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Early-season fires in boreal black spruce forests produce pyrogenic carbon with low intrinsic recalcitrance

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Abstract. Pyrogenic carbon (PyC), a major by-product of wildfires in boreal forests, plays several critical roles in soil biogeochemical processes. However, PyC properties, including its potential recalcitrance, may vary depending on its formation conditions. Our study aimed to characterize the chemical and physical properties of PyC formed under variable fire severity in Eastern Canada boreal forests; these latter represent an important fraction of fire-affected circumboreal ecosystems. A total of 267 PyC samples, produced by early-season wildfires in 2005–2007, were collected ≤5 years after fire from the forest floors of 14 black spruce sites distributed across Quebec, to cover the range of fire severity encountered in these forests. Early-season fires occur frequently in Eastern Canada, and are predicted to increase in regional and global scenarios of future fire regimes associated with climate change. Selected PyC samples were analyzed using elemental analysis, solid-state 13C nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy, and surface area analysis. The NMR spectra of the PyC collected on low-fire-severity sites were dominated by peaks indicative of cellulose, while those for PyC from higher-severity sites were dominated by a broad peak assigned to aromatic carbons. Atomic H/C and O/C ratios decreased with increasing fire severity. By comparing field samples to samples produced in the laboratory under controlled formation conditions, we were able to infer that the temperature of formation in the field was low (75–250°C). In addition, for all PyC samples, the aromatic carbon: total carbon ratio was small, suggesting that PyC produced by early-season fires in these boreal forests may be susceptible to relatively rapid degradation. Taken together, our data suggest that boreal PyC may not be as recalcitrant as previously assumed, and that its influence on soil biogeochemical processes may be short lived.

Key words: 13C NMR; boreal forest; Canada; fire severity; forest floor; pyrogenic carbon.

INTRODUCTION

Worldwide, boreal ecosystems cover 24 × 107 km2, and the associated boreal forest soils, which store more carbon per unit area than permafrost soils (Deluca and Boisvenue 2012), represent an immense carbon pool estimated at 227 × 1012 kg (Kasischke 2000). The boreal forest is characterized by recurring wildfires that produce significant amounts of CO2 (Bond-Lamberty et al. 2007, van Bellen et al. 2010). In black spruce boreal forests of Eastern Canada, the combustion of the thick forest floors is often incomplete and pyrogenic carbon (PyC), also called black carbon, is a major by-product. In addition to its potential importance as a global carbon sink, there is evidence that PyC plays a central role in soil fertility, in particular by stimulating microbial activity and nutrient cycling after fire (Wardle et al. 1998, DeLuca et al. 2006).

Combustion-derived PyC consists of multiple possible end-products, and it is difficult to outline distinctive classes with quantitative boundaries along the PyC continuum (Masiello 2004, Lehmann and Joseph 2009). While PyC is generally considered an important component of the stable soil carbon pool (Kasischke 2000, Preston and Schmidt 2006), some studies caution against the assumption that all PyC is recalcitrant (Hockaday et al. 2006, Czimczik and Masiello 2007, Hammes et al. 2008, Preston 2009). As pointed out by Preston et al. (2006), only part of the PyC continuum with sufficiently low H/C and O/C ratios and highly condensed aromatic structures, should be associated with long-term stability. Similarly, PyC porosity and surface area will directly affect the extent of its role in retaining water, nutrients, and/or tannins, and its potential to provide habitats for microorganisms (Zackrisson et al. 1996, Hockaday et al. 2006). Thus, a detailed knowledge of PyC chemical composition and physical properties is a prerequisite to determine both its...
fate and functions in terrestrial ecosystems (Keiluweit et al. 2010).

Variation in formation conditions, such as fuel type, maximum temperature reached during combustion, abundance of oxygen, and duration of charring, can result in major differences in PyC properties (Soucémariamadin et al. 2013). In the field, differences in biophysical conditions, and associated fuel availability, create spatial variation in wildfire intensity (Sousa 1984), and consequently severity (e.g., Turner and Romme 1994, van Wagendock 2006). Fire thus results in a mosaic of forest vegetation and soils burned to varying degrees (Turner and Romme 1994), and in a range of formation conditions for PyC. Spatial variability in fire severity and formation conditions occurs at scales ranging from thousands of square kilometers to small patches of a few square decimeters. While that has yet to be fully characterized, it is likely that PyC residues have properties that vary within tree stands and across the landscape.

