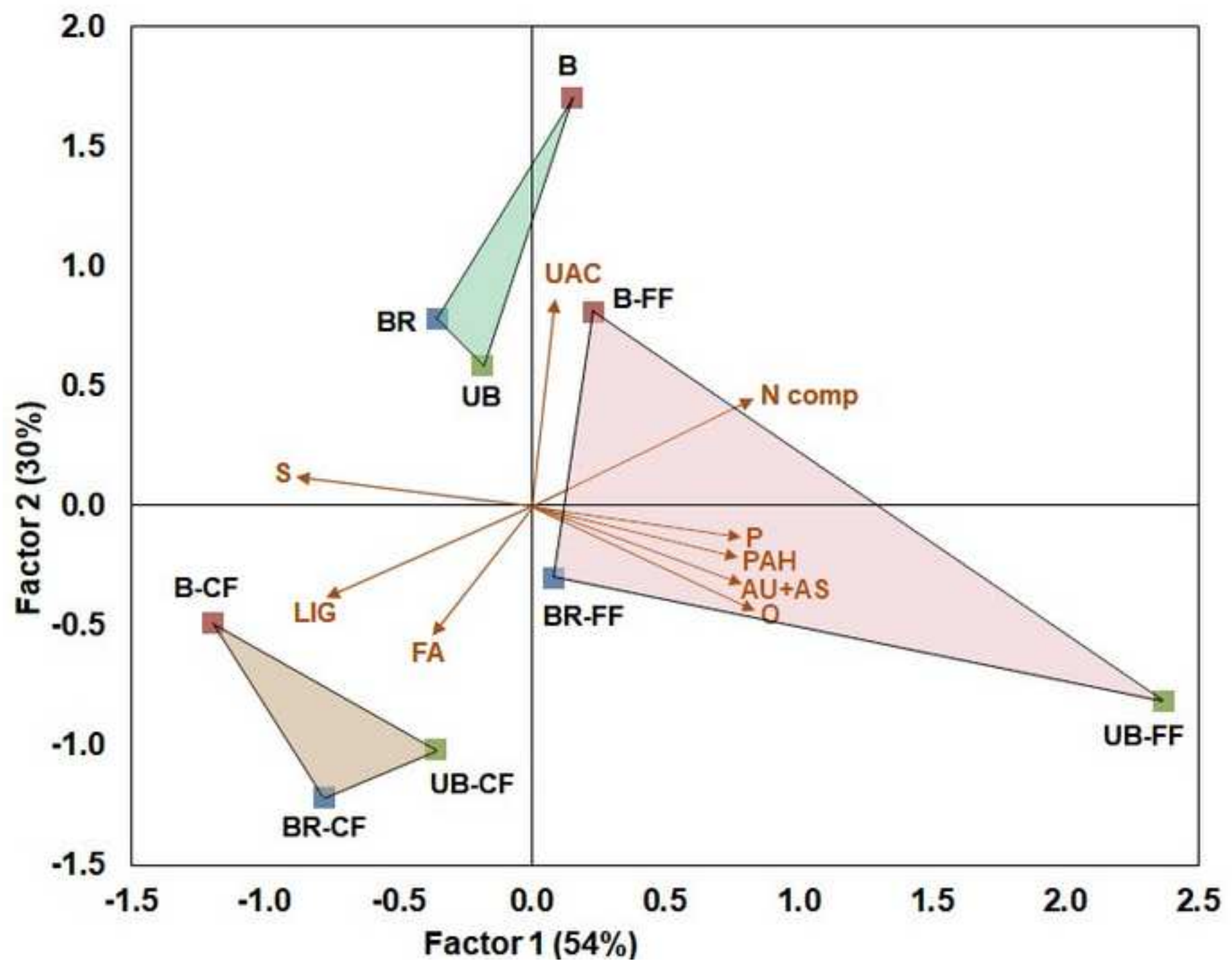
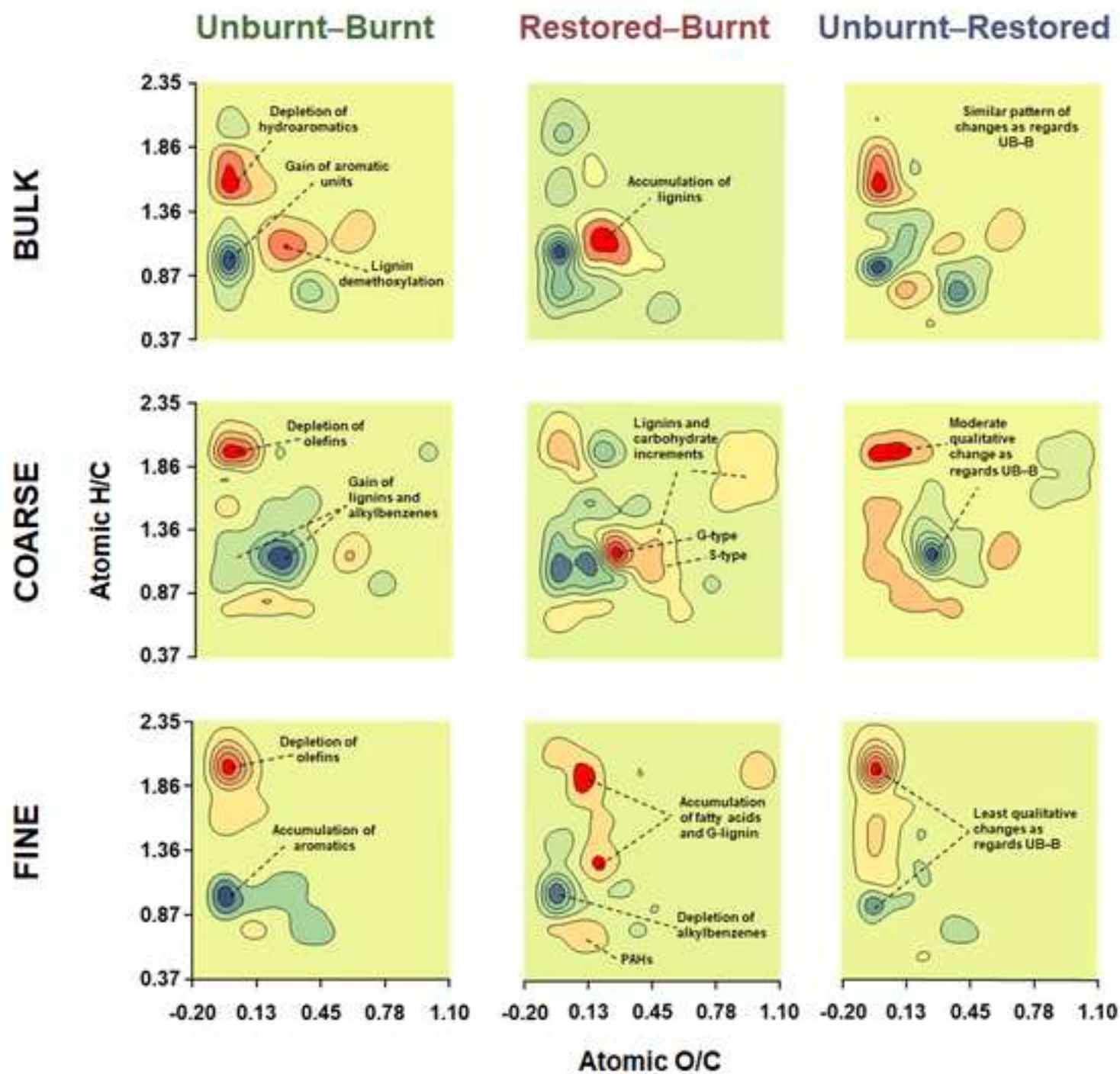


Figure 4

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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