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

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Highlights

- Soil organic layer chemical transformations during a boreal forest fire determined
- Transformations correlated with temperature-time profiles during the fire
- T and heating durations correlated with C%, thermal recalcitrance and aromaticity
- Key changes occurred at higher T than found previously in laboratory experiments
- Increases in boreal fire severity likely to lead to more recalcitrant soil carbon

Abstract

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

During this typical boreal crown fire average maximum temperature (T_{max}) at the forest floor was 745 ºC ($550<T_{max}<976$ ºC) with the average heating duration (t) >300 ºC being 176 s (65<t<364 s). Significant correlations were detected between the chemical characteristics of the pyrogenic (charred) forest floor layer and the temperature-time profiles at the corresponding sampling points. Higher T_{max} and associated prolonged heating durations correlated with greater C enrichments, increased thermal

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recalcitrance and degree of aromaticity of the pyrogenic organic matter. These changes were particularly pronounced for T_{max}>600-700 ^{0}C, which is higher than the range of 300-500 ^{0}C for aromaticity development previously reported from laboratory experiments. One reason for this discrepancy could be the generally much longer heating durations used in laboratory studies, and we therefore advise caution when extrapolating findings from laboratory studies to wildfire conditions.

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

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

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1. Introduction

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

Alterations of the quantity and composition of SOM by fire are many and very diverse (González-Pérez et al., 2004). They are not only relevant to the C budget but also affect many ecosystem properties and functions, such as microbial dynamics, nutrient cycles and vegetation succession (Holden et al., 2015; Schmidt et al., 2011; Turetsky et al., 2011). Quantitatively, fire can lead to a substantial depletion of the SOM stock by, for example, combustion of organic horizons (Kane et al., 2007) or loss of mineral soil by enhanced post-fire erosion (Pingree et al., 2012), but it can also result in an increase of SOM content by incorporation of dead and charred biomass from vegetation and litter (Santín et al., 2008). Fire effects on SOM composition range from negligible to the loss of labile components and enrichment of pyrogenic recalcitrant forms (González-Pérez et al., 2004). An increase of labile compounds could also occur by inputs of dead, but uncharred, vegetation (Alexis et al., 2007).

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

The current understanding of the relationships between fire parameters and SOM changes is largely based on laboratory experiments (e.g. Badía-Villas et al., 2014; Verdes and Salgado, 2011), which are not necessarily representative of field conditions, due to, for example, different heating durations and oxygen availability (Alexis et al., 2010; Atanassova and Doerr, 2010; Spokas, 2010). To date, the relationships between SOM transformations and specific fire parameters have not been directly examined in a wildfire context. This study addresses this research gap by utilizing a high-intensity experimental boreal forest fire to elucidate specific relationships between transformations of the organic top soil layer (the forest floor) and temperature-time profiles. Forest floor samples taken before and after fire were analyzed by elemental and $\delta^{13}C$ analysis, differential scanning calorimetry (DSC) and ^{13}C nuclear magnetic resonance (NMR). Temperatures were continuously monitored during the fire at 18 sampling points using thermocouples placed at the forest floor surface and at the forest floor/mineral soil interface. Examining these relationships does not only help to understand real wildfire conditions and the processes occurring under these, but it can also provide insights into potential effects of the already increasing fire occurrence and severity in the boreal regions driven by the changing climate.

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2. Material and Methods

2.1 Study site and the FireSmart experimental forest fire

An experimental forest fire aimed at simulating wildfire conditions was conducted as part of the Canadian Boreal Community FireSmart Project at Fort Providence, Northwest Territories, Canada (61^{0}34’55’’N, 117^{0}11’55’’W). This boreal region has a dry, subhumid continental climate with low annual precipitation (300 mm) and a wildfire season lasting from May to September. The terrain is flat with an elevation of 160 m.a.s.l. (Alexander et al. 2004). The experimental plot (1.7 ha) was a mature stand of jack pine (*Pinus banksiana*) originating from a stand-replacing fire in 1931, with a tree density (live and dead) of 7600 stems ha^{-1} and average tree height of 14 m. The understorey was very sparse (<0.1 stems m^{-2}) with a few jack pine and black spruce (*Picea mariana*) saplings and shrubs. The soils in the experimental plot are stony sandy loams derived from fluvio-glacial deposits with a distinct organic surface layer, the forest floor (hereafter abbreviated as FF) . This organic soil layer, the FF, had an average thickness of 6.5 cm and was composed of mosses, lichens, needles, fermented litter and humidified organic material (Santín et al., 2015b). In this study woody debris <0.5 cm diameter were also considered as part of the FF.

