

1           **Forest floor chemical transformations in a boreal forest fire**  
2           **and their correlations with temperature and heating duration**

3           Cristina Santín<sup>1</sup>, Stefan H. Doerr<sup>1\*</sup>, Agustín Merino<sup>2</sup>, Robert Bryant<sup>1</sup>, Neil J.  
4           Loader<sup>1</sup>

5           <sup>1</sup>Department of Geography, College of Science, Swansea University, Singleton Park, Swansea  
6           SA2 8PP, UK; [c.s.nuno@swansea.ac.uk](mailto:c.s.nuno@swansea.ac.uk); [s.doerr@swansea.ac.uk](mailto:s.doerr@swansea.ac.uk) \*corresponding author;  
7           [r.bryant@swansea.ac.uk](mailto:r.bryant@swansea.ac.uk); [n.j.loader@swansea.ac.uk](mailto:n.j.loader@swansea.ac.uk)

8           <sup>2</sup>Department of Soil Science and Agricultural Chemistry, University of Santiago de Compostela,  
9           27002 Lugo, Spain; [agustin.merino@usc.es](mailto:agustin.merino@usc.es)

10  
11       **Abstract**

12       Boreal soils account for ~30% of the global soil organic carbon (C) stock. Wildfires are  
13       an important perturbation of this C pool, particularly affecting the top organic soil layer,  
14       which constitutes the forest floor. Alterations to the forest floor by fire are relevant to the  
15       soil C balance and have profound implications for soil properties. However, relationships  
16       between forest floor transformations and actual wildfire characteristics have not been  
17       established to date due to the logistical challenges of obtaining the necessary fire  
18       behaviour data, together with associated pre- and post-fire sample material. We used a  
19       high-intensity experimental wildfire to address this research gap, which enabled us to  
20       determine chemical transformations in a Canadian boreal forest in relation to  
21       temperature-time profiles for 18 sampling points during the fire. Forest floor samples  
22       taken pre- and post-fire were characterized using elemental and  $\delta^{13}\text{C}$  analysis,  
23       differential scanning calorimetry and  $^{13}\text{C}$  nuclear magnetic resonance.

24       During this typical boreal crown fire average maximum temperature ( $T_{\text{max}}$ ) at the forest  
25       floor was 745 °C ( $550 < T_{\text{max}} < 976$  °C) with the average heating duration ( $t$ ) >300 °C being  
26       176 s ( $65 < t < 364$  s). Significant correlations were detected between the chemical  
27       characteristics of the pyrogenic (charred) forest floor layer and the temperature-time  
28       profiles at the corresponding sampling points. Higher  $T_{\text{max}}$  and associated prolonged  
29       heating durations correlated with greater C enrichments, increased thermal recalcitrance  
30       and degree of aromaticity of the pyrogenic organic matter. These changes were  
31       particularly pronounced for  $T_{\text{max}} > 600\text{-}700$  °C, which is higher than the range of 300-500  
32       °C for aromaticity development previously reported from laboratory experiments. One  
33       reason for this discrepancy could be the generally much longer heating durations used  
34       in laboratory studies, and we therefore advise caution when extrapolating findings from  
35       laboratory studies to wildfire conditions.

36 Almost half of the initial total C stock in the forest floor (20 Mg C ha<sup>-1</sup>) was affected by  
37 fire, with ~24% of this fire-affected C transformed to pyrogenic organic matter. This  
38 pyrogenic material possessed variable, yet distinct, chemical characteristics when  
39 compared to unburnt forest floor, including higher recalcitrance and associated  
40 resistance to biological degradation. As some boreal regions already show a rise in fire  
41 severity and area burned linked to climate change, our findings suggest a potential  
42 accompanying increase in the more stable organic carbon stock, with important  
43 implications for the functioning and turnover of organic matter in boreal soils.

44 **Keywords:** pyrogenic carbon, black carbon, biochar, carbon isotopes, wildfire, *Canadian*  
45 *Boreal Community FireSmart Project.*

46

## 48 **1. Introduction**

49 Fire is one of the most frequent and recurrent perturbations in a wide range of  
50 environments, with profound effects on ecosystem properties and functions including the  
51 carbon (C) cycle (Reichstein et al., 2013). Fire not only alters C stocks by releasing C  
52 stored in the dead and living vegetation to the atmosphere, but also changes the quantity  
53 and composition of the soil organic matter (SOM) pool. In the boreal region, fire is one  
54 of the dominant drivers of the C balance (Bond-Lamberty et al., 2007), with, on average,  
55 over 464 Mha burnt annually and associated emissions of  $\sim 2.5 \text{ Pg C yr}^{-1}$  (period 2001-  
56 2010, Randerson et al., 2012). In recent decades, boreal ecosystems have undergone  
57 profound changes in response to climatic change, including an increase in wildfire activity  
58 (Kelly et al., 2013). This upward trend is expected to be further enhanced by the end of  
59 this century (Flannigan et al., 2013; Héon et al., 2014). In boreal regions, the top organic  
60 soil layer, the forest floor, is the fuel component most affected by fire, accounting for up  
61 to 85% of the total fuel burnt (Amiro et al., 2001; de Groot et al., 2009). Given that around  
62 30% of the global soil organic C stock is held in the boreal regions (Scharlemann et al.,  
63 2014), a full understanding of fire effects on boreal soils is of global importance.  
64 However, the relationships between fire characteristics and alterations of the soil organic  
65 C stock in the boreal ecosystems, and beyond, are still not well understood (Kane et al.,  
66 2010; Turetsky et al., 2011).

67 Alterations of the quantity and composition of SOM by fire are many and very diverse  
68 (González-Pérez et al., 2004). They are not only relevant to the C budget but also affect  
69 many ecosystem properties and functions, such as microbial dynamics, nutrient cycles  
70 and vegetation succession (Holden et al., 2015; Schmidt et al., 2011; Turetsky et al.,  
71 2011). Quantitatively, fire can lead to a substantial depletion of the SOM stock by, for  
72 example, combustion of organic horizons (Kane et al., 2007) or loss of mineral soil by  
73 enhanced post-fire erosion (Pingree et al., 2012), but it can also result in an increase of

74 SOM content by incorporation of dead and charred biomass from vegetation and litter  
75 (Santín et al., 2008). Fire effects on SOM composition range from negligible to the loss  
76 of labile components and enrichment of pyrogenic recalcitrant forms (González-Pérez et  
77 al., 2004). An increase of labile compounds could also occur by inputs of dead, but  
78 uncharred, vegetation (Alexis et al., 2007).

79 In order to elucidate SOM transformations by fire, many studies have compared SOM  
80 quantity and characteristics of wildfire-affected soils with those of unburnt soils in similar  
81 areas, either soon (Mastrolonardo et al., 2014) or sometime after burning (Dymov and  
82 Gabov, 2015; Santín et al., 2008). This approach, however, leaves substantial  
83 uncertainties regarding actual fire characteristics and the representativeness of unburnt  
84 samples as substitutes for pre-fire soil conditions (Bormann et al., 2008). Prescribed fires  
85 (i.e. controlled burns for fuel management and/or ecological purposes) have also been  
86 used to examine the transformations of SOM, litter and vegetation by fire (Alexis et al.,  
87 2010, 2007), as the scheduling of the fire allows pre-fire and post-fire sampling and in-  
88 fire monitoring. Unfortunately, most prescribed fires are carried out at lower fire  
89 intensities and higher fuel moisture contents than is typical for wildfires, and/or at sites  
90 with modified fuel conditions, and are, therefore, not fully representative of wildfire  
91 conditions (Santín et al., 2015a). Other studies have explored relationships between  
92 transformations of organic matter and inferred soil burn severity as a proxy for fire  
93 conditions (e.g. Merino et al., 2015, 2014; Vega et al., 2013). None of these approaches,  
94 however, allows direct characterisation of the relationships between actual fire  
95 parameters (i.e. temperature, heating duration, oxygen availability) and SOM  
96 transformations.

97 The current understanding of the relationships between fire parameters and SOM  
98 changes is largely based on laboratory experiments (e.g. Badía-Villas et al., 2014;  
99 Verdes and Salgado, 2011), which are not necessarily representative of field conditions,  
100 due to, for example, different heating durations and oxygen availability (Alexis et al.,

101 2010; Atanassova and Doerr, 2010; Spokas, 2010). To date, the relationships between  
102 SOM transformations and specific fire parameters have not been directly examined in a  
103 wildfire context. This study addresses this research gap by utilizing a high-intensity  
104 experimental boreal forest fire to elucidate specific relationships between  
105 transformations of the organic top soil layer (the forest floor) and temperature-time  
106 profiles. Forest floor samples taken before and after fire were analyzed by elemental and  
107  $\delta^{13}\text{C}$  analysis, differential scanning calorimetry (DSC) and  $^{13}\text{C}$  nuclear magnetic  
108 resonance (NMR). Temperatures were continuously monitored during the fire at 18  
109 sampling points using thermocouples placed at the forest floor surface and at the forest  
110 floor/mineral soil interface. Examining these relationships does not only help to  
111 understand real wildfire conditions and the processes occurring under these, but it can  
112 also provide insights into potential effects of the already increasing fire occurrence and  
113 severity in the boreal regions driven by the changing climate.