This study provides a complete characterization of wildfire-produced PyC, knowledge that is scarce in boreal ecosystems. Further, it explores how formation conditions influence PyC properties and hence its potential for recalcitrance and importance in regulating post-fire soil nutrient cycling. In 2005–2007, high fire activity, with an especially early onset, burned over 1.2 Mha in northern Quebec. This provided the opportunity to study the influence of early-season wildfires on PyC properties. This is of particular significance, as current climate models predict an increase in fire frequency for this region, and a potential shift in fire seasonality toward the spring (Flannigan et al. 2005, Wotton et al. 2010). We collected and analyzed PyC samples using a set of analytical methods to: (1) identify the range of variation in their properties, and (2) determine how these properties may be related to fire severity. We hypothesized that variations in fire severity would correspond to a continuum of PyC properties. We further focused on PyC properties that directly affect its potential for degradation, including its elemental and macromolecular composition, as well as on several key physical characteristics that control its biogeochemical function in boreal black spruce ecosystems, including porosity and surface area.

### Materials and Methods

#### Field sampling

A total of 14 fires, ranging in size from 330 to 56 000 ha, were selected in 2010 from the black spruce–feathermoss bioclimatic domain of Quebec (Appendix A: Fig. A1). This domain covers a third of the provincial territory, and is characterized by an average precipitation ranging from 850 mm/yr in the west to 1020 mm/yr in the east (Bergeron et al. 2004, Cyr et al. 2007). Mean annual temperature ranges from −2°C in the north to just above 0°C in the south (Carrier 1996). The majority of soils are Humo-Ferric Podzols (Soil Classification Working Group 1998).

Within each fire, 2–4 topographic gradients (toposequences) were established inside an intact burnt stand, i.e., burnt but not salvage-logged. Three 20 × 20 m square plots were positioned on each topographic gradient, and within each plot, nine round microplots (1.5 m diameter) were sampled. We assessed both the aboveground (aerial severity) and belowground (soil severity) impacts of fire at the plot and microplot scale.
To estimate aerial fire severity, we evaluated three burn characteristics of the trees remaining on the plot: scorch height, abundance of twigs, and presence of bark splitting (Ryan 2002 and references therein). Preliminary field observations indicated that aboveground fire severity was fairly homogeneous across and within sites, in that most trees were dead and burned over the full bole height.

As opposed to aerial fire severity, the amount and visual appearance of organic matter left post-fire at the soil level varied greatly among both topographic gradients and microplots at each topographic position. Thus, we chose to further characterize soil fire severity to capture the range of fire severity at the sites. To estimate soil fire severity, we evaluated the impact of fire on the consumption of the forest floor layers (i.e., burning class), and we determined the main substrate type present within each microplot (Appendix B: Table B1). We used four burning classes: unburnt/scorched; slightly, moderately, and severely burnt; and five substrate classes: burnt forest floor; mineral soil; dead wood; rock; unburnt forest floor. Consequently, at the soil level, six fire severity classes (0–low to 5–high) were defined, were randomly chosen among the collected samples and further analyzed. This led to a total of 33 field PyC samples for detailed analysis (Appendix B: Table B1).

**PyC set produced under controlled laboratory conditions**

We compared the field PyC samples to a PyC reference set, produced under controlled laboratory conditions (Soucémarianadin et al. 2013). To produce the controlled PyC set, we selected biomass representing the most common fuels available in Quebec black spruce–feathermoss forests, including *Sphagnum* sp. and *Pleurozium schreberi*, bark, branches, and needles from black spruce, branches and needles from jack pine, and twigs and leaves from Labrador tea (*Rhododendron groenlandicum*). The charcoalification experiments were performed in a muffle furnace under controlled maximum temperature (MT), which varied between 75°C and 800°C for charring durations between 0.5 and 24 hours. We adjusted the amount of oxygen present during PyC formation by either placing the fuels in a moisture tin with a cap pierced with tiny holes (tin = partial pyrolysis), or by tightly wrapping them in tinfoil before putting them in a sand bath (SB = full pyrolysis). We submitted the samples from the PyC reference set to the same analyses as the field PyC.

**Characterization of PyC chemical properties**

Carbon, hydrogen, and nitrogen concentrations were determined by dry combustion on finely ground PyC samples using a CE440 Elemental Analyzer (Exeter Analytical, Chelmsford, Massachusetts, USA). The total ash and oxygen contents were estimated by difference from the sample ash-free mass obtained after six hours at 750°C, in accordance with ASTM Standard D1762-84 (ASTM 2007). Solid-state 13C NMR spectroscopy with magic angle spinning (MAS) was used to characterize PyC macromolecular structure.

