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Paper:

Dlapa, P., Bodí, M., Mataix-Solera, J., Cerdà, A. & Doerr, S. (2014). Organic matter and wettability characteristics of wildfire ash from Mediterranean conifer forests. *CATENA*
<http://dx.doi.org/10.1016/j.catena.2014.06.018>

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1 **Organic matter and wettability characteristics of wildfire ash from**
2 **Mediterranean conifer forests**

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13

14 **Abstract**

15 After a fire, an ash layer is commonly present, which influences soil properties and hillslope hydrology.
16 The wettability of ash, which can vary from highly absorbent to water repellent, is an important
17 characteristic in this context. Recent work has suggested that ash wettability is related to its degree of
18 combustion, which in turn, can be expected to determine ash chemical composition. In this paper we
19 therefore examine the relationship between ash water repellency and ash chemical composition. Ten ash
20 samples with different wettability were each taken from four burned Mediterranean forest sites located at
21 Albaida (A), Lliber (L), Navalón (N), and Pinoso (P), in the east of Spain. The persistence of water
22 repellency of samples was assessed by the Water Drop Penetration Time (WDPT) test and Fourier
23 Transform-Infrared (FT-IR) analysis was applied to characterise sample chemical composition. Ash water
24 repellency varied from wettable to severely water repellent and differed in terms of maximum WDPT and
25 percentage of water repellent samples between the four locations. In all FT-IR spectra obtained, the
26 absorbance bands assigned to organic matter and carbonates were dominant. They are subject to change
27 during progressive combustion. The ratios of relevant peak areas were calculated, i.e. between aliphatic
28 bands in the 3000-2800 cm⁻¹ region, other organic matter bands in the 1800-1200 cm⁻¹ region, and of the
29 calcite band at 875 cm⁻¹. These ratios are related to organic matter and calcite contents in ash samples and
30 proved to be closely linked to measured WDPT values through an exponential relationship. Organic
31 matter content in all water repellent ash samples was more than twice higher than the carbonate content.

32 From the results obtained it is concluded that the water repellency or wettability of wildfire ash is driven
33 by the ratio of remaining organic matter to emerging carbonates, which in turn, is related with fire
34 severity.

35

36 *Keywords:* Wildfire, ash composition, FT-IR spectroscopy, water repellency

37

38 **1. Introduction**

39 Following a wildfire or prescribed fire, ash commonly covers the soil surface for some time until
40 it is removed by wind or water erosion. This layer can be up to many centimetres thick and can affect soil
41 erosion (Cerdà, 1998a) and runoff generation processes and rates (Cerdà, 1998b). In recent years the
42 relationship between ash characteristics and soil hydrology has been explored in several studies. For
43 example, Cerdà and Doerr (2008) examined the potential impact of ash deposits immediately following a
44 forest fire in a Mediterranean forest using simulated rainfall and found that the ash cover substantially
45 reduced surface runoff and erosion. Also using rainfall simulations following experimental burns in a
46 conifer forest in Montana, Woods and Balfour (2010) confirmed the importance of water storage capacity
47 of ash, but also found that, for a specific soil texture, ash could reduce infiltration into soil due to pore
48 clogging. Another factor, which is important in the effect of ash in hydro-geomorphological responses, is
49 the wettability of ash itself. In most of the literature, ash is referred to as being highly wettable (e.g. Cerdà
50 and Doerr, 2008; Doerr et al., 2006; Woods and Balfour, 2010), whereas in some studies ash has also
51 been suggested to be water repellent, albeit with no further quantification (Gabet and Sternberg, 2008;
52 Khanna et al., 1996; Stark, 1977). More recently, Bodi et al. (2011) evaluated 48 ash samples taken from
53 a range of Mediterranean wildfire sites and found that over 30% of samples exhibited water repellency
54 with persistence levels ranging from low to extreme. The water repellency levels correlated with organic
55 carbon contents in the ash material. It can therefore be supposed that ash properties will depend strongly
56 on the ash chemical composition.