## 114 2. Material and Methods

### 115 2.1 Study site and the FireSmart experimental forest fire

116 An experimental forest fire aimed at simulating wildfire conditions was conducted as part  
117 of the Canadian Boreal Community FireSmart Project at Fort Providence, Northwest  
118 Territories, Canada (61°34'55"N, 117°11'55"W). This boreal region has a dry, subhumid  
119 continental climate with low annual precipitation (300 mm) and a wildfire season lasting  
120 from May to September. The terrain is flat with an elevation of 160 m.a.s.l. (Alexander et  
121 al. 2004). The experimental plot (1.7 ha) was a mature stand of jack pine (*Pinus*  
122 *banksiana*) originating from a stand-replacing fire in 1931, with a tree density (live and  
123 dead) of 7600 stems ha<sup>-1</sup> and average tree height of 14 m. The understorey was very  
124 sparse (<0.1 stems m<sup>-2</sup>) with a few jack pine and black spruce (*Picea mariana*) saplings  
125 and shrubs. The soils in the experimental plot are stony sandy loams derived from fluvio-  
126 glacial deposits with a distinct organic surface layer, the forest floor (hereafter  
127 abbreviated as FF) . This organic soil layer, the FF, had an average thickness of 6.5 cm  
128 and was composed of mosses, lichens, needles, fermented litter and humidified organic  
129 material (Santín et al., 2015b). In this study woody debris <0.5 cm diameter were also  
130 considered as part of the FF.

131 The fire was started at 16h on 23 June 2012 with a line ignition initiated along the upwind  
132 east edge of the plot using a Terra torch (Fig. 1). The ambient temperature was 28 °C  
133 and relative humidity was 22% with winds of 10–12 km h<sup>-1</sup>. The last rain (0.5 mm),  
134 occurred 6 days previously with a total precipitation over the preceding month of 4.3 mm  
135 (more information in Santín et al., 2015b).

### 136 2.2 Temperature recording and forest floor sampling

137 Before the fire, three parallel transects of 18 m length were established 7.5 m apart in  
138 the direction of the prevailing wind (E-W) (Fig. 1). These were instrumented at a spacing  
139 of 2 m with thermocouples connected to data loggers (Lascar, Easylog) that recorded

140 temperatures at the FF surface and the FF/mineral soil interface every second (1Hz)  
141 (Fig. 2a&b). In total, 27 points (9 per transect) were monitored. In our study area, the FF  
142 developed under jack pine does not present well differentiated layers and, for simplicity,  
143 was sampled as a single FF layer (Preston et al., 2006). The FF was sampled along two  
144 parallel lines between the three sampling transects with 20 X 20 cm sampling squares  
145 (n = 10). The total depth of the FF was measured at each corner of the 20 X 20 cm  
146 square and the entire layer was carefully collected. At the centre of these same points,  
147 samples of the underlying mineral soil were taken using a 5 X 5 cm soil corer (n = 10).

148 The morning after the fire, the FF was sampled again, this time distinguishing between  
149 the top charred layer (hereafter, pyrogenic FF layer; Fig. 2c) and the unburnt layer  
150 underneath (hereafter, post-fire unburnt FF layer). Samples were taken adjacent to the  
151 thermocouples, at every sampling point along the three sampling transects (i.e., n = 27).  
152 The pyrogenic FF layer was sampled using a 30 X 30 cm square. The depth of the  
153 pyrogenic FF layer was measured at each corner of the square and the entire layer was  
154 collected. The same procedure was used to sample the underlying unburnt layer but  
155 using a subsquare of 10 X 10 cm in the centre of the sampling point. The mineral soil  
156 was then sampled using a 5 X 5 cm soil corer at the same locations.

### 157 *2.3 Forest floor characterization*

158 All samples were oven-dried at 65 °C to constant weight and cleaned by hand to remove  
159 any “cross-contamination” that had occurred during sampling. The unburnt FF samples  
160 were thus cleaned of any charred particles and mineral soil (<6% dry weight) and the  
161 pyrogenic FF samples from any visually uncharred materials (<7% dry weight) derived  
162 from the unburnt FF layer underneath. All samples were subsequently weighed and  
163 subsamples ground for further analyses. Presence of carbonates was tested by addition  
164 of 10% HCl to a set of representative subsamples (Rayment and Lyons, 2011).

#### 165 *2.3.1 Elemental and $\delta^{13}\text{C}$ analysis*

166 Total C and nitrogen (N) contents (%) and stable C isotope ratios ( $\delta^{13}\text{C}$ ) were determined  
167 by quantitative combustion and conversion to  $\text{CO}_2$  and  $\text{N}_2$  using an ANCA GSL elemental  
168 analyser interfaced with a Sercon 20/20 mass spectrometer. Stable C isotope ratios  
169 ( $\delta^{13}\text{C}$ ) expressed as per-mille (‰) and deviations from the Vienna Pee Dee Belemnite  
170 standard (VPDB) were also determined on the resulting  $\text{CO}_2$ . Analytical precision over  
171 the experiment for the analysis of an internal laboratory CN standard (Acetanilide,  
172 Elemental Micro Analysis Ltd. UK) was mean  $-30.12\text{‰}$   $\delta^{13}\text{C}$  ( $\sigma_{n-1} = 0.06$   $n=10$ ),  $10.16\%$   
173 N ( $\sigma_{n-1} = 0.29$   $n=10$ ), and  $70.18\%$  C ( $\sigma_{n-1} = 2.00$   $n=10$ ); and for a commercial  
174 microcrystalline cellulose powder (Sigma Aldrich, UK. No. C-8002 Lot. 92F-0243) was  
175 mean  $-23.89\text{‰}$   $\delta^{13}\text{C}$ , ( $\sigma_{n-1} = 0.06$   $n=3$ ) and  $41.38\%$  C ( $\sigma_{n-1} = 0.25$   $n = 3$ ). These results  
176 compare favourably with the analytical precision of the methods typically reported for  
177 %C, %N and  $\delta^{13}\text{C}$  determinations (Loader et al., 2013; McCarroll and Loader, 2004).

### 178 2.3.2 Differential scanning calorimetry (DSC)

179 DSC thermographs were obtained using a differential scanning calorimeter Q100, TA  
180 instrument. Two replicates of each sample (10 mg) were placed in open aluminium pans  
181 under a flow of dry air at  $2.1 \text{ kg cm}^{-2} \text{ min}^{-1}$  and exposed to a temperature increase of  $10$   
182  $^{\circ}\text{C min}^{-1}$  from  $50$  to  $600$   $^{\circ}\text{C}$ . Samples of Indium (mp:  $156.6$   $^{\circ}\text{C}$ ) were used to calibrate  
183 the calorimeter. The heat of combustion (Q) was determined by integrating the  
184 thermographs with respect to time over the exothermic region ( $150 < T < 600$   $^{\circ}\text{C}$ ). The  
185 region  $T < 150^{\circ}\text{C}$  was not considered as it is dominated by endothermic reactions  
186 associated with water loss (Fernández et al., 2011). Thermograms were normalized to  
187 each sample's total organic C content (Leifeld et al., 2015). The areas under the  
188 thermographs were divided into three temperature regions representing different levels  
189 of resistance to thermal oxidation (Merino et al., 2015, 2014; Rovira et al., 2008): labile  
190 organic matter, mainly comprising carbohydrates, proteins and other aliphatic  
191 compounds ( $150 < T_1 < 375$   $^{\circ}\text{C}$ ); recalcitrant organic matter, such as lignin or other  
192 polyphenols ( $375 < T_2 < 475$   $^{\circ}\text{C}$ ); and highly recalcitrant organic matter, such as



193 polycondensed aromatic forms ( $475 < T_3 < 600$  °C). The resulting partial heats of  
194 combustion representing these three regions were calculated as  $q_1$ ,  $q_2$  and  $q_3$ . The  
195 temperature at which 50% of the total energy is released under the given conditions ( $T_{50}$ ),  
196 as well as the temperatures of the maximum combustion peak in each temperature  
197 region ( $T_1$ ,  $T_2$  and  $T_3$ , respectively) were also determined.

### 198 *2.3.3 Solid state $^{13}\text{C}$ cross polarization-magic angle spinning (CP-MAS) Nuclear* 199 *Magnetic Resonance (NMR) spectroscopy*

200 Solid-state  $^{13}\text{C}$  CP-MAS NMR analyses were carried out on a selected subset of  
201 samples: two pre-fire FF samples and three pairs of post-fire pyrogenic + unburnt FF  
202 samples taken at sampling points at which maximum temperatures during the fire ( $T_{\text{max}}$ )  
203 covered a range of recorded  $T_{\text{max}}$ s: sample n.2,  $T_{\text{max}}=550$  °C; sample n.13,  $T_{\text{max}}=683$  °C;  
204 and sample n.20,  $T_{\text{max}}=950$  °C (for the complete range of  $T_{\text{max}}$ s see Table S1).