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

2.2 Temperature recording and forest floor sampling

Before the fire, three parallel transects of 18 m length were established 7.5 m apart in the direction of the prevailing wind (E-W) (Fig. 1). These were instrumented at a spacing of 2 m with thermocouples connected to data loggers (Lascar, Easylog) that recorded temperatures at the FF surface and the FF/mineral soil interface every second (1Hz) (Fig. 2a&b). In total, 27 points (9 per transect) were monitored. In our study area, the FF developed under jack pine does not present well differentiated layers and, for simplicity, was sampled as a single FF layer (Preston et al., 2006).The FF was sampled along two parallel lines between the three sampling transects with 20 X 20 cm sampling squares (n = 10). The total depth of the FF was measured at each corner of the 20 X 20 cm square and the entire layer was carefully collected. At the centre of these same points, samples of the underlying mineral soil were taken using a 5 X 5 cm soil corer (n = 10).

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

2.3 Forest floor characterization

All samples were oven-dried at 65 ^{0}C to constant weight and cleaned by hand to remove any “cross-contamination” that had occurred during sampling. The unburnt FF samples were thus cleaned of any charred particles and mineral soil (<6% dry weight) and the pyrogenic FF samples from any visually uncharred materials (<7% dry weight) derived from the unburnt FF layer underneath. All samples were subsequently weighed and subsamples ground for further analyses. Presence of carbonates was tested by addition of 10% HCl to a set of representative subsamples (Rayment and Lyons, 2011).

2.3.1 Elemental and δ^{13}C analysis

Total C and nitrogen (N) contents (%) and stable C isotope ratios (δ^{13}C) were determined by quantitative combustion and conversion to CO_2 and N_2 using an ANCA GSL elemental analyser interfaced with a Sercon 20/20 mass spectrometer. Stable C isotope ratios (δ^{13}C) expressed as per-mille (‰) and deviations from the Vienna Pee Dee Belemnite standard (VPDB) were also determined on the resulting CO_2. Analytical precision over the experiment for the analysis of an internal laboratory CN standard (Acetanilide, Elemental Micro Analysis Ltd. UK) was mean -30.12‰ δ^{13}C (σ_{n-1}= 0.06 n=10), 10.16% N (σ_{n-1}= 0.29 n=10), and 70.18% C (σ_{n-1}= 2.00 n=10); and for a commercial microcrystalline cellulose powder (Sigma Aldrich, UK. No. C-8002 Lot. 92F-0243) was mean −23.89‰ δ^{13}C, (σ_{n-1} = 0.06 n=3) and 41.38 % C (σ_{n-1} = 0.25 n = 3). These results compare favourably with the analytical precision of the methods typically reported for %C, %N and δ^{13}C determinations (Loader et al., 2013; McCarroll and Loader, 2004).

2.3.2 Differential scanning calorimetry (DSC)

DSC thermographs were obtained using a differential scanning calorimeter Q100, TA instrument. Two replicates of each sample (10 mg) were placed in open aluminium pans under a flow of dry air at 2.1 kg cm^{-2} min^{-1} and exposed to a temperature increase of 10 ^{0}C min^{-1} from 50 to 600 °C. Samples of Indium (mp: 156.6 ^{0}C) were used to calibrate the calorimeter. The heat of combustion (Q) was determined by integrating the thermographs with respect to time over the exothermic region (150<T<600 ºC). The region T<150°C was not considered as it is dominated by endothermic reactions associated with water loss (Fernández et al., 2011). Thermograms were normalized to each sample's total organic C content (Leifeld et al., 2015). The areas under the thermographs were divided into three temperature regions representing different levels of resistance to thermal oxidation (Merino et al., 2015, 2014; Rovira et al., 2008): labile organic matter, mainly comprising carbohydrates, proteins and other aliphatic compounds (150<T_1<375 ºC); recalcitrant organic matter, such as lignin or other polyphenols (375<T_2<475 ºC); and highly recalcitrant organic matter, such as polycondensed aromatic forms (475<T_3<600 ºC). The resulting partial heats of combustion representing these three regions were calculated as q1, q2 and q3. The temperature at which 50% of the total energy is released under the given conditions (T_{50}), as well as the temperatures of the maximum combustion peak in each temperature region (T1, T2 and T3, respectively) were also determined.

2.3.3 Solid state ^{13}C cross polarization-magic angle spinning (CP-MAS) Nuclear Magnetic Resonance (NMR) spectroscopy

Solid-state ^{13}C CP-MAS NMR analyses were carried out on a selected subset of samples: two pre-fire FF samples and three pairs of post-fire pyrogenic + unburnt FF samples taken at sampling points at which maximum temperatures during the fire (T_{max}) covered a range of recorded T_{maxs}: sample n.2, T_{max}=550 ^{0}C; sample n.13, T_{max}=683 ^{0}C; and sample n.20, T_{max}=950 ^{0}C (for the complete range of T_{maxs} see Table S1).