57 Ash from forest fire is a complex mixture composed of organic and inorganic particles. It is well
58 established that ash properties are changing with heating (e.g. Ubeda et al., 2009), In the case of organic
59 matter, combustion or pyrolysis lead to complete destruction of some components and the transformation
60 to new substances of others. Previous work has shown that the chemical composition of forest fire ash can

61 be very variable and depends on various factors like burning temperature, type of plant species, part of
62 plant combusted, time of exposition, fuel arrangement and package conditions of combustion, etc.
63 (Liodakis et al., 2005; Pereira et al., 2011). The residual organic carbon is a darkening pigment in ash and
64 its colour lightness is suggested to indicate the degree of combustion completeness (Goforth et al., 2005).
65 In wood ash, dominant elements are calcium, potassium, magnesium, silicon, manganese, aluminium,
66 phosphorus, sulphur, iron, sodium and zinc (Liodakis et al., 2007; Etiegni and Campbell, 1991). Although
67 conditions during laboratory burning experiments may differ substantially from those during wildfires
68 and the results must be carefully compared, model laboratory experiments may give some useful
69 information on the relationships between ash composition and temperature reached. Thus Misra et al.
70 (1993) investigated relationships between wood ash properties and heating temperature. CaCO_3 and
71 $\text{K}_2\text{Ca}(\text{CO}_3)_2$ were the main compounds in ash produced at 600 °C, whereas CaO and MgO were
72 identified in 1300 °C ash. Ulery et al. (1993) reported calcite as the major inorganic component in wood
73 ash. Úbeda et al. (2009) observed formation of CaCO_3 at temperatures from 350 to 550 °C and Woods
74 and Balfour (2010) observed (in polarized light) white ash with calcite as infillings between larger
75 particles in thin sections. The pH and calcium carbonate content in ash were reported to increase with
76 lighter colour, while total nitrogen and organic carbon content increased with darker colour (Goforth et
77 al., 2005). More recently Gabet and Bookter (2011) analysed ash produced by the burning of Ponderosa
78 pine wood (*Pinus ponderosa*). The elemental composition was dominated by Ca, K, Mg, P, Mn, Fe and
79 Al. Mineralogical analysis revealed the presence of calcite, quartz and feldspars. There are various
80 hypotheses about the origin of calcite in ash materials. The most frequent explanation of calcite origin is
81 that calcium oxide is produced during wood combustion and subsequently transformed to hydroxide and
82 carbonate due to reaction with atmospheric water vapour and CO_2 (e.g. Ulery et al, 1993; Goforth et al.,
83 2005). It was also pointed out that rapid evaporation of plant cell water during burning may lead to the
84 increase in solution concentration and precipitation of well developed calcite crystals from a saturated
85 solution (Ulery et al, 1993). Additionally, Quintana et al. (2007) detected transformation of whewellite
86 (calcium oxalate) into calcite at around 400 °C in both the organic horizon and the plant leaves.

87 In this study we applied Fourier Transform Infrared spectroscopy (FT-IR) to a variety of ash
88 samples in order to provide a better understanding of ash chemical composition and its relationship with
89 ash wettability. To our knowledge, FT-IR has not been applied to wildfire ash samples before, however,
90 D'Acqui et al. (2010) demonstrated the suitability of FT-IR spectroscopy for determination of properties
91 for soils from the Mediterranean region and this technique might prove useful for ash. Features observed
92 in the FT-IR spectrum may not only provide information on the composition of ash material, but may also

93 indicate conditions during burning (various compounds or functional groups have different thermal
94 stability) and resulting physical and chemical ash properties. Soil organic matter, for example, has been
95 shown to give characteristic absorbance bands in FT-IR spectrum. The peaks at 2920 and 2860 cm^{-1} are
96 due to stretching vibration of methylene groups ($-\text{CH}_2-$) (Ellerbrock et al., 2005; Kaiser and Ellerbrock,
97 2005). These groups build aliphatic hydrocarbons, which are considered to contribute to water repellency
98 occurrence in soils. Capriel et al. (1995) proposed the use of absorbance bands 3000-2800 cm^{-1} as index
99 of hydrophobicity and Simkovic et al. (2008) showed that thermal destruction of these peaks had been
100 accompanied with elimination of the soil water repellency. Two other absorbance bands at 1740 to 1720
101 cm^{-1} and 1640 to 1620 cm^{-1} represent C=O groups in aldehydes, ketones and carboxylic acids (Chapman
102 et al., 2001; Ellerbrock et al., 2005; Kaiser and Ellerbrock, 2005). The adjacent region at 1620 to 1600
103 cm^{-1} is associated with aromatic C=C vibrations (Kaiser and Ellerbrock, 2005; Dick et al., 2006).

104 Absorbance bands observable in FT-IR spectra have various implications for the temperature a
105 material has been exposed to. For example, clay minerals may dehydroxylate during heating, indicated by
106 disappearance of stretching of the O-H vibration bands and the Al-O-H deformation band. Kaolinite
107 dehydroxylates at $\sim 450-650$ °C and smectites at about 600-800 °C (Kurap et al., 2010). Many organic
108 substances have less thermal stability than kaolinite. Amongst them, the condensed organic fraction is
109 more stable than aliphatic hydrocarbons. Simkovic et al. (2008) observed removal of the aliphatic
110 absorbance bands in the region of 3000-2800 cm^{-1} at temperatures slightly above 200 °C. Even at
111 temperatures below 200 °C some changes in the IR spectrum may occur due to volatilization of water and
112 some organic substances.