205 Analyses were performed using an Agilent Varian VNMRS-500-WB spectrometer,  
206 operated at a proton resonance frequency of 500 MHz and using a zirconia rotor of  
207 160 $\mu\text{L}$ . C chemical shifts were referenced to the C methylene signal of solid adamantane  
208 at 28.92 ppm. Cross Polarization Magic Angle Spinning (CPMAS) analysis was carried  
209 out under the following conditions: contact time 1 ms, inter-scan delay 1 s (a proton  $T_1$   
210 experiment was performed to check the suitability of this time), and MAS rate 12 kHz.  
211 The number of scans was ca. 10000-35000. The cross polarization time was set at 1 ms.  
212 In the CPMAS technique, the sensitivity to  $^{13}\text{C}$  is increased by polarization transfer from  
213 the  $^1\text{H}$  to the  $^{13}\text{C}$  spin system. This may obscure the relative intensity distribution in a  $^{13}\text{C}$   
214 NMR spectrum of pyrogenic material due to inefficient cross polarization of C in highly-  
215 condensed structures (Smernik et al., 2002). However, Knicker et al. (2005b) have  
216 shown that, in contrast to soot and other very recalcitrant forms of pyrogenic and black  
217 carbon, charred vegetation residues and burnt SOM do not usually contain a substantial  
218 proportion of highly-condensed graphite-like structures, and, therefore, quantitative  
219 analysis by the CPMAS NMR technique is possible for this type of samples.

220 The NMR spectra were processed and the areas of the different signals were integrated  
221 and quantified using the MestreNova software 8.1.0 (Mestrelab Research Inc, University  
222 of Santiago de Compostela). For quantification, the spectra were divided into four regions  
223 representing different chemical environments of the  $^{13}\text{C}$  nucleus: alkyl C (0–45 ppm), O-  
224 alkyl C (45–110 ppm), olefinic and aromatic C (110–160 ppm), and carbonyl C (160–210  
225 ppm). Corrections of the regions' intensities due to spinning side bands were made  
226 according to Knicker et al. (2005a). The degree of aromaticity (%) was calculated  
227 according to Hatcher et al. (1981):  $\text{aromatic-C} \times 100 / (\text{alkyl C} + \text{O-alkyl-C} + \text{aromatic-C})$ .

#### 228 *2.4 Statistical analyses*

229 Statistical analyses were performed with the software IBM SPSS Statistics 19.  
230 Differences in FF characteristics before and after fire were investigated using 'fire effect'  
231 as the independent factor in one-factor ANOVAs (providing three classes: pre-fire; post-  
232 fire unburnt and post-fire pyrogenic). The equality of variances was assessed using  
233 Levene's homoscedasticity test. In the cases where differences in arithmetic means  
234 among classes were statistically significant and variances for those classes equal, the  
235 *post-hoc* Duncan's multiple range test was performed to identify classes with significantly  
236 different means. In the cases of unequal variance, the post-hoc Tamhane's T2 test was  
237 performed instead of Duncan's. Spearman's rank correlation coefficients ( $\rho$ ) were  
238 calculated to identify any correlations between variables. The level of significance used  
239 for all the tests was 5 % (i.e.  $\alpha = 0.05$ ).

## 240 3. Results

### 241 3.1 Fire characteristics

242 The experimental fire was a high-intensity crown fire with a head fire intensity of ~8000  
243 kW m<sup>-1</sup>, a flame height of 5-6 m above canopy level and a spread rate of ~6–7 m min<sup>-1</sup>  
244 (Fig. 1). This fire behaviour is in the typical range for boreal crown fires (De Groot et al.,  
245 2013a; De Groot et al., 2009).

246 The burning of this 1.7 ha plot, from ignition at its flank to extinction of the flaming  
247 combustion, lasted approx. 16 minutes. Figure 2b shows typical temperature-time  
248 profiles recorded during the experimental fire at the FF surface and the FF/mineral soil  
249 interface. Of the 27 thermocouples installed, 18 thermocouples successfully recorded  
250 data at the FF surface (the other 9 failed). Average T<sub>max</sub> was 745 °C (range 550-976 °C,  
251 Table S1). A T<sub>max</sub> >600 °C was recorded at 16 sampling points, >700 °C at 9 sampling  
252 points and only 4 sampling points registered T<sub>max</sub> >900 °C. The average durations of  
253 T>300 °C, T>500°C and T>700 °C were 180 s (range 65-364 s), 81 s (range 24-176 s)  
254 and 21 s (range 0-72 s) respectively. Typical times to reach T<sub>max</sub> from 40°C at the FF  
255 surface ranged from ~50 to 200 s with times to return to 40° C ranging from ~500 to  
256 >2000s. It is worth stressing the high spatial variability on the fire's thermal signature at  
257 the FF surface even at the small spatial scale at which our thermocouples were deployed  
258 (270 m<sup>2</sup>, see Fig 1). Sensors only 2 m apart registered T<sub>max</sub> that differed by up to 350 °C  
259 (Table S1).

260 At the interface of FF/mineral soil, 21 of 27 loggers successfully recorded data and T<sub>max</sub>  
261 never exceeded 60 °C (average 24°C, range 7- 60 °C). Based on these data and the fact  
262 that the mineral soil was waterlogged before and after the fire due to the shallow water  
263 table, the direct effect of fire on the properties of the organic matter in the mineral soil  
264 was considered negligible.

### 265 3.2 Forest floor C stocks

266 The FF (Fig. 2a) had an average depth to the mineral soil of  $6.5 \pm 1.8$  cm (mean  $\pm$  standard  
267 deviation;  $n=108$ ) and a bulk density of  $0.063 \pm 0.014$  g cm<sup>-3</sup> ( $n=10$ ). The fire consumed  
268 part of the FF and generated a continuous upper layer of charred (pyrogenic) FF ( $1.3 \pm 0.6$   
269 cm depth;  $n=108$ ; bulk density  $0.034 \pm 0.018$  g cm<sup>-3</sup>;  $n=27$ ; Fig. 2c). The uncharred FF  
270 remaining underneath had a depth of  $3.9 \pm 1.2$  cm ( $n=108$ ) and a bulk density of  
271  $0.098 \pm 0.030$  g cm<sup>-3</sup> ( $n=27$ ). Santín et al. (2015b) determined the variation of the different  
272 forest C stocks for this experimental wildfire by statistical bootstrap procedures and  
273 estimated that almost half of the initial C stock in the FF ( $19.7 \pm 6.2$  Mg C ha<sup>-1</sup>) was either  
274 emitted to the atmosphere ( $6.0 \pm 4.4$  Mg C ha<sup>-1</sup>) or transformed into a pyrogenic FF layer  
275 ( $1.9 \pm 0.4$  Mg C ha<sup>-1</sup>), with the rest remaining unaffected, i.e. unburnt ( $9.9 \pm 1.7$  Mg C ha<sup>-1</sup>).  
276 This represents a conversion to pyrogenic C of 24.5 % of the FF C affected by fire and  
277  $\sim 10$  % of the initial FF C stock.

278 During the fire, some material from the overstory fell to the ground and became part of  
279 the pyrogenic FF layer. However, this contribution was quantitatively very low ( $\sim 15$  % of  
280 the pyrogenic FF layer weight, Santín et al., 2015b) and thus, these overstory inputs are  
281 expected to have had limited effects on the characteristics of the pyrogenic FF layer.

282 The inorganic C concentration in the pyrogenic FF samples was very low (no  
283 effervescence was observed after addition of 10% HCl so, according to the commonly  
284 used classification of Rayment and Lyons (2011), inorganic C concentration is  $<1$  %).  
285 Therefore, total C was considered equivalent to total organic C.

### 286 *3.3 C and N concentrations, $\delta^{13}\text{C}$ signatures and C:N ratios in the forest floor*

287 Before the fire the FF had average concentrations of 40.5 % C, 1.0 % N and a  $\delta^{13}\text{C}$   
288 signature of  $-28.1$  ‰ (Table 1). After the fire, the pyrogenic FF layer showed significantly  
289 higher C and N concentrations (54.1 % and 1.3 % respectively), and a more negative  
290  $\delta^{13}\text{C}$  signature ( $-28.9$  ‰  $\delta^{13}\text{C}$ ), whereas the unburnt FF layer had similar values to the

291 pre-fire FF (36.9 % C, 1.1 % N, and -28.1 ‰  $\delta^{13}\text{C}$ ; Table 1). The C:N ratio was the highest  
292 for the pyrogenic FF (43.8) and the lowest in the post-fire unburnt FF (32.7; Table 1).

### 293 *3.4 Thermostability of the forest floor: DSC analysis*

294 All DSC thermograms displayed three exotherm bands with maxima at 333-348 °C (T1),  
295 380-433 °C (T2) and 480-506 °C (T3) (Fig. 3 and Table 1), assigned to labile, recalcitrant  
296 and highly recalcitrant organic matter, respectively (Merino et al., 2015, 2014; Rovira et  
297 al., 2008).

298 Pyrogenic FF showed higher  $T_{50}$  and  $q3(\%)$ , but lower  $q1(\%)$  and  $q2(\%)$  than pre- and  
299 post-fire unburnt FF (Table 1), which indicates a greater thermal recalcitrance of the  
300 pyrogenic samples. The main peaks indicated by T1 and T2 occurred at higher  
301 temperatures in the pyrogenic FF whereas the T3 occurred at lower temperatures in  
302 comparison with pre- and post-fire unburnt FF (Table 1). No significant differences were  
303 found between the thermostability of the pre-fire and the post-fire unburnt FF (Table 1;  
304 Fig. 3b).