Analyses were performed using an Agilent Varian VNMRS-500-WB spectrometer, operated at a proton resonance frequency of 500 MHz and using a zirconia rotor of 160μL. C chemical shifts were referenced to the C methylene signal of solid adamantane at 28.92 ppm. Cross Polarization Magic Angle Spinning (CPMAS) analysis was carried out under the following conditions: contact time 1 ms, inter-scan delay 1 s (a proton T1 experiment was performed to check the suitability of this time), and MAS rate 12 kHz. The number of scans was ca. 10000-35000. The cross polarization time was set at 1 ms. In the CPMAS technique, the sensitivity to ^{13}C is increased by polarization transfer from the ^{1}H to the ^{13}C spin system. This may obscure the relative intensity distribution in a ^{13}C NMR spectrum of pyrogenic material due to inefficient cross polarization of C in highly-condensed structures (Smernik et al., 2002). However, Knicker et al. (2005b) have shown that, in contrast to soot and other very

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recalcitrant forms of pyrogenic and black carbon, charred vegetation residues and burnt SOM do not usually contain a substantial proportion of highly-condensed graphite-like structures, and, therefore, quantitative analysis by the CPMAS NMR technique is possible for this type of samples.

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

2.4 Statistical analyses

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

3. Results

3.1 Fire characteristics

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

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

At the interface of FF/mineral soil, 21 of 27 loggers successfully recorded data and T_{max} never exceeded 60 ^{0}C (average 24^{0}C, range 7- 60 ^{0}C). Based on these data and the fact that the mineral soil was waterlogged before and after the fire due to the shallow water table, the direct effect of fire on the properties of the organic matter in the mineral soil was considered negligible.

3.2 Forest floor C stocks

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

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

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

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

Before the fire the FF had average concentrations of 40.5 % C, 1.0 % N and a $\delta^{13}C$ signature of -28.1 ‰ (Table 1). After the fire, the pyrogenic FF layer showed significantly higher C and N concentrations (54.1 % and 1.3 % respectively), and a more negative $\delta^{13}C$ signature (-28.9 ‰ $\delta^{13}C$), whereas the unburnt FF layer had similar values to the pre-fire FF (36.9 % C, 1.1 % N, and -28.1 ‰ $\delta^{13}C$; Table 1). The C:N ratio was the highest for the pyrogenic FF (43.8) and the lowest in the post-fire unburnt FF (32.7; Table 1).

3.4 Thermostability of the forest floor: DSC analysis

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

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

Regarding the effect of fire characteristics on properties of the pyrogenic FF, as T_{max} increased, the corresponding DSC curves of the pyrogenic FF samples shifted to higher temperatures (Fig. 3a). This indicates a progressive loss of the most thermolabile compounds (q1) and enrichment in recalcitrant (q2) and highly recalcitrant (q3) compounds with increasing fire temperatures. The increase of T_{max} from 550 to 680 ^{0}C mainly translated into a decrease in q1 and an increase in q2 (Fig. 3a), whereas the increase of T_{max} from 680 to 950 ^{0}C resulted mainly in an enrichment of highly recalcitrant compounds in the q3 region (Fig. 3a). Only 3 samples are displayed in Fig. 3 as examples, however, the observed differences are consistent for all the samples analysed: the samples subjected to T_{max} <700 ^{0}C (n=9) presented higher q1 (39±3%)

and lower q3 values (11±2%) than the samples subjected to T_{max} >700 ^{0}C (n=9), (q1= 31±5% and q3 = 18±8%; for individual values see Table S1).

3.5 Forest floor composition: Solid-state ^{13}C NMR

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

Spectra of the pyrogenic FF are very different to the pre-fire FF (Fig. 4a), with an evident loss of O-alkyl-C compounds by charring, a slight relative increase of alkyl compounds and a substantial presence of newly-formed pyrogenic aromatic compounds, as indicated by the broad peak around 130 ppm (Skjemstad et al., 2002). Higher signal intensities in the aromatic region of the pyrogenic FF sample spectra were found for those samples subjected to higher T_{max} during the fire (Fig. 4a and 4b). The degree of aromaticity increased from 38 % for the sample subjected to T_{max} 550 ^{0}C to 60 % and 64 % in samples subjected to T_{max} of 680 and 950 ^{0}C, respectively.