113 Given the potential of FT-IR spectra in the evaluation of ash composition, the aim of this study
114 was to apply FT-IR to ash samples taken from wildfires of different severity in order to (i) characterize
115 ash composition and (ii) evaluate the potential relationship of ash composition with ash water repellency.

116

117 **2. Materials and methods**

118 2.1. Site description and ash samples

119 Ash samples were taken from four Mediterranean sites located in the provinces of Alicante and
120 Valencia, eastern Spain: Albaida (A), Lliber (L), Navalón (N), and Pinoso (P). Prior to the fires, all sites
121 were dominated by *Pinus halepensis* Miller. The understory comprised mainly of *Quercus coccifera*,

122 *Rosmarinus officinalis* and *Brachypodium retosum*. Occurrence of other species (*Cistus albidus*, *Erica*
123 *multiflora*, *Juniperus oxycedrus*, *Pistacia lentiscus*, and *Ulex parviflorus*) varied depending on the
124 quantity of precipitation and the time since the previous fire. Fire severity at the four locations had been
125 classified according to ash colour as moderate-severe, moderate, severe, and moderate-severe,
126 respectively (Bodi et al., 2011). At each site, ten ash samples were taken randomly from underneath pine
127 trees and understorey vegetation (Table 1). The samples were air-dried and used for subsequent analyses.
128 More details about sites, sampling and samples are given in the study by Bodi et al. (2011), which
129 focused on wettability of ash and its relationship to plant species, burn severity and total organic carbon
130 content.

131 2.2. Ash water repellency

132 Persistence of water repellency was assessed by widely used water drop penetration time
133 (WDPT) test (Doerr, 1998). Ash samples were placed in Petri dishes and WDPT measurements were
134 carried out after two weeks equilibration in a climate chamber (manufacturer Memmert HPP 108) at a
135 constant temperature of 20°C and a relative air humidity of 50% (Doerr et al., 2002). Three drops of
136 distilled water were placed onto the surface of each ash sample using a dropper and actual time required
137 for complete penetration of the droplet was recorded. In order to reduce evaporation Petri dishes were
138 covered following drop placement testing. The average of the three WDPT values was used for
139 assessment of particular ash sample. The following classes of persistence of water repellency were
140 distinguished: wettable (<5 s), slightly water repellent (5 – 60 s), strongly water repellent (60 – 600 s),
141 severely water repellent (600 – 3600 s) and extremely water repellent (> 3600 s) (Dekker and Ritsema,
142 1995).

143 2.3. FT-IR spectroscopy

144 The ash samples were ground to powder in an agate mill prior FT-IR analysis. The samples were
145 pressed into KBr pellets with sample/KBr ratio 2/200 mg. Infrared spectral analysis was carried out in the
146 mid-infrared wavelength range (wavenumbers from 4000 to 400 cm⁻¹) and results obtained in the form of
147 absorbance values. One hundred and twenty eight scans at a resolution of 4 cm⁻¹ were averaged for each
148 spectrum. FT-IR spectra were measured on a NICOLET Magna IR 750 spectrometer with a DTGS
149 detector and OMNIC 8.1 software that was used for background corrections.

150 In order to compare and quantify any differences between the ash samples as regards FT-IR
151 spectra, an additional treatment of the data sets was carried. OMNIC 8.1 software was used for fitting of
152 individual peaks to a complex set of overlapping peaks in a spectrum. The software automatically
153 adjusted the peak centre, height and width to produce a composite spectrum that matches the original.
154 Peak fitting was applied to selected absorbance bands after the baseline correction. The results obtained
155 were used to identify bands in which relative decrease or increase of absorbance was prevailing as a result
156 of combustion. Particularly the wavelength regions 3000–2800 and 1800–1200 cm^{-1} were taken for
157 detailed mathematical treatment in order to separate absorbance bands assigned to organic matter and
158 calcite in ash samples. Subsequently ratios of peak areas were calculated.