305 Regarding the effect of fire characteristics on properties of the pyrogenic FF, as  $T_{\text{max}}$   
306 increased, the corresponding DSC curves of the pyrogenic FF samples shifted to higher  
307 temperatures (Fig. 3a). This indicates a progressive loss of the most thermolabile  
308 compounds ( $q1$ ) and enrichment in recalcitrant ( $q2$ ) and highly recalcitrant ( $q3$ )  
309 compounds with increasing fire temperatures. The increase of  $T_{\text{max}}$  from 550 to 680 °C  
310 mainly translated into a decrease in  $q1$  and an increase in  $q2$  (Fig. 3a), whereas the  
311 increase of  $T_{\text{max}}$  from 680 to 950 °C resulted mainly in an enrichment of highly recalcitrant  
312 compounds in the  $q3$  region (Fig. 3a). Only 3 samples are displayed in Fig. 3 as  
313 examples, however, the observed differences are consistent for all the samples  
314 analysed: the samples subjected to  $T_{\text{max}} < 700$  °C ( $n=9$ ) presented higher  $q1$  ( $39\pm 3\%$ )  
315 and lower  $q3$  values ( $11\pm 2\%$ ) than the samples subjected to  $T_{\text{max}} > 700$  °C ( $n=9$ ), ( $q1=$   
316  $31\pm 5\%$  and  $q3 = 18\pm 8\%$ ; for individual values see Table S1).

### 317 3.5 Forest floor composition: Solid-state $^{13}\text{C}$ NMR

318 The  $^{13}\text{C}$  NMR spectra of the pre-fire FF (Fig. 4a) were dominated by the signal attributed  
319 to O-alkyl structures, mainly cellulose and hemicellulose (73 ppm and 103 ppm). The  
320 contribution of the signal in the alkyl region was also notable (Fig. 4b) and dominated by  
321 a peak at 30 ppm, attributed to polymethylene C (lipids, cutin) (Almendros et al., 2000).  
322 The most intense aromatic C signals occurred at 145, 148 and 153 ppm, which are  
323 assigned to lignin and tannins (Preston et al., 1997). Signals from pyrogenic materials  
324 were not evident in the aryl region. A prominent lignin signal was also identified at 56  
325 ppm (Kögel-Knabner, 2002). Note that in Fig. 4 only one of the two pre-fire FF samples  
326 analysed is shown as the two spectra were nearly identical.

327 Spectra of the pyrogenic FF are very different to the pre-fire FF (Fig. 4a), with an evident  
328 loss of O-alkyl-C compounds by charring, a slight relative increase of alkyl compounds  
329 and a substantial presence of newly-formed pyrogenic aromatic compounds, as  
330 indicated by the broad peak around 130 ppm (Skjemstad et al., 2002). Higher signal  
331 intensities in the aromatic region of the pyrogenic FF sample spectra were found for  
332 those samples subjected to higher  $T_{\text{max}}$  during the fire (Fig. 4a and 4b). The degree of  
333 aromaticity increased from 38 % for the sample subjected to  $T_{\text{max}}$  550  $^{\circ}\text{C}$  to 60 % and 64  
334 % in samples subjected to  $T_{\text{max}}$  of 680 and 950  $^{\circ}\text{C}$ , respectively.

335 The spectra of the post-fire unburnt FF samples were all similar, irrespective of the  $T_{\text{max}}$   
336 to which they were exposed during the fire (Fig. 4a). They were also similar to the pre-  
337 fire FF spectra described above, with a slightly higher contribution of alkyl compounds  
338 (Fig. 4a and 4b).

### 339 3.6 Correlations between fire characteristics and forest floor transformations

340 Spearman's rank correlation coefficients ( $\rho$ ) between some characteristics of the  
341 pyrogenic FF layer and fire parameters, and their level of significance are given in Table

342 2. A complete set of correlations for all pyrogenic FF characteristics and fire parameters  
343 analysed can be found in Table S2.

344 Some of the characteristics of the pyrogenic FF showed correlations with each other:  
345 %C was positively correlated to  $T_{50}$  and negatively correlated to %N and  $q_1$ , whereas  
346 %N showed a positive correlation to  $q_1$  and a negative correlation to %C and  $T_{50}$  (Table  
347 2). This indicates that the increase of thermal recalcitrance had an associated  
348 enrichment of C and a concomitant loss of N. Moreover, the  $\delta^{13}\text{C}$  signature of the  
349 pyrogenic FF showed a negative correlation with  $q_2$  and a positive correlation with  $q_3$   
350 ( $\rho=-0.624$  and  $\rho=0.649$ ; Table S2).

351 Regarding relationships between fire parameters and pyrogenic FF characteristics,  $T_{\text{max}}$   
352 was positively correlated to %C and  $T_{50}$ , and negatively correlated to  $q_1$  (Table 2), which  
353 indicates that higher  $T_{\text{max}}$  led to an increase in the thermal recalcitrance of the pyrogenic  
354 FF. Heating durations of  $T>300\text{ }^{\circ}\text{C}$  and  $>400\text{ }^{\circ}\text{C}$  were positively correlated with %N, and  
355 those of  $T>600\text{ }^{\circ}\text{C}$  and  $>700\text{ }^{\circ}\text{C}$  showed significant positive correlations with the DSC  
356 parameter  $T_{50}$  and negative correlations with the DSC parameter  $q_1$ . The duration of  
357 heating  $>700\text{ }^{\circ}\text{C}$  also showed a positive correlation with %C (Table 2).

358 No significant correlations were found between characteristics of the FF layer remaining  
359 unburnt after the fire and any of the fire parameters determined (Table S3).

## 360 4. Discussion

### 361 4.1 Transformations of the forest floor and their correlations with fire temperature-time 362 profiles

#### 363 4.1.1 The pyrogenic FF layer

364 The pyrogenically altered (charred) FF layer following this forest fire (Fig. 2c) exhibited  
365 typical characteristics of charred organic products, such as higher C concentration,  
366 enhanced thermal recalcitrance and higher aromaticity when compared with unburnt  
367 organic matter (Knicker, 2007). This largely results from degradation of the most  
368 thermolabile compounds, mainly O-alkyl structures, and concomitant formation of more  
369 refractory aromatic structures (Knicker et al., 2008). The observed decrease in the  $\delta^{13}\text{C}$   
370 signature ( $\sim 0.8\text{‰}$ ) after charring is attributed to the loss of the isotopically heavier  
371 cellulose-type compounds (Bird and Ascough, 2012). This observation agrees with the  
372 reported loss of O-alkyl compounds (Section 3.5). A very similar change in the  $\delta^{13}\text{C}$   
373 signature of the litter layer was observed by Alexis et al. (2010) before and after a  
374 prescribed fire in a scrub-oak ecosystem.

375 In addition to the observation of these general changes with burning, our experimental  
376 design also allowed the establishment of direct correlations between specific wildfire  
377 parameters and some features of the pyrogenic FF. The most relevant fire parameter  
378 was  $T_{\text{max}}$ , where increased values were associated with higher %C and concomitant  
379 decreases in %N. Increasing  $T_{\text{max}}$  was also associated with enhancement in thermal  
380 recalcitrance of the pyrogenic FF and loss of thermally labile compounds (see DSC  
381 analyses, Section 3.3). These observations were also consistent with the decrease of O-  
382 alkyl compounds and the increase in the degree of aromaticity reported by  $^{13}\text{C}$  NMR  
383 analyses (Section 3.4). In addition to this, positive correlations were detected between  
384 the concentrations of N and the heating durations when  $T > 300\text{ }^{\circ}\text{C}$  and  $T > 400\text{ }^{\circ}\text{C}$ , but  
385 not at any temperatures above these (Table 2). This could indicate relative N enrichment



386 at lower temperatures ( $T < 400$  °C), when O and H are preferentially lost by dehydration  
387 and dehydroxylation reactions (Knicker et al., 2008), and a subsequent loss of N at  
388 temperatures  $T \sim 500$  °C (Bodí et al., 2014), with the remaining fraction locked into N-  
389 heteroaromatic C forms (Knicker, 2010). The  $\delta^{13}\text{C}$  signature of the pyrogenic FF showed  
390 no significant trends with  $T_{\text{max}}$  or heating durations (Table S2). This is in contrast to  
391 results reported for laboratory-produced chars by Wurster et al. (2015, 2013), who found  
392 progressively lower isotope composition at higher charring temperatures relative to the  
393 original material.

394 The general trends for FF transformations observed for this wildfire are in agreement  
395 with those detected under laboratory conditions (Ascough et al., 2008; Keiluweit et al.,  
396 2010), however, the range of temperatures and the heating durations reported here differ  
397 substantially from those used in laboratory experiments. Ascough et al. (2011) detected  
398 the main chemical changes in laboratory-produced charcoals at  $\sim 400$  °C ( $\text{O}_2$ -limited  
399 atmosphere, 60 min exposure), with charcoal produced at  $>400$  °C being chemically more  
400 homogeneous (largely aromatic) and chemically recalcitrant than charcoal produced at  
401 300 °C. McBeath et al. (2011) also produced charcoal under laboratory conditions ( $\text{O}_2$ -  
402 deprived atmosphere, 5 h exposure) and found that aromaticity increased up to 400 °C  
403 (reaching  $>85\%$  by 350 °C), whereas at  $T > 400$  °C condensation of the already  
404 predominant aromatic fraction increased. Similar results have been found by Wurster et  
405 al. (2013) and McBeath et al. (2015), who suggested that at  $T > 500$  °C there was mainly  
406 an increase of condensation of the already dominant aromatic fraction, as smaller  
407 aromatic clusters ( $<7$  rings) combined into those of 7-14 rings. Therefore, it seems that,  
408 under laboratory conditions, even if the characteristics of pyrogenic organic materials are  
409 partially conditioned by the properties of the source material, at temperatures  $>300$ -400  
410 °C all materials develop highly aromatic structures and their characteristics and  
411 properties tend to converge (Almendros et al., 2003; Keiluweit et al., 2010; Knicker,

412 2007). Importantly, these findings appear to be consistent for a range of materials from  
413 grass to wood.