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

3.6 Correlations between fire characteristics and forest floor transformations

Spearman's rank correlation coefficients (ρ) between some characteristics of the pyrogenic FF layer and fire parameters, and their level of significance are given in Table 2. A complete set of correlations for all pyrogenic FF characteristics and fire parameters analysed can be found in Table S2.

Some of the characteristics of the pyrogenic FF showed correlations with each other: %C was positively correlated to T_{50} and negatively correlated to %N and q1, whereas %N showed a positive correlation to q1 and a negative correlation to %C and T_{50} (Table 2). This indicates that the increase of thermal recalcitrance had an associated enrichment of C and a concomitant loss of N. Moreover, the $\delta^{13}C$ signature of the pyrogenic FF showed a negative correlation with q2 and a positive correlation with q3 (ρ=-0.624 and ρ=0.649; Table S2).

Regarding relationships between fire parameters and pyrogenic FF characteristics, T_{max} was positively correlated to %C and T_{50}, and negatively correlated to q1 (Table 2), which indicates that higher T_{max} led to an increase in the thermal recalcitrance of the pyrogenic FF. Heating durations of T>300 ^{0}C and >400 ^{0}C were positively correlated with %N, and those of T>600 ^{0}C and >700 ^{0}C showed significant positive correlations with the DSC parameter T_{50} and negative correlations with the DSC parameter q1. The duration of heating >700 ^{0}C also showed a positive correlation with %C (Table 2).

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

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4. Discussion

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

4.1.1 The pyrogenic FF layer

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

In addition to the observation of these general changes with burning, our experimental design also allowed the establishment of direct correlations between specific wildfire parameters and some features of the pyrogenic FF. The most relevant fire parameter was T_{max}, where increased values were associated with higher %C and concomitant decreases in %N. Increasing T_{max} was also associated with enhancement in thermal recalcitrance of the pyrogenic FF and loss of thermally labile compounds (see DSC analyses, Section 3.3). These observations were also consistent with the decrease of O-alkyl compounds and the increase in the degree of aromaticity reported by ^{13}C NMR analyses (Section 3.4). In addition to this, positive correlations were detected between the concentrations of N and the heating durations when T>300 ^{0} C and T>400 ^{0} C, but not at any temperatures above these (Table 2). This could indicate relative N enrichment at lower temperatures (T<400 ^{0}C), when O and H are preferentially lost by dehydration and dehydroxylation reactions (Knicker et al., 2008), and a subsequent loss of N at temperatures T~500 ^{0}C (Bodí et al., 2014), with the remaining fraction locked into N-heteroaromatic C forms (Knicker, 2010). The δ^{13}Csignature of the pyrogenic FF showed no significant trends with T_{max} or heating durations (Table S2). This is in contrast to results reported for laboratory-produced chars by Wurster et al. (2015, 2013), who found progressively lower isotope composition at higher charring temperatures relative to the original material.

The general trends for FF transformations observed for this wildfire are in agreement with those detected under laboratory conditions (Ascough et al., 2008; Keiluweit et al., 2010), however, the range of temperatures and the heating durations reported here differ substantially from those used in laboratory experiments. Ascough et al. (2011) detected the main chemical changes in laboratory-produced charcoals at ~400 ^{0}C (O_2-limited atmosphere, 60 min exposure), with charcoal produced at >400^{0}C being chemically more homogeneous (largely aromatic) and chemically recalcitrant than charcoal produced at 300 ^{0}C. McBeath et al. (2011) also produced charcoal under laboratory conditions (O_2-deprived atmosphere, 5 h exposure) and found that aromaticity increased up to 400 ^{0}C (reaching >85% by 350 ^{0}C), whereas at T>400 ^{0}C condensation of the already predominant aromatic fraction increased. Similar results have been found by Wurster et al. (2013) and McBeath et al. (2015), who suggested that at T>500 ^{0}C there was mainly an increase of condensation of the already dominant aromatic fraction, as smaller aromatic clusters (<7 rings) combined into those of 7-14 rings. Therefore, it seems that, under laboratory conditions, even if the characteristics of pyrogenic organic materials are partially conditioned by the properties of the source material, at temperatures >300-400 ^{0}C all materials develop highly aromatic structures and their characteristics and properties tend to converge (Almendros et al., 2003;

Keiluweit et al., 2010; Knicker, 2007). Importantly, these findings appear to be consistent for a range of materials from grass to wood.