159 *2.4. Organic matter and carbonate contents*

160 Total contents of organic matter and inorganic carbonates were determined by differential thermal
161 analysis. The analysis was performed on TGA-DTA system (SDT 2960, manufacturer TA Instruments,
162 New Castle, USA) with a 90 $\text{cm}^3 \text{min}^{-1}$ standard air flow rate from 20 to 1000 °C. Measurements were
163 performed at 10 °C/min heating rate. Decrease of weight between 200 and 600 °C was used for
164 determination of the soil organic matter/carbon content. Inorganic carbonate content was determined from
165 the weight loss between 600 and 800 °C.

166 *2.5. Digital microscopy*

167 A digital microscope (Keyence VHX 1000, Camera VHX 1100, Lens x 20-200 VH Z20W, Lens
168 x100-1000 VH Z100W, Motorized Stand VHX-S50) was used to observe the morphologies of the ash
169 materials at magnification x30-700.

170 *2.6. Statistical analysis*

171 The variability of WDPT values among the four study sites was evaluated with Kruskal-Wallis
172 test. This test was adopted because the WDPT values do not respect the normality. Kruskal-Wallis test is
173 the non-parametric analogue of ANOVA test, which does not make assumptions about normality. During
174 the analysis each measured value was substituted with the rank in the overall data set. The sum of the
175 ranks was calculated for each group and statistical parameter H was calculated. The p value
176 corresponding to chi-square equal to H was determined when the degrees of freedom were number of
177 study sites minus 1. Significant H values from the Kruskal-Wallis test indicate significant difference
178 among evaluated groups.

179

180 3. Results and discussion

181 3.1. Ash water repellency

182 Water repellency of ashes from the four locations were highly variable, ranging from wettable to
183 severely water repellent (Table 2). Statistically significant result of the Kruskal-Wallis test
184 confirmed that WDPT values were significantly different among the four wildfire sites ($H =$
185 11.4 ; $d.f. = 3$; $p = 0.0099$). There are differences in the sites as regards the maximum WDPT values
186 reached amongst the 10 samples, decreasing in order $L1 > A7 > P6 > N5$. Similarly, when sites are
187 arranged according to occurrence of samples with WDPT above 60 s, the same order emerges: L (6
188 samples) $> A(3) > P(2) > N(0)$, which corresponds fully with sites ordered by increasing fire severity
189 (Table 1). Heating and pyrolysis of organic material has been shown to lead to an increase, and at higher
190 temperature, destruction of soil water repellency (DeBano et al. 1979; Bryant et al. 2005) and Bodí et al.
191 (2011) found that for ash generated in the laboratory under oxygen containing atmosphere at temperatures
192 exceeding ~ 350 to 400 °C, water repellency was absent.

193 This explains the correspondence of WDPT values to the differences in wildfire severities at
194 selected study sites. Thus the highest temperatures related to ash production would be expected at site N
195 where all samples were wettable or only slightly water repellent. In contrast, at site L, affected by low fire
196 severity, over half of the ash samples were strongly water repellent. Noticeable is the occurrence of
197 severely water repellent samples together with wettable samples within sites L, N and P. This may
198 indicate either a strong heterogeneity of the medium and high burn severity sites, or a very strong
199 sensitivity of water repellent properties to the composition of combusted ash materials.

200 The observed variability in ash water repellency may affect hydrological responses of burned
201 sites. The net impact of ash material on hydrological processes continues to be a matter of debate. Some
202 authors suggest that the presence of ash increases surface runoff due to surface sealing (e.g. Gabet and
203 Sternberg, 2008; Onda et al., 2008) while others reported that its water absorbent nature decreases surface
204 runoff (Cerdà and Doerr, 2008; Woods and Balfour, 2008; Larsen et al., 2009; Kinner and Moody, 2010).
205 The effect of ash water repellency itself on surface runoff has not been investigated in detail to date, but it
206 is speculated here that at patches where ash is water repellent, net runoff generation will be greater than at
207 patches where the ash layer has a similar depth, but is wettable.

208 3.2. FT-IR spectra characteristics

209 Accordingly the FT-IR spectra of the least and the most combusted ash samples from the four
210 study sites are described as follows. The samples were selected according to relative proportion of the
211 absorbance bands assigned to organic matter and calcite. The absorbance bands are expected to broadly
212 represent the degree of organic matter combustion of samples. Figure 1 shows the characteristic
213 absorbance bands in the FT-IR spectra of the least combusted sample A7. The broad absorbance band at
214 3368 cm^{-1} corresponds to O–H stretching vibrations in water and hydroxyl groups in various organic and
215 inorganic substances (Gerzabek et al., 2006). Relatively intensive bands at 2926 and 2854 cm^{-1} from C–H
216 stretching vibrations are attributed to aliphatic hydrocarbons (Ellerbrock et al., 2005). Absorbance bands
217 occurring as a shoulder at 1731 and a peak at 1607 cm^{-1} are typical for C=O vibrations in carboxylic
218 groups and for C=C vibrations in aromatics, respectively (Dick et al., 2006). Several more or less
219 intensive bands are caused by presence of calcite (CaCO_3) at 2516 , 1797 , 1426 , 875 , and 713 cm^{-1}
220 (Tatzber et al., 2007).