414 Our data suggest that under the typical wildfire conditions studied here, the T threshold  
415 for the most substantial chemical changes in the FF was not ~300-400 °C but followed  
416 exposure to  $T_{\max} > 600-700$  °C, as indicated by significant correlations between % C,  
417 thermal recalcitrance ( $T_{50}$  and  $q_1$ ) and the durations in and above this T range (Table 2).  
418 It is also important to consider that there were no significant correlations between these  
419 parameters for heating within lower temperature thresholds (in the range  $300 < T < 500$  °C;  
420 Table 2). The  $^{13}\text{C}$  NMR spectra of selected samples also indicate that the main increase  
421 in the degree of aromaticity (%) occurred between the sample subjected to  $T_{\max}$  of 550  
422 °C (38%) to the sample subjected to  $T_{\max}$  of 680 °C (60%) (Fig. 4). The difference in the  
423 degree of aromaticity between the samples subjected to 680 °C and 950 °C was much  
424 smaller (60% and 65%, see Fig. 4), and the main chemical differences between them  
425 could be an increase in the condensation of the already predominant aromatic fraction  
426 (McBeath et al., 2011). However, this speculation cannot be confirmed by the analyses  
427 performed here.

428 In a previous field study, Alexis et al. (2010) used thermo-sensitive paints to obtain  
429 approximate maximum temperatures during a prescribed shrub fire and found an  
430 increase of the aromatic C contribution in charred litter from ~40% for  $T_{\max}$  ~380 °C to  
431 58% for  $T_{\max}$  ~650 °C ( $n=4$ ). Unfortunately, maximum temperatures reported during the  
432 fire did not exceed ~650 °C nor did the paints provide records of temperature with time.  
433 These results, overall, are in support of the findings from our study, with the most notable  
434 being that under actual fire conditions higher temperatures ( $600 < T < 700$  °C) may be  
435 required to transform the organic matter into highly aromatic and thermally recalcitrant  
436 forms than has been previously assumed based on temperature thresholds determined  
437 in laboratory studies ( $\sim 300 < T < 500$  °C).

438 The discrepancies discussed here between the effect of specific  $T_{\max}$  under field vs.  
439 laboratory conditions may be due to the variation of other critical fire parameters that  
440 influence pyrogenic matter production (Santín et al., 2015a): the period of exposure  
441 (heating duration) and the availability of oxygen.

442 Our experimental wildfire had a spread rate of 6-7 m min<sup>-1</sup>. This spread rate resulted in  
443 average heating durations of the FF of >300 °C ~180 s, >500 °C ~ 81 s, >700 °C ~21 s.  
444 This fire was relatively slow-moving compared with even more intense boreal crown  
445 wildfires (Taylor et al., 2004). A more intense and faster fire front would probably produce  
446 higher  $T_{\max}$  in the FF, but even shorter heating durations close to the peak T values, than  
447 those reported here. In most laboratory studies, soils and organic materials have been  
448 exposed to a constant maximum temperature for many minutes or even hours (Ascough  
449 et al., 2008; Badía-Villas et al., 2014; McBeath et al., 2015; Wurster et al., 2013). Hence  
450 it is likely that these long heating durations lead to significant penetration of heat and  
451 mass transfer of volatile products, allowing chemical transformations to proceed at  
452 temperatures lower than those during actual wildfire conditions.

453 In addition to heating duration, the availability of oxygen will influence the balance  
454 between combustion, gasification and pyrolysis and, therefore, will also condition the  
455 amount and characteristics of pyrogenic products (Ascough et al., 2008; Loader and  
456 Buhay, 1999). Laboratory studies have been carried mostly under reduced and oxygen-  
457 restricted atmospheres (Ascough et al., 2011), which may not reflect conditions  
458 experienced during wildfire. To what degree this may be the case represents an area for  
459 future investigation as the determination of oxygen levels in the FF during this wildfire  
460 was not possible.

461 Apart from the fire characteristics discussed above, fuel properties could play a role in  
462 causing the differences observed between field and laboratory experiments. Fuel  
463 arrangement, moisture and particle size can also affect fire characteristics and, therefore,  
464 the properties of the resulting pyrogenic products (Brewer et al., 2013). Future research

465 should be aimed to gain insights into the specific effects of these parameters on the  
466 production and characteristics of pyrogenic organic matter.

#### 467 *4.1.2. The post-fire unburnt FF layer*

468 The lack of any significant correlations between the fire parameters analysed and the  
469 characteristics of the lower part of the FF layer that remained unburnt (i.e. visibly  
470 uncharred after fire), together with the similarity in properties of this post-fire unburnt FF  
471 layer and the pre-fire FF, suggest that the fire had little direct impact on it. The only  
472 notable differences between the pre-fire FF and the post-fire unburnt FF layer were the  
473 higher C:N ratios and contribution of alkyl-type compounds in the latter (Table 1 and Fig.  
474 4). These differences could be due to the fact that the part of the FF layer that remained  
475 unburnt after the fire was the deepest (i.e. closest to the mineral soil), and, therefore, the  
476 most humified (Almendros et al., 2000).

#### 477 *4.2 Wider implications: soil organic carbon stocks and future wildfire trends*

478 The characteristics of this experimental high-intensity crown fire were representative of  
479 typical wildfire conditions in this boreal region of Canada (De Groot et al., 2013a). In  
480 general, North American boreal wildfires are stand-replacing crown fires whereas the  
481 Eurasian boreal fire regime is characterized by surface fires, which are less intense,  
482 smaller in size, but more frequent (De Groot et al., 2013a). Despite these differences in  
483 fire dynamics, the organic top soil layer, the FF, is the fuel component most affected by  
484 fire in the boreal region worldwide (De Groot et al., 2013a). Our experimental wildfire  
485 substantially altered the FF C stock, burning almost half of it and converting ~10% of this  
486 initial FF C stock to pyrogenic C (i.e. 24% of the fire-affected FF C) (Santín et al., 2015b).  
487 However, the fire did not directly alter the mineral soil C stock. This is typical for boreal  
488 forest fires, which rarely burn through the entire depth of the FF layer down to the mineral  
489 soil (De Groot et al., 2009).

490 As residence times of pyrogenic organic matter (PyOM) are generally one or two orders  
491 of magnitude longer than those of its unburnt precursors (Santín et al., 2015a), PyOM  
492 inputs from wildfires can substantially decrease the overall turnover rate of the whole soil  
493 organic C stock (Lehmann et al., 2008). In addition to this, PyOM also affects soil fauna,  
494 microbial activity and community composition (Ameloot et al., 2013), post-fire nutrient  
495 dynamics (Michelotti and Miesel, 2015), native SOM decomposition (Maestrini et al.,  
496 2014), and C and N emissions from soils (Bergeron et al., 2013; Zhang et al., 2015). The  
497 magnitude and direction of these changes will be influenced by the amount and  
498 characteristics of PyOM. Therefore, PyOM production within the FF during boreal fires  
499 is quantitatively and qualitatively important and should be considered when addressing  
500 C fluxes during fire and post-fire C dynamics.

501 Previous studies have already highlighted the high variability in the composition of PyOM  
502 generated by wildfire (McBeath et al., 2013; Michelotti and Miesel, 2015). Our results  
503 support these findings: even within a relatively homogeneous fuel (FF) and at a small  
504 spatial scale (270 m<sup>2</sup>), differences in fire parameters resulted in substantial variability of  
505 PyOM characteristics. In addition to this, our findings correlate, for the first time, this  
506 variability in characteristics of the pyrogenic FF with temperature-time profiles registered  
507 during the fire: higher temperatures and heating durations correspond with increased  
508 degree of aromaticity and thermal recalcitrance of the PyOM. These chemical properties,  
509 in turn, have been shown to strongly affect the rate of decomposition of PyOM (Nguyen  
510 et al., 2010; Harvey et al., 2012). For instance Baldock and Smernik (2002) reported a  
511 decrease of mineralization with increasing production temperature for charred pine wood  
512 and attributed this to the concomitant increase in aromaticity. Therefore, it is reasonable  
513 to conclude that higher temperatures and prolonged heating could lead to a higher  
514 resistance to biological degradation of the PyOM produced.

515 Recent increases in wildfire activity, both in terms of the area affected, and the intensities  
516 and severities of the fires, have been reported in the boreal regions (Kelly et al., 2013).

517 This trend is expected to be enhanced further in the near future (De Groot et al., 2013b;  
518 Héon et al., 2014). De Groot et al. (2013b) predicted associated substantial increases of  
519 the consumption of the FF, especially in western Canada. Therefore, if the trends  
520 observed in this experimental wildfire are also applicable to more severe fires, the  
521 predicted future increases in fire intensity and severity would be expected to lead to  
522 higher recalcitrance of the PyOM produced and hence enhance the capacity of soils to  
523 act as long-term C sinks. The specific tradeoffs between C emitted and C locked up as  
524 PyOM during fires, and their impact in local and global C fluxes and budgets, are yet to  
525 be fully elucidated (Lehman et al. 2008; Santin et al. 2015a). The results presented here  
526 contribute to addressing this issue and therefore to reducing uncertainties in the role of  
527 wildfires in the global C balance.