Our data suggest that under the typical wildfire conditions studied here, the T threshold for the most substantial chemical changes in the FF was not ~300-400 ^{0}C but followed exposure to T_{max} >600-700 ^{0}C, as indicated by significant correlations between % C, thermal recalcitrance (T_{50} and q1) and the durations in and above this T range (Table 2). It is also important to consider that there were no significant correlations between these parameters for heating within lower temperature thresholds (in the range 300<T<500 ^{0}C; Table 2). The ^{13}C NMR spectra of selected samples also indicate that the main increase in the degree of aromaticity (%) occurred between the sample subjected to T_{max} of 550 ^{0}C (38%) to the sample subjected to T_{max} of 680 ^{0}C (60%) (Fig. 4). The difference in the degree of aromaticity between the samples subjected to 680 ^{0}C and 950 ^{0}C was much smaller (60% and 65%, see Fig. 4), and the main chemical differences between them could be an increase in the condensation of the already predominant aromatic fraction (McBeath et al., 2011). However, this speculation cannot be confirmed by the analyses performed here.

In a previous field study, Alexis et al. (2010) used thermo-sensitive paints to obtain approximate maximum temperatures during a prescribed shrub fire and found an increase of the aromatic C contribution in charred litter from ~40% for T_{max} ~380 ºC to 58% for T_{max} ~650 ºC (n=4). Unfortunately, maximum temperatures reported during the fire did not exceed ~650 ºC nor did the paints provide records of temperature with time. These results, overall, are in support of the findings from our study, with the most notable being that under actual fire conditions higher temperatures (600<T<700 °C) may be required to transform the organic matter into highly aromatic and thermally recalcitrant forms than has been previously assumed based on temperature thresholds determined in laboratory studies (~300<T<500 ^{0}C).

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

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

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

Apart from the fire characteristics discussed above, fuel properties could play a role in causing the differences observed between field and laboratory experiments. Fuel arrangement, moisture and particle size can also affect fire characteristics and, therefore, the properties of the resulting pyrogenic products (Brewer et al., 2013). Future research should be aimed to gain insights into the specific effects of these parameters on the production and characteristics of pyrogenic organic matter.

4.1.2. The post-fire unburnt FF layer

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

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

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

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

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

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

5. Conclusions

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

This study overcomes these limitations by using an experimental forest fire that represented typical boreal wildfire conditions. This allowed us to establish, for the first time, correlations between temperature-time profiles obtained under wildfire conditions and the characteristics of the pyrogenic products present in the FF after the fire. Higher T_{max} reached during the fire and associated longer heating durations correlated with greater C enrichment, increased thermal recalcitrance and associated aromaticity of the pyrogenic FF layer, particularly for T_{max} >600 ^{0}C. This T_{max} is substantially higher than the range of $300<T<500$ ^{0}C widely reported for development of aromaticity based on laboratory tests, which have tended to involve unrealistically long heating durations compared to those typical for actual wildfires.

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

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Table captions

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

Table 2. Spearman's rank correlation coefficients (ρ) between selected characteristics of the pyrogenic FF layer (C and N concentrations (%), and DSC parameters: T_{50} and q1) and key fire parameters (maximum temperature reached during fire (T_{max}, ^{0}C), and heating durations (s) >300, 400, 500, 600 and 700 ^{0}C). For correlations among other variables analyzed in this study see Table S2.

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Figure captions

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

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

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

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

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	C (%)	N (%)	C:N	$\delta^{13}C$	T50 (°C)	q1 (%)	q2 (%)	q3 (%)	T1 (°C)	T2(°
Pre-fire FF	40.5 ± 6.4 ^{a}	1.0 ± 0.2 ^{a}	39.4 ± 8.2 ^{a}	-28.1 ± 0.3 ^{a}	378 ± 6 ^{a}	49 ± 3 ^{a}	42 ± 3 ^{a}	9 ± 2 ^{a}	340 ± 2 ^{a}	420 ±
pyrogenic FF	54.1 ± 6.3 ^{b}	1.3 ± 0.2 ^{b}	43.8 ± 13.0 ^{ac}	-28.9 ± 0.5 ^{b}	407 ± 14 ^{b}	35 ± 6 ^{b}	51 ± 4 ^{b}	15 ± 7 ^{b}	343 ± 4 ^{ac}	427 ±
Post-fire unburn FF	36.9 ± 6.3 ^{a}	1.1 ± 0.2 ^{a}	32.7 ± 5.2 ^{ab}	-28.1 ± 0.3 ^{a}	376 ± 5 ^{a}	50 ± 3 ^{a}	39 ± 2 ^{a}	11 ± 2 ^{ab}	338 ± 3 ^{ab}	413 ±

n=10 for pre-fire FF and n= 27 for post-fire FF. Different superscript letters indicate groups with significantly different means for each parameter (more details in Sec