221 A mixture of inorganic particles is represented by absorbance bands typical for primary silicate
222 minerals and clays (Farmer, 1974). These components are less sensitive to heating compared to organic
223 matter (Simkovic et al., 2008; Kurap et al., 2010). Thus, the intensive band at 1033 cm^{-1} is attributed to
224 Si-O stretching vibrations. Absorbance bands of Si-O-Al at 535 cm^{-1} and Si-O-Si at 472 cm^{-1} (bending
225 vibrations), weak shoulders of O–H stretching bands at 3697 and 3621 cm^{-1} and an Al-O-H deformation
226 band at 912 cm^{-1} , which all are typical for clay minerals, are also present (Farmer, 1974).

227 Very notable for the studied ashes is the presence of calcium oxalate (whevellite), which can be
228 identified according to absorbance band at 1317 cm^{-1} . It also has less intensive bands at 780 and 516 cm^{-1}
229 (Li et al., 2004), which overlap with absorbance bands of silicates.

230 In the most combusted ash sample A3, absorbance bands belonging to organic substances almost
231 disappeared. In the $2800\text{-}3000\text{ cm}^{-1}$ region the dominant absorption are ascribed to a combination bands
232 of calcite with peak maxima at 2981 and 2874 cm^{-1} (Tatzber et al., 2007; D'Acqui et al., 2010; Kurap et
233 al., 2010). Calcite absorbance bands predominate in the whole spectrum. Also bands assigned to admixed
234 silicate minerals are present, including the quartz doublet at 797 and 779 cm^{-1} (Reig et al., 2002). In a
235 study by Che et al. (2011) O-H stretching and deformation bands in kaolinite became weaker at $400\text{ }^\circ\text{C}$
236 and disappeared at $500\text{ }^\circ\text{C}$. Thus, the presence of kaolinite (as evidenced by absorbance band at 3697 cm^{-1}
237 and by O-H stretching and deformation bands) is probably caused by mixing of ash material with less

238 affected mineral soil during sampling. Almost complete destruction of organic matter in the ash material
239 corresponds with the moderate-severe fire severity.

240 A similar pattern with respect to FT-IR features is evident amongst samples at remaining three
241 sites with only small variations (Fig. 2 – 4). In all spectra the absorbance bands assigned to organic matter
242 and carbonates are dominant features and they are subject to change during progressive combustion. With
243 increasing combustion, the absorbance bands assigned to organic matter at 2928-2925, 2854 and 1619-
244 1615 cm^{-1} are relatively decreasing with respect to absorbance bands of carbonates at 1439-1432 and 877-
245 875 cm^{-1} . However, in highly combusted samples, the peaks in the range of 3000-2800 cm^{-1} (organic
246 matter) are very weak and superimposed with calcite combination bands at 2981 and 2874 cm^{-1} .

247 After peak deconvolution the absorbance bands assigned to organic matter and calcite were
248 separated in the 3000-2800 cm^{-1} and 1800-1200 cm^{-1} regions. Six individual absorbance bands were
249 distinguished in the 3000-2800 cm^{-1} region (Fig. 5). The methylene peaks occur at 2923 and 2852 cm^{-1}
250 together with weaker methyl peaks at 2956 and 2895 cm^{-1} . As the peak areas of the methyl and methylene
251 groups are decreasing, the calcite combination bands at 2978 and 2873 cm^{-1} are increasing in more
252 combusted ash samples. In the 1800-1200 cm^{-1} region (Fig. 6) organic matter peaks attributed to
253 carboxylic and aromatic groups at 1707 cm^{-1} and 1600 cm^{-1} , respectively, were separated from calcite
254 peak at 1435 cm^{-1} .

255 Individual peak areas assigned to organic matter in the regions 3000-2800 cm^{-1} (Fig. 5) and 1800-
256 1200 cm^{-1} (Fig. 6) together with a calcite peak at 875 cm^{-1} were taken for further evaluation of the
257 relationships between the ash WDPT values and the FT-IR compositional characteristics of the ash
258 samples. The peaks, and ratios of peak areas, were determined for each sample and obtained results are
259 listed in Table 2. The ratios of the absorbance bands were highly variable in the ash samples and showed
260 a high sensitivity to burning impact on the ash properties. It is presupposed that evaluated parameters of
261 the FT-IR spectrum reflects adequately major changes of the organic and inorganic compounds in the
262 ashes and that these parameters are suitable for explanation and interpretation of observed changes in ash
263 water repellency.