## 528 **5. Conclusions**

529 Investigation of the conditions governing transformation of SOM by wildfire is  
530 experimentally very challenging and our knowledge to date has been derived largely  
531 from laboratory experiments and low-intensity prescribed fires, which may not be  
532 particularly representative of typical wildfire conditions. Furthermore, organic matter  
533 transformations are driven by several factors (fire characteristics, soil type, organic  
534 matter and vegetation characteristics), resulting in very high variability even over short  
535 spatial scales, which adds to this challenge.

536 This study overcomes these limitations by using an experimental forest fire that  
537 represented typical boreal wildfire conditions. This allowed us to establish, for the first  
538 time, correlations between temperature-time profiles obtained under wildfire conditions  
539 and the characteristics of the pyrogenic products present in the FF after the fire. Higher  
540  $T_{\max}$  reached during the fire and associated longer heating durations correlated with  
541 greater C enrichment, increased thermal recalcitrance and associated aromaticity of the  
542 pyrogenic FF layer, particularly for  $T_{\max} > 600$  °C. This  $T_{\max}$  is substantially higher than

543 the range of  $300 < T < 500$  °C widely reported for development of aromaticity based on  
544 laboratory tests, which have tended to involve unrealistically long heating durations  
545 compared to those typical for actual wildfires.

546 PyOM production within the FF during boreal fires is quantitatively and qualitatively  
547 important and should not be overlooked when studying C fluxes and dynamics both  
548 during and after fire. The correlations established here between PyOM characteristics  
549 and fire conditions could help in the understanding of the effects on soil C dynamics of  
550 the changing climate in this region. The predicted increases in boreal fire severity would  
551 lead to the production of more recalcitrant and biologically stable PyOM, which in turn,  
552 would reduce soil organic C turnover rates. Whilst the net effects of climate change on  
553 C stocks in boreal regions remain the subject of much debate, this mechanism could be  
554 an important positive driver affecting the C sequestration capability of fire-affected boreal  
555 soils.

556 **Acknowledgements**

557 C.S. is grateful to the Spanish Ministry of Education for a mobility postdoctoral fellowship  
558 (EX2010–0498) and to the University of Oviedo (Spain), her previous affiliation.  
559 Fieldwork and laboratory analyses were supported by the College of Science of Swansea  
560 University. Funding by the The Leverhulme Trust (Grant RPG-2014-095) enabled  
561 manuscript preparation. Special thanks go to Ray Ault (FP-Innovations), and Larry Nixon  
562 and Danny Beaulieu (Environment and Natural Resources, GNT) for enabling us to  
563 participate in the Fire-Smart project. Thanks also to Dr Caroline Preston (NRCan), the  
564 staff of FP-Innovations, Alberta Environment and Sustainable Resource Development,  
565 and the NT Government for their support during fieldwork. Soil analyses (solid-state <sup>13</sup>C  
566 NMR Nuclear Magnetic Resonance, Differential Scanning Calorimetry and Infrared  
567 Fourier Transform) were carried out in RIAIDT, University of Santiago de Compostela,  
568 Spain, by Ms Montse Gómez.

569 **References**

- 570 Alexis, M.A., Rasse, D.P., Rumpel, C., Bardoux, G., Péchot, N., Schmalzer, P., Drake,  
571 B., Mariotti, A., 2007. Fire impact on C and N losses and charcoal production in a  
572 scrub oak ecosystem. *Biogeochemistry* 82, 201–216. doi:10.1007/s10533-006-  
573 9063-1
- 574 Alexis, M.A., Rumpel, C., Knicker, H., Leifeld, J., Rasse, D., Péchot, N., Bardoux, G.,  
575 Mariotti, A., 2010. Thermal alteration of organic matter during a shrubland fire: A  
576 field study. *Org. Geochem.* 41, 690–697. doi:10.1016/j.orggeochem.2010.03.003
- 577 Almendros, G., Dorado, J., González-Vila, F.J., Blanco, M.J., Lankes, U., 2000. <sup>13</sup>C  
578 NMR assessment of decomposition patterns during composting of forest and  
579 shrub biomass. *Soil Biol. Biochem.* 32, 793–804. doi:10.1016/S0038-  
580 0717(99)00202-3
- 581 Almendros, G., Knicker, H., González-Vila, F.J., 2003. Rearrangement of carbon and  
582 nitrogen forms in peat after progressive thermal oxidation as determined by solid-  
583 state <sup>13</sup>C- and <sup>15</sup>N-NMR spectroscopy. *Org. Geochem.* 34, 1559–1568.  
584 doi:10.1016/S0146-6380(03)00152-9
- 585 Ameloot, N., Graber, E.R., Verheijen, F.G.A., De Neve, S., 2013. Interactions between  
586 biochar stability and soil organisms: Review and research needs. *Eur. J. Soil Sci.*  
587 64, 379–390. doi:10.1111/ejss.12064



- 588 Amiro, B.D., Todd, J.B., Wotton, B.M., Logan, K.A., Flannigan, M.D., Stocks, B.J.,  
589 Mason, J.A., Martell, D.L., Hirsch, K.G., 2001. Direct carbon emissions from  
590 Canadian forest fires, 1959-1999. *Can. J. For. Res.* 31, 512–525.  
591 doi:10.1139/x00-197
- 592 Ascough, P.L., Bird, M.I., Francis, S.M., Thornton, B., Midwood, A. J., Scott, A. C.,  
593 Apperley, D., 2011. Variability in oxidative degradation of charcoal: Influence of  
594 production conditions and environmental exposure. *Geochim. Cosmochim. Acta*  
595 75, 2361–2378. doi:10.1016/j.gca.2011.02.002
- 596 Ascough, P.L., Bird, M.I., Wormald, P., Snape, C.E., Apperley, D., 2008. Influence of  
597 production variables and starting material on charcoal stable isotopic and  
598 molecular characteristics. *Geochim. Cosmochim. Acta* 72, 6090–6102.  
599 doi:10.1016/j.gca.2008.10.009
- 600 Atanassova, I., Doerr, S.H., 2010. Organic compounds of different extractability in total  
601 solvent extracts from soils of contrasting water repellency. *Eur. J. Soil Sci.* 61,  
602 298–313. doi:10.1111/j.1365-2389.2009.01224.x
- 603 Badía-Villas, D., González-Pérez, J.A., Aznar, J.M., Arjona-Gracia, B., Martí-Dalmau,  
604 C., 2014. Changes in water repellency, aggregation and organic matter of a mollic  
605 horizon burned in laboratory: Soil depth affected by fire. *Geoderma* 213, 400–407.  
606 doi:10.1016/j.geoderma.2013.08.038
- 607 Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of  
608 thermally altered *Pinus resinosa* (Red pine) wood. *Org. Geochem.* 33, 1093–1109.  
609 doi:10.1016/S0146-6380(02)00062-1
- 610 Bergeron, S.P., Bradley, R.L., Munson, A., Parsons, W., 2013. Physico-chemical and  
611 functional characteristics of soil charcoal produced at five different temperatures.  
612 *Soil Biol. Biochem.* 58, 140–146. doi:10.1016/j.soilbio.2012.11.017
- 613 Bird, M.I., Ascough, P.L., 2012. Isotopes in pyrogenic carbon: A review. *Org.*  
614 *Geochem.* 42, 1529–1539. doi:10.1016/j.orggeochem.2010.09.005
- 615 Bodí, M.B., Martín, D.A., Balfour, V.N., Santín, C., Doerr, S.H., Pereira, P., Cerdà, A.,  
616 Mataix-Solera, J., 2014. Wildland fire ash: Production, composition and eco-hydro-  
617 geomorphic effects. *Earth-Science Rev.* 130, 103–127.  
618 doi:10.1016/j.earscirev.2013.12.007
- 619 Bond-Lamberty, B., Peckham, S.D., Ahl, D.E., Gower, S.T., 2007. Fire as the dominant  
620 driver of central Canadian boreal forest carbon balance. *Nature* 450, 89–92.  
621 doi:10.1038/nature06272
- 622 Bormann, B.T., Homann, P.S., Darbyshire, R.L., Morrissette, B.A., 2008. Intense forest  
623 wildfire sharply reduces mineral soil C and N: the first direct evidence. *Can. J. For.*  
624 *Res.* 38, 2771–2783. doi:10.1139/X08-136
- 625 Brewer, N.W., Smith, A.M.S., Hatten, J.A., Higuera, P.E., Hudak, A.T., Ottmar, R.D.,  
626 Tinkham, W.T., 2013. Fuel moisture influences on fire-altered carbon in  
627 masticated fuels: An experimental study. *J. Geophys. Res. Biogeosciences* 118,  
628 30–40. doi:10.1029/2012JG002079