We carried out the 13C NMR experiments using a Chemagnetics CMX Infinity 200 Spectrometer (Varian, Palo Alto, California, USA), and a 7.5 mm Chemagnetics double resonance MAS probe to spin the samples at 5 kHz. Experimental settings were the same as those used for the PyC reference set (Soucémarianadin et al. 2013), except that for the field PyC samples we acquired 8580–8624 scans for the cross-polarization (CP) spectra, and 888 scans for the direct polarization (DP) spectra. We divided the 13C NMR spectra into the following four carbon regions: carbonyl (215–165 ppm); aromatic and phenolic (165–110 ppm); O-alkyl and di-O-alkyl (110–45 ppm); alkyl (45–0 ppm). We corrected for the spinning side-bands using the regions with large
chemical shifts (290–215 ppm), following the same methodology as Baldock and Smernik (2002).

Usually studies employ the CP technique, as it generally allows for the acquisition of $^{13}$C NMR spectra in less time. However, the CP efficiency for chars is reduced (Baldock and Smernik 2002) because of the absence of particularly mobile $^1$H nuclei (Smernik et al. 2002). To verify that spectra acquired with CP were representative, we used the more quantitative DP technique (Preston and Schmidt 2006) on a subset of samples. Applying Smernik and Oades’ (2000) methodology, we used spin counting to determine if the DP spectra were quantitative for the various carbons present in the samples (Appendix C: Table C1). From these results, and by comparing CP and DP spectra, we concluded that the CP spectra represented the distribution of the total intensity quite accurately ($\pm 7\%$), further indicating that the CP efficiency for the aromatic/quaternary carbons was about the same as for the aliphatic carbons. Therefore, we used the results derived from the CP spectra for the remainder of the study.

Characterization of PyC physical properties

We characterized BET (Brunauer et al. 1938) specific surface area (multipoint) and pore size distribution from nitrogen adsorption and desorption isotherms measured at 77.3K on an Autosorb 1MP surface area analyzer (Quantachrome Instruments Corporation, Boynton Beach, Florida, USA). Prior to analysis, we outgassed samples at room temperature or 105°C for 19–26 hours. We derived the BET surface areas (SA) from a multipoint plot over a range of relative pressure, $P/P_0 = 0.05$–0.35 (7–8 data points). We performed the calculation of the different pore volumes using Autosorb 1 for Windows 1.52.

We assessed PyC heterogeneity, notably the size and shape of pores, by scanning electron microscopy (SEM). High-resolution digital images of the surfaces of different PyC samples were obtained using a field emission SEM (JEOL 6301F; JEOL Limited, Akashima, Tokyo, Japan) with magnifications ranging from 25× to 50 000×. Before imaging them through the SEM, we coated the samples with gold (Nanotech SEMPrep 2 sputter coater; Nanotech, Utica, New York, USA) to increase their conductivity.

Statistical analyses

We used a one-way ANOVA to investigate changes in PyC chemical characteristics using the $^{13}$C NMR and elemental results of the 33 field PyC samples in relation to fire severity classes. The experimental units were the microplots and their associated fire severity classes. When data did not follow the ANOVA assumptions, we used a Mood’s median test and a Kruskall-Wallis non-parametric test. All comparisons were considered significant at $\alpha$ of 0.05. We performed all statistical analyses with SAS 9.2 (SAS 2010).

Results

PyC physical and elemental properties

As can be seen on the SEM micrographs (Fig. 1), the bulk of the cell structures of the original plant materials remained unaltered. Microorganisms were visible on most samples. In particular, we were able to observe bacteria as well as various fungal structures, such as hyphae and hyphal tubes. The PyC samples correspond-
ing to a class 0 fire severity had a slightly higher surface area (2.3 m²/g) than those associated with a high fire severity (SA = 1.1 m²/g and 1.6 m²/g for class 2 and class 5, respectively). Overall, all analyzed samples exhibited very low specific surface area (i.e.; < 3 m²/g), and porosity was dominated by macropores (Table 1). Moreover, these values were similar to results obtained for unburnt fuels.

The carbon content of the samples increased from 47% to 60% with increasing fire severity (Table 1; Appendix B: Table B1). The PyC collected on the low fire severity sites (classes 0 and 1) showed a significantly lower carbon content than PyC from the high fire severity sites (classes 4 and 5). The oxygen content steadily decreased with increasing fire severity (46% to 36%), while the hydrogen content remained constant (5%) from class 0 to 2, before decreasing to 4% for class 5. The nitrogen content was only weakly related to fire severity; it increased slightly up to class 3 (1.1% to 1.8%) and then appeared to reach a plateau (Table 1). The ash content ranged from 4% to 34%; it increased slightly from class 0 to 3, then more importantly from class 4 to class 5 (Table 1). The atomic H/C and O/C ratios both decreased with increasing fire severity (Fig. 2). PyC from classes 0 and 1 had significantly higher atomic ratios than PyC from classes 4 and 5 (H/C ratio) and classes 2, 4, and 5 (O/C ratio).