264

265 *3.3. Ash water repellency vs. ash composition*

266 Combustion of plant biomass and litter material induces two processes, which can be considered
267 as concurrent with respect to ash water repellency or wettability. Whether ash material will be water
268 repellent or wettable depends on the relative proportion of hydrophilic and hydrophobic surfaces. The
269 properties of organic matter, found in ash, are changing during burning processes (Úbeda et al., 2009) and
270 charred particles formed by organic matter can be considered as the source of hydrophobic surfaces
271 (Almendros et al, 1992; Knicker, 2007; Bodí et al., 2011). Overall, however, the effect of burning (i.e.
272 combustion) is a gradual decrease in organic matter content, which leads to an absolute decrease of
273 hydrophobic surfaces in ash material. From the FT-IR spectra of ash samples it is evident that absorbance
274 bands assigned to functional groups of organic matter in both the 3000-2800 cm^{-1} region and the 1800-
275 1200 cm^{-1} region are decreasing during combustion and these changes are closely correlated (Fig. 7).

276 Organic matter combustion is accompanied by the synthesis of inorganic substances with
277 hydrophilic surfaces. Particularly carbonates are typically formed during organic matter burning under
278 conditions commonly occurring during wildfires. While charred organic matter is a darkening pigment in
279 ash, the lighter colour in ash is associated with an increase of the calcium carbonate content (Goforth et
280 al., 2005). Calcium carbonate (calcite) has a higher free energy than water and therefore has hydrophilic
281 surface (Keller and Luner, 2000). In partially combusted ash hydrophobic organic and hydrophilic
282 inorganic surfaces will both be present. These components will be responsible for the net water
283 repellent/wettable character of the ash material. In the less combusted ash material examined here, the
284 plant tissue residues are still recognizable (Fig. 8a) and the ash layer exhibits water repellent properties.
285 While plant residues are absent in the strongly combusted ash (Fig. 8b), whitish calcite crystals are
286 present (Fig. 9), which facilitate ash wettability.

287 Based on the above assumptions, FT-IR characteristics may be identified that correlate with
288 WDPT values. Particularly, parameters directly related to organic matter and carbonate contents could be
289 considered as properties related to ash wettability or water repellency. In FT-IR spectra of ash samples,
290 certain peaks (peak areas) are clearly related to organic matter and carbonate contents as described above
291 and could be used for such purposes.

292 Several absorbance bands in FT-IR spectra can be assigned to various functional groups of ash
293 organic mater. Some of them were previously reported to be linked to soil water repellency or wettability
294 (Simkovic et al., 2008; Ellerbrock et al., 2005). The most promising are absorbance bands between 3000
295 and 2800 cm^{-1} corresponding to aliphatic functional groups. This region is closely related to the aliphatic
296 fraction of organic matter and had been satisfactorily applied with respect to soil water repellency by

297 Simkovic et al. (2008). Ellerbrock et al. (2005) used ratio of two absorbance bands representing
298 hydrophobic groups ($3020\text{-}2800\text{ cm}^{-1}$) and hydrophilic groups ($1740\text{-}1710\text{ cm}^{-1}$ and $1640\text{-}1620\text{ cm}^{-1}$) as
299 the explaining parameter for contact angle values, used as a measure of water repellency in soils.
300 However, the adjacent region between 1620 and 1600 cm^{-1} can also be attributed to aromatic C=C
301 vibrations (Kaiser and Ellerbrock, 2005; Dick et al., 2006), which represent hydrophobic groups.
302 Gerzabek et al. (2006) showed a quantitative relationship between the FT-IR bands and soil organic
303 matter content in non-calcareous bulk mineral soil. Thus, a broad spectrum region with a maximum
304 between 1620 and 1600 cm^{-1} may also be considered as suitable because there are several overlapping
305 peaks in this region belonging to various functional groups of organic matter and this complex absorbance
306 band can be related as a whole to organic matter content in the ash material.