- 629 De Groot, W.J., Cantin, A.S., Flannigan, M.D., Soja, A.J., Gowman, L.M., Newbery, A.,  
630 2013a. A comparison of Canadian and Russian boreal forest fire regimes. *For.*  
631 *Ecol. Manage.* 294, 23–34. doi:10.1016/j.foreco.2012.07.033
- 632 De Groot, W.J., Flannigan, M.D., Cantin, A.S., 2013b. Climate change impacts on  
633 future boreal fire regimes. *For. Ecol. Manage.* 294, 35–44.  
634 doi:10.1016/j.foreco.2012.09.027
- 635 De Groot, W.J., Pritchard, J.M., Lynham, T.J., 2009. Forest floor fuel consumption and  
636 carbon emissions in Canadian boreal forest fires. *Can. J. For. Res.* 39, 367–382.  
637 doi:10.1139/X08-192
- 638 Dymov, A., Gabov, D.N., 2015. Geoderma Pyrogenic alterations of Podzols at the  
639 North-east European part of Russia : Morphology, carbon pools , PAH content.  
640 *Geoderma* 241-242, 230–237. doi:10.1016/j.geoderma.2014.11.021
- 641 Fernández, J.M., Plante, A.F., Leifeld, J., Rasmussen, C., 2011. Methodological  
642 considerations for using thermal analysis in the characterization of soil organic  
643 matter. *J. Therm. Anal. Calorim.* 104, 389–398. doi:10.1007/s10973-010-1145-6
- 644 Flannigan, M., Cantin, A.S., De Groot, W.J., Wotton, M., Newbery, A., Gowman, L.M.,  
645 2013. Global wildland fire season severity in the 21st century. *For. Ecol. Manage.*  
646 294, 54–61. doi:10.1016/j.foreco.2012.10.022
- 647 González-Pérez, J.A., González-Vila, F.J., Almendros, G., Knicker, H., 2004. The effect  
648 of fire on soil organic matter--a review. *Environ. Int.* 30, 855–870.  
649 doi:10.1016/j.envint.2004.02.003
- 650 Harvey, O.R., Kuo, L.J., Zimmerman, A.R., Louchouart, P., Amonette, J.E., Herbert,  
651 B.E., 2012. An index-based approach to assessing recalcitrance and soil carbon  
652 sequestration potential of engineered black carbons (biochars). *Environ. Sci.*  
653 *Technol.* 46, 1415–1421. doi:10.1021/es2040398
- 654 Hatcher, P.G., Schnitzer, M., Dennis, L.W., Maciel, G.E., 1981. Aromaticity of humic  
655 substances in soils. *Soil Sci. Soc. Am. J.* 45, 1089–1094.
- 656 Héon, J., Arseneault, D., Parisien, M., 2014. Resistance of the boreal forest to high  
657 burn rates. *Proc. Natl. Acad. Sci.* doi:10.1073/pnas.1409316111
- 658 Holden, S.R., Berhe, A.A., Treseder, K.K., 2015. Decreases in soil moisture and  
659 organic matter quality suppress microbial decomposition following a boreal forest  
660 fire. *Soil Biol. Biochem.* 87, 1–9. doi:10.1016/j.soilbio.2015.04.005
- 661 Kane, E.S., Hockaday, W.C., Turetsky, M.R., Masiello, C. a., Valentine, D.W., Finney,  
662 B.P., Baldock, J. a., 2010. Topographic controls on black carbon accumulation in  
663 Alaskan black spruce forest soils: Implications for organic matter dynamics.  
664 *Biogeochemistry* 100, 39–56. doi:10.1007/s10533-009-9403-z
- 665 Kane, E.S., Kasischke, E.S., Valentine, D.W., Turetsky, M.R., McGuire, A. D., 2007.  
666 Topographic influences on wildfire consumption of soil organic carbon in interior  
667 Alaska: Implications for black carbon accumulation. *J. Geophys. Res.*  
668 *Biogeosciences* 112, 1–11. doi:10.1029/2007JG000458

- 669 Keiluweit, M., Nico, P.S., Johnson, M., Kleber, M., 2010. Dynamic molecular structure  
670 of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44, 1247–  
671 1253. doi:10.1021/es9031419
- 672 Kelly, R., Chipman, M.L., Higuera, P.E., Stefanova, I., Brubaker, L.B., Hu, F.S., 2013.  
673 Recent burning of boreal forests exceeds fire regime limits of the past 10,000  
674 years. *Proc. Natl. Acad. Sci. U. S. A.* 110, 13055–60.  
675 doi:10.1073/pnas.1305069110
- 676 Knicker, H., 2010. “Black nitrogen” - an important fraction in determining the  
677 recalcitrance of charcoal. *Org. Geochem.* 41, 947–950.  
678 doi:10.1016/j.orggeochem.2010.04.007
- 679 Knicker, H., 2007. How does fire affect the nature and stability of soil organic nitrogen  
680 and carbon? A review. *Biogeochemistry* 85, 91–118. doi:10.1007/s10533-007-  
681 9104-4
- 682 Knicker, H., Hilscher, A., González-Vila, F.J., Almendros, G., 2008. A new conceptual  
683 model for the structural properties of char produced during vegetation fires. *Org.*  
684 *Geochem.* 39, 935–939. doi:10.1016/j.orggeochem.2008.03.021
- 685 Knicker, H., González-Vila, F.J., Polvillo, O., González, J., Almendros, G., 2005a. Fire-  
686 induced transformation of C- and N- forms in different organic soil fractions from a  
687 Dystric Cambisol under a Mediterranean pine forest (*Pinus pinaster*). *Soil Biol.*  
688 *Biochem.* 37, 701–718. doi:10.1016/j.soilbio.2004.09.008
- 689 Knicker, H., Totsche, K.U., Almendros, G., González-Vila, F.J., 2005b. Condensation  
690 degree of burnt peat and plant residues and the reliability of solid-state VACP  
691 MAS 13C NMR spectra obtained from pyrogenic humic material. *Org. Geochem.*  
692 36, 1359–1377. doi:10.1016/j.orggeochem.2005.06.006
- 693 Kögel-Knabner, I., 2002. The macromolecular organic composition of Plant and  
694 microbial residues as inputs to soil organic matter. *Soil Biol. Biochem.* 34, 139–  
695 162. doi:10.1016/S0038-0717(01)00158-4
- 696 Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K.,  
697 Woodbury, P., Krull, E., 2008. Australian climate–carbon cycle feedback reduced  
698 by soil black carbon. *Nat. Geosci.* 1, 832–835. doi:10.1038/ngeo358
- 699 Leifeld, J., Heiling, M., Hajdas, I., 2015. Age and thermal stability of particulate organic  
700 matter fractions indicate the presence of black carbon in soil. *Radiocarbon* 57, 99–  
701 107.
- 702 Loader, N., Buhay, W., 1999. Rapid catalytic oxidation of CO to CO(2) - On the  
703 development of a new approach to on-line oxygen isotope analysis of organic  
704 matter. *Rapid Commun. Mass Spectrom.* 13, 1828–1832. doi:10.1002/(SICI)1097-  
705 0231
- 706 Loader, N.J., Young, G.H.F., Grudd, H., McCarroll, D., 2013. Stable carbon isotopes  
707 from Torneträsk, northern Sweden provide a millennial length reconstruction of  
708 summer sunshine and its relationship to Arctic circulation. *Quat. Sci. Rev.* 62, 97–  
709 113. doi:10.1016/j.quascirev.2012.11.014

- 710 Maestrini, B., Nannipieri, P., Abiven, S., 2014. A meta-analysis on pyrogenic organic  
711 matter induced priming effect. *GCB Bioenergy*. doi:10.1111/gcbb.12194
- 712 Mastrolonardo, G., Francioso, O., Di Foggia, M., Bonora, S., Rumpel, C., Certini, G.,  
713 2014. Application of thermal and spectroscopic techniques to assess fire-induced  
714 changes to soil organic matter in a Mediterranean forest. *J. Geochemical Explor.*  
715 143, 174–182. doi:10.1016/j.gexplo.2014.04.010
- 716 McBeath, A., Wurster, C.M., Bird, M.I., 2015. Influence of feedstock properties and  
717 pyrolysis conditions on biochar carbon stability as determined by hydrogen  
718 pyrolysis. *Biomass and Bioenergy* 73, 155–173.  
719 doi:10.1016/j.biombioe.2014.12.022
- 720 McBeath, A. V., Smernik, R.J., Krull, E.S., 2013. A demonstration of the high variability  
721 of chars produced from wood in bushfires. *Org. Geochem.* 55, 38–44.  
722 doi:10.1016/j.orggeochem.2012.11.006
- 723 McBeath, A. V., Smernik, R.J., Schneider, M.P.W., Schmidt, M.W.I., Plant, E.L., 2011.  
724 Determination of the aromaticity and the degree of aromatic condensation of a  
725 thermosequence of wood charcoal using NMR. *Org. Geochem.* 42, 1194–1202.  
726 doi:10.1016/j.orggeochem.2011.08.008
- 727 McCarroll, D., Loader, N.J., 2004. Stable isotopes in tree rings. *Quat. Sci. Rev.* 23,  
728 771–801. doi:10.1016/j.quascirev.2003.06.017
- 729 Merino, A., Chávez-vergara, B., Salgado, J., Fonturbel, M.T., García-oliva, F., Vega,  
730 J.A., 2015. Catena Variability in the composition of charred litter generated by wild  
731 fire in different ecosystems 133, 52–63.
- 732 Merino, A., Ferreira, A., Salgado, J., Fontúrbel, M.T., Barros, N., Fernández, C., Vega,  
733 J.A., 2014. Use of thermal analysis and solid-state <sup>13</sup>C CP-MAS NMR  
734 spectroscopy to diagnose organic matter quality in relation to burn severity in  
735 Atlantic soils. *Geoderma* 226-227, 376–386. doi:10.1016/j.geoderma.2014.03.009
- 736 Michelotti, L., Miesel, J., 2015. Source material and concentration of wildfire-produced  
737 pyrogenic carbon influence post-fire soil nutrient dynamics. *Forests* 6, 1325–1342.  
738 doi:10.3390/f6041325
- 739 Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S., Masiello, C., 2010.  
740 Temperature sensitivity of black carbon decomposition and oxidation. *Environ.*  
741 *Sci. Technol.* 44, 3324–3331.
- 742 Pingree, M.R. a, Homann, P.S., Morrisette, B., Darbyshire, R., 2012. Long and short-  
743 term effects of fire on soil charcoal of a conifer forest in Southwest Oregon.  
744 *Forests* 3, 353–369. doi:10.3390/f3020353
- 745 Preston, C.M., Trofymow, T.J.A., Niu, J., Sayer, B.G., 1997. C nuclear magnetic  
746 resonance spectroscopy with cross-polarization and magic-angle spinning  
747 investigation of the proximate-analysis fractions used to assess litter quality in  
748 decomposition studies. *Can. J. Bot.* 75, 1601–1613. doi:10.1139/b97-872
- 749 Preston, C.M., Bhatti, J.S., Flanagan, L.B., Norris, C., 2006. Stocks, chemistry, and  
750 sensitivity to climate change of dead organic matter along the Canadian boreal