**PyC molecular composition**

The cross-polarization 13C NMR spectra acquired for the field PyC associated with low fire severity showed a distribution of carbon groups very similar to that in unburnt fuels (Fig. 3a; Appendix C: Table C2). Spectra were dominated by carbohydrates, as confirmed by the presence of peaks representative of cellulose and hemicelluloses; i.e., at 62, 72–75, and 105 ppm (Wikberg and Maunu 2004, Melkior et al. 2012), and showed limited presence of lignin. Lignin was identified by peaks between 110 and 165 ppm, the aromatic carbons appearing in several (mostly) broad peaks of weak intensity (Fig. 3a; Appendix C: Table C2).

Spectra from PyC collected on sites associated with fire severity classes 2 and 3 were very similar (Fig. 3b). They differed from the PyC spectra associated with fire severity classes 0 and 1 by an increase in the contribution of the alkyl carbons (peaks at ~30 ppm) and the emergence of two peaks characteristic of aromatic carbons: one at 130 ppm assigned to polyaromatic hydrocarbons (Baldock and Smernik 2002), and one at 150 ppm ascribable to O-substituted aromatic carbons (furans). In the spectra of PyC associated with class 4–fire severity, the relative contribution of the two peaks in the aromatic region, as well as the peak in the alkyl region, continued to increase (Fig. 3b). Conversely, the contribution of signals relative to cellulose (72 and 105 ppm) decreased. The broad peak centered at 30 ppm also became slightly narrower, suggesting that the variability in the composition of the alkyl groups was decreasing. In contrast, the 13C NMR spectra obtained for the PyC associated with high fire severity (class 5) was dominated by broad peaks related to aromatic and phenolic carbons. They were similar to spectra of fuels thermally treated at 250°C under pyrolytic conditions (Fig. 3c). These spectra were dominated by two broad peaks: one in the aromatic and phenolic regions, and the other one in the alkyl region. Peaks associated with cellulose (centered at 84 ppm and 89 ppm but also at 74 ppm and 65 ppm) were almost absent for the PyC produced from *Rhododendron* and *Sphagnum* at 250°C, and were entirely absent for the PyC produced under oxic conditions. On the other hand, hemicelluloses (173 ppm) and lignin (56 ppm) structures were still clearly visible. Finally, for the class 5 PyC, carbohydrates and lignin biomolecules were still present, even though their relative contribution substantially decreased (Fig. 3b).

With increasing fire severity, we observed a statistically significant increase in the aromatic and phenolic carbon contributions (Table 1). There was also a small (nonsignificant) increase in the contribution of the carbonyl carbons. Furthermore, PyC exhibited a higher proportion of alkyl carbons, corresponding with the emergence of the broad peak centered at 30 ppm (Fig. 3a). Overall, from low to high fire severity, the 13C NMR spectra shifted from intensity dominated by O-alkyl and di-O-alkyl signals (cellulose and hemicelluloses) to intensity dominated by peaks associated with aryl
and alkyl functional groups. The contribution of the O-alkyl and di-O-alkyl carbon was significantly different between fire severity classes 0–1, and class 5. These observations are consistent with those from the calculated atomic ratios, that is, an increase in aromatic content (Fig. 2).

Properties of the PyC reference set

We incorporated the results of the PyC produced under controlled conditions on the PyC continuum (Fig. 4) to follow how chemical and physical properties change with an increasing maximum temperature of formation. Values and observations summarized in Fig.
are derived entirely from results of PyC produced in the laboratory under full pyrolysis (Soucénarianadin et al. 2013). With increasing maximum temperature, we observed a degradation of the fuel macromolecules (cellulose, hemicelluloses, and lignin) and formation of aromatic structures, with a concomitant increase in PyC carbon content and a decrease in H/C and O/C ratios, consistent with the NMR results, i.e., an increase in carbon condensation. As for PyC physical properties, an increase in the maximum temperature induced an increase in PyC specific surface area, with a shift from a porosity dominated by macropores to a porosity dominated by micropores. This was accompanied by a progressive destruction of the cell structures of the fuel. Overall, the physical and chemical properties of the field PyC matched the properties of the laboratory PyC produced at low temperatures ranging between 75°C and 250°C (Figs. 2 and 4).