307 Similarly, for carbonates, a number of absorbance bands can be distinguished, but many of them
308 are overlapping with organic matter bands or with bands from other inorganic substances. For example,
309 the combination bands of calcite (2982 and 2875 cm^{-1}) lie in the aliphatic region of organic matter. The
310 bands at 2513 and 1798 cm^{-1} are weak and may overlap with other absorbance bands of organic matter.
311 The most intensive absorbance band around 1427 cm^{-1} is wide and overlapping with many other bands of
312 organic and inorganic origin and the same is true for the 712 cm^{-1} band. The most promising FT-IR
313 absorbance band representing calcite content in the ash samples can be considered to be the peak at 875
314 cm^{-1} . Reig et al. (2002) used peaks at 875 and 712 cm^{-1} for FT-IR quantitative analysis of calcite in
315 geological samples. In the analysed ash samples the peak at 875 cm^{-1} is narrow, selective and distinct
316 enough for approximation of variable calcite content in the evaluated ash samples.

317 Based on the above-discussed assumptions, the ratios of responsible peak areas were calculated –
318 namely, ratios of aliphatic peaks in the $3000\text{-}2800\text{ cm}^{-1}$ region and of organic matter peaks in the 1800-
319 1200 cm^{-1} region to calcite peak at 875 cm^{-1} . These ratios are directly related to the ratio of organic matter
320 to calcite content in ash material. Calculated values are listed together with measured WDPT values in
321 Table 2. The relationships between the ratio of organic matter to calcite absorbance bands and logWDPT
322 values are given in Figs. 10 and 11. The relationship with the aliphatic region ($2800\text{-}3000\text{ cm}^{-1}$) is less
323 sensitive for more combusted ashes (because aliphatic peaks are very weak), but both relationships have a
324 very similar character.

325 The relationship between the logWDPT and the ratio of ash organic matter to ash calcite (peak
326 areas in the $1800\text{-}1200\text{ cm}^{-1}$ region divided by peak area at 875 cm^{-1}) probably corresponds very well to
327 the actual composition of ash material with respect to ratio of organic matter and calcite contents. As can

328 be seen in Fig. 11 this relationship is not linear and can be approximated with an exponential function.
329 From the obtained diagram follows that ash water repellency will not change gradually with changes in
330 ash composition. The function has a characteristic shape with a flat top and a steep decrease in logWDPT
331 at low values of the organic matter/calcite ratio. The ash behaviour is thus expected to be very sensitive to
332 ash composition especially at ratios where exponential function is sharply decreasing (Fig. 11). There is a
333 relatively narrow area in the diagram where the water repellent ash changes to being wettable.

334 There is close relationship between the FT-IR data and the ratio between organic matter and
335 carbonate contents as can be seen in Figs. 12 and 13. All water repellent ash samples are found above the
336 dashed line, which denotes the ratio of organic matter to carbonate contents of 2:1 (for weight
337 percentages). This means that water repellency occurs only in the ash samples where the organic matter
338 content is more than twice higher than the content of carbonates. From Figs. 12 and 13 it can be
339 concluded that water repellency or wettability of wildfire ashes will be driven by the ratio of remaining
340 organic matter to emerging carbonates. This ratio will depend on the burning conditions during the fire.
341 Ash organic matter mineralisation (combustion) will increase with increasing burning temperature and
342 duration, but will depend also on the original properties of burned organic matter and oxygen availability.
343 The calcium carbonate formation depends among other factors, of the plant flammability. The same
344 temperature can produce different severities in species with different flammability, and located in
345 different environments (Ubeda et al., 2009). Thus ash water repellency can be different in fires produced
346 with the same temperature in the same ecosystem, and between the same specie located in different areas.
347 Variations in these parameters will result in the occurrence of ashes with very variable wettabilities at
348 burned sites. The resulting ash properties in turn can lead to contrasting effects as regards soil behaviour
349 and hydrogeomorphological responses of hillslopes following fire.

350 The results presented in this paper are an extension of knowledge about ash water repellency, reported by
351 Bodi et al. (2011). Our new results show a very narrow boundary line between wettable and water
352 repellent ash. The threshold is determined by the relationship between the content of organic matter and
353 carbonates in the ash. FT-IR spectroscopy has proven to be very fast and inexpensive alternative for
354 evaluation of ash composition with respect to possible occurrence of ash water repellency. But this
355 boundary between water repellent and wettable ash also determines the different post-fire consequences.
356 The water repellency implicates various negative effects which are frequently referred for water repellent
357 soils (Doerr et al., 2000; Shakesby and Doerr, 2006). Among the most serious consequences of post-fire
358 water repellency must be included enhanced surface runoff and erosion, occurrence of dry patches,

359 decreased germination, etc. Although we can not assume that water repellent ash layer will be preserved
360 for a longer time, ash particles can become part of the soil and affect its properties. A similar effect of ash
361 on soil water repellency has been already reported by Bodí et al. (2011). Therefore we can not exclude
362 even the long-term consequences in case of formation of water repellent ash.