- 751 forest transect case study. *Clim. Change* 74, 233–251. doi:10.1007/s10584-006-  
752 0466-8
- 753 Randerson, J.T., Chen, Y., Van Der Werf, G.R., Rogers, B.M., Morton, D.C., 2012.  
754 Global burned area and biomass burning emissions from small fires. *J. Geophys.*  
755 *Res. Biogeosciences* 117. doi:10.1029/2012JG002128
- 756 Rayment, G.E., Lyons, D., 2011. *Soil Chemical Methods - Australasia*. CSIRO Publ.  
757 Victoria, 482 pp..
- 758 Reichstein, M., Bahn, M., Ciais, P., Frank, D., Mahecha, M.D., Seneviratne, S.I.,  
759 Zscheischler, J., Beer, C., Buchmann, N., Frank, D.C., Papale, D., Rammig, A.,  
760 Smith, P., Thonicke, K., van der Velde, M., Vicca, S., Walz, A., Wattenbach, M.,  
761 2013. Climate extremes and the carbon cycle. *Nature* 500, 287–95.  
762 doi:10.1038/nature12350
- 763 Rovira, P., Kurz-Besson, C., Coûteaux, M.M., Ramón Vallejo, V., 2008. Changes in  
764 litter properties during decomposition: A study by differential thermogravimetry  
765 and scanning calorimetry. *Soil Biol. Biochem.* 40, 172–185.  
766 doi:10.1016/j.soilbio.2007.07.021
- 767 Santín, C., Doerr, S.H., Kane, E.S., Masiello, C. a., Ohlson, M., de la Rosa, J.M.,  
768 Preston, C.M., Dittmar, T., 2015a. Towards a global assessment of pyrogenic  
769 carbon from vegetation fires. *Glob. Chang. Biol.* n/a–n/a. doi:10.1111/gcb.12985
- 770 Santín, C., Doerr, S.H., Preston, C.M., González-Rodríguez, G., 2015b. Pyrogenic  
771 organic matter production from wildfires: a missing sink in the global carbon cycle.  
772 *Glob. Chang. Biol.* 21, 1621–1633. doi:10.1111/gcb.12800
- 773 Santín, C., Knicker, H., Fernández, S., Menéndez-Duarte, R., Álvarez, M.Á., 2008.  
774 Wildfires influence on soil organic matter in an Atlantic mountainous region (NW of  
775 Spain). *Catena* 74, 286–295. doi:10.1016/j.catena.2008.01.001
- 776 Scharlemann, J.P., Tanner, E.V., Hiederer, R., Kapos, V., 2014. Global soil carbon:  
777 understanding and managing the largest terrestrial carbon pool. *Carbon Manag.* 5,  
778 81–91. doi:10.4155/cmt.13.77
- 779 Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. a.,  
780 Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. a. C., Nannipieri, P.,  
781 Rasse, D.P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter  
782 as an ecosystem property. *Nature* 478, 49–56. doi:10.1038/nature10386
- 783 Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J., 2002. Charcoal Carbon in  
784 U.S. Agricultural Soils. *Soil Sci. Soc. Am. J.* 66, 1249. doi:10.2136/sssaj2002.1249
- 785 Smernik, R.J., Baldock, J.A., Oades, J.M., Whittaker, A.K., 2002. Determination of  
786 T1rhoH relaxation rates in charred and uncharred wood and consequences for  
787 NMR quantitation. *Solid State Nucl. Magn. Reson.* 22, 50–70.  
788 doi:10.1006/snmr.2002.0064
- 789 Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C  
790 molar ratios. *Carbon Manag.* 1, 289–303. doi:10.4155/cmt.10.32

- 791 Taylor, S.W., Wotton, B.M., Alexander, M.E., Dalrymple, G.N., 2004. Variation in wind  
792 and crown fire behaviour in a northern jack pine – black spruce forest. *Can. J. For.*  
793 *Res.* 34, 1561–1576. doi:10.1139/x04-116
- 794 Turetsky, M.R., Kane, E.S., Harden, J.W., Ottmar, R.D., Manies, K.L., Hoy, E.,  
795 Kasischke, E.S., 2011. Recent acceleration of biomass burning and carbon losses  
796 in Alaskan forests and peatlands. *Nat. Geosci.* 4, 27–31. doi:10.1038/ngeo1027
- 797 Vega, J.A., Fontúrbel, T., Merino, A., Fernández, C., Ferreiro, A., Jiménez, E., 2013.  
798 Testing the ability of visual indicators of soil burn severity to reflect changes in soil  
799 chemical and microbial properties in pine forests and shrubland. *Plant Soil* 369,  
800 73–91. doi:10.1007/s11104-012-1532-9
- 801 Verdes, P. V., Salgado, J., 2011. Changes induced in the thermal properties of Galizian  
802 soils by the heating in laboratory conditions. *J. Therm. Anal. Calorim.* 104, 177–  
803 186. doi:10.1007/s10973-010-1173-2
- 804 Wurster, C.M., McBeath, A. V., Bird, M.I., 2015. The carbon isotope composition of  
805 semi-labile and stable pyrogenic carbon in a thermosequence of C3 and C4  
806 derived char. *Org. Geochem.* 81, 20–26. doi:10.1016/j.orggeochem.2015.01.008
- 807 Wurster, C.M., Saiz, G., Schneider, M.P.W., Schmidt, M.W.I., Bird, M.I., 2013.  
808 Quantifying pyrogenic carbon from thermosequences of wood and grass using  
809 hydrogen pyrolysis. *Org. Geochem.* 62, 28–32.  
810 doi:10.1016/j.orggeochem.2013.06.009
- 811 Zhang, H., Voroney, R.P., Price, G.W., 2015. Effects of temperature and processing  
812 conditions on biochar chemical properties and their influence on soil C and N  
813 transformations. *Soil Biol. Biochem.* 83, 19–28. doi:10.1016/j.soilbio.2015.01.006
- 814

815 **Table captions**

816 **Table 1.** Arithmetic mean ( $\pm$  standard deviation) of %C, %N, C:N ratio,  $\delta^{13}\text{C}$  signature  
817 and DSC main parameters of the three types of forest floor samples investigated.

818

819 **Table 2.** Spearman's rank correlation coefficients ( $\rho$ ) between selected characteristics  
820 of the pyrogenic FF layer (C and N concentrations (%), and DSC parameters:  $T_{50}$  and  
821  $q_1$ ) and key fire parameters (maximum temperature reached during fire ( $T_{\text{max}}$ ,  $^{\circ}\text{C}$ ), and  
822 heating durations (s) >300, 400, 500, 600 and 700  $^{\circ}\text{C}$ ). For correlations among other  
823 variables analyzed in this study see Table S2.

824 **Figure captions**

825 **Figure 1.** Aerial view of the forest plot (shortly after ignition) burnt by the FireSmart  
826 experimental 'wildfire' (June 2012) with location of the sampling transects and ignition  
827 front. The circle SZ1 is marking the location of a survival zone designed for fire-fighting  
828 safety research. Sample numbers were continuous starting at the East end of T1 (sample  
829 n.1) and finishing at the West end of T3 (sample n.27).

830 **Figure 2.** (a) Forest floor before fire with thermocouple inserted; (b) examples of typical  
831 temperature-time profiles recorded during the experimental fire at the forest floor surface  
832 (solid line) and at the forest floor/mineral soil interface (dashed line); (c) forest floor after  
833 the fire with the horizontal bar of the 'depth of burn pin' indicating the consumption depth.

834 **Figure 3.** Examples of differential scanning calorimetry thermograms of the pyrogenic  
835 forest floor (a) and unburnt forest floor (b). These samples were collected at sampling  
836 points affected by different maximum fire temperatures (in brackets). The same samples  
837 were used for  $^{13}\text{C}$  CP NMR analysis (see Fig. 4).

838 **Figure 4.** (a) Solid-state  $^{13}\text{C}$  CP MAS NMR spectra of selected forest floor samples. (b)  
839  $^{13}\text{C}$  intensity distribution (%) in the MAS  $^{13}\text{C}$  CP MAS NMR spectra of the selected  
840 samples. These samples were collected at sampling points affected by different  
841 maximum temperatures during fire as indicated in brackets (a) and in the legend (b).