**DISCUSSION**

**Formation conditions for the field PyC**

Hammes et al. (2006) reported that an atomic H/C ratio >0.5 characterizes chars formed at temperatures <500°C. By comparing results from the field samples (Table 1) and the PyC produced under controlled laboratory conditions (Fig. 2), we can conclude that the high atomic ratio values obtained for the field PyC samples were characteristic of a low temperature of formation. Both elemental analysis and $^{13}$C NMR spectroscopy confirmed that all field PyC samples were the products of forest floor exposed to temperatures ranging from 75°C to 250°C. Results also suggested that pyrolysis conditions prevailed during the production of this PyC, indicating formation by smoldering fire. Wildfires progress through different phases (DeBano et al. 1998); a crown fire associated with flaming combustion generally transitions to a smoldering fire, affecting the forest floor through glowing combustion. If the forest floor is dry, the combustion is more complete and the organic layer is almost entirely consumed; this was not the case in the present study. The absence of a relationship between aerial fire severity and soil fire severity further suggests that the fire behavior in the canopy and at soil level was disconnected. Under these conditions, fire severity at the soil level is driven by microscale patterns, such as differences in microtopography, rather than flammability of the canopy. The C content of the PyC produced by wildfire (Table 1; Appendix B: Table B1) was slightly lower (<60%) than the values obtained for the PyC produced under controlled conditions at similar temperatures (Fig. 4), suggesting a more complete combustion in the former context (Krull et al. 2009).

Under observed field conditions of the highest fire severity (class 5), the $^{13}$C NMR spectra indicate that the forest floor underwent thermal alterations. Specifically, there was a visible decrease in peaks associated with cellulose and hemicellulose, accompanied by a relative increase in the contribution of peaks associated with lignin. A potential explanation is that while cellulose and hemicellulose were subject to (thermal) degradation, the temperature remained below the pyrolysis temperature of lignin (280°–500°C [Miyanishi 2001]), consequently increasing its relative contribution to the total signal intensity. For the highest fire severity class, aromatic
non-oxygenated carbons (signal at 130 ppm) dominated the $^{13}$C NMR spectra, suggesting that at this stage, condensation of the original macromolecules into aromatic polymers had begun. This suggests an increase in condensation with severity, which agrees with the observed decrease in atomic H/C and O/C ratios along the same severity gradient. To further illustrate this phenomenon, we calculated the degree of aromatization, which corresponds to the ratio (atomic and phenolic C [165–110 ppm]) to (O-alkyl and di-O-alkyl C + alkyl C [110–0 ppm]), and is an indicator of the increasingly condensed nature of chars (Keiluweit et al. 2010). As expected, there was an increase in the degree of aromatization with increasing fire severity (Table 1).

Surface area and pore volume have been shown to be principally controlled by maximum temperature (Brown et al. 2006) and duration of charring (Rutherford et al. 2005). Both are expected to increase with harsher formation conditions, including higher maximum temperature and/or longer charring duration. Hammes et al. (2006) reported PyC surface areas < 25 m$^2$/g for low temperatures of formation (<500°C), while high temperatures (500–1000°C) led to surface areas of 214–336 m$^2$/g. Rutherford et al. (2005) also reported a very small micropore volume (≤0.001 cm$^3$g$^{-1}$) for pine wood and pine bark treated at 250°C. The low values we measured on our samples confirm the low temperatures of formation, corroborating the chemical analysis results. The absence of major destruction of the fuel cell structures, as observed on the SEM micrographs (Fig. 1), confirms an average low formation temperature across the severity gradient. The relative contribution of microporosity remained constant with increasing fire severity, suggesting that the temperature of PyC formation was too low to create new microporosity. These results match changes in chemical structure suggested by the $^{13}$C NMR spectra (Fig. 3b), where it is evident that the conversion of alkyl to aromatic carbon remained incomplete. The rigid structure that fused-ring aromatic carbons provide and in which micropores develop was not yet fully established (Rutherford et al. 2005). In addition, at low temperatures, a certain proportion of the porosity, especially the microporosity, could have been occluded by tars and other condensed volatiles (Downie et al. 2009). This process can also disrupt pore continuity, leading to small specific surface areas and pore volumes. Finally, a low surface area could also be associated with low thermal ramping (Brown et al. 2006). Wildfire thermal rates are typically low, characterized by values between 2°C and 17°C/min for natural smoldering combustion (Miyahishi 2001), and a slow thermal ramping rate (0.5°C–3.3°C/min) tends to produce chars with low surface area (<0.5 m$^2$/g).

The chemical characteristics of PyC produced in