363 **4. Conclusions**

364 Comparison between study sites affected by different fire severities showed consistent differences
365 in ash wettabilities. The occurrence of strongly to severely water repellent ash samples (WDPT > 60 s)
366 varied from 70% to 0% for sites with low-moderate to severe wildfires respectively. Maximum WDTP
367 values amongst samples follow the same fire severity order. A suspected relationship between the degree
368 of ash water repellency with ash composition was supported by data obtained on ash composition using
369 FT-IR.

370 FT-IR data showed that key changes in ash composition comprise a decrease of organic matter
371 content and increase of carbonate content with increasing fire severity. Relative changes in the proportion
372 of absorbance bands may be potentially used for estimation of wildfire ash properties and effects on
373 detrimental post-fire hydro-geomorphological impacts. A comparison of peak areas between the spectra
374 from the samples affected by wildfires of different severity suggests that the FT-IR spectrum regions
375 attributed to organic matter and calcite are the most informative with respect to water repellency
376 occurrence and severity. The ratio of absorbance bands belonging to organic matter and calcite is the
377 parameter suggested to determine whether ash material will be water repellent or wettable. Function
378 fitting this relationship showed that ash WDPT values are strongly sensitive to the organic matter/calcite
379 ratio. The relationship also explains why ash water repellency can be very variable even within sites of
380 seemingly uniform burn severity.

381 Organic matter content in all water repellent ash samples was more than twice higher than the
382 carbonate content. This compositional boundary also determines post-fire effects of ash layer. Water
383 repellent ash layer will enhance surface runoff formation and soil erosion. While these effects of ash layer
384 are expected to have only short-term effect, we can not exclude long term impact of ash water repellency
385 on post-fire processes when the ash particles become part of the soil.

386

387 **Acknowledgements**

388 This research was supported by the Research and Development Operational Programme,
389 the project Excellence Centre of Integral Territory Flood Protection, code ITMS 26240120004,
390 funded by the ERDF.

391

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- 501

502 **Figure captions**

503

504 Fig. 1. FT-IR spectra of the most (upper) and the least (lower) combusted ash samples from the Albaida
505 study site.

506 Fig. 2. FT-IR spectra of the most (upper) and the least (lower) combusted ash samples from the Lliber
507 study site.

508 Fig. 3. FT-IR spectra of the most (upper) and the least (lower) combusted ash samples from the
509 Navalón study site.

510 Fig. 4. FT-IR spectra of the most (upper) and the least (lower) combusted ash samples from the Pinoso
511 study site.

512 Fig. 5. Example of the peak deconvolution in the 3000-2800 cm^{-1} region in the ash sample A9 from the
513 Albaida study site.

514 Fig. 6. Example of the peak deconvolution in the 1800-1200 cm^{-1} region in the ash sample A9 from the
515 Albaida study site.

516 Fig. 7. Relationship between relative intensity of absorbance bands assigned to aliphatic hydrocarbons
517 ($A_{3000-2800}$) and carboxylic and aromatic groups ($A_{1800-1200}$), plotted on a logarithmic x and y axis.

518 Fig. 8. The morphology of the ash material as observed with a digital microscope (Keyence VHX 1000)
519 at low magnification: a) needle residues with preserved morphology in the least combusted
520 water repellent ash (Sample A7) and b) most combusted wettable ash (Sample A3) without any
521 visible plant residues.

522 Fig. 9. Whitish calcite crystals on the surface of most combusted wettable ash (Sample A3) as observed
523 with digital microscope (Keyence VHX 1000) at high magnification.

524 Fig. 10. Relationship between the ash water repellency (log WDPT) and the peak area ratio of
525 absorbance bands assigned to aliphatic hydrocarbons ($A_{3000-2800}$) and to calcite (A_{875})

526 Fig. 11. Relationship between ash water repellency (log WDPT) and the peak area ratio of absorbance
527 bands assigned to organic matter (carboxylic and aromatic groups, $A_{1800-1200}$) and to calcite (A_{875})

528 Fig. 12. Relationship between the ratio of organic matter (OM) and inorganic carbonate (IC) contents
529 and the peak area ratio of absorbance bands assigned to aliphatic hydrocarbons ($A_{3000-2800}$) and to
530 calcite (A_{875})

531 Fig. 13. Relationship between the ratio of organic matter (OM) and inorganic carbonate (IC) contents
532 and the peak area ratio of absorbance bands assigned to organic matter (carboxylic and aromatic
533 groups, $A_{1800-1200}$) and to calcite (A_{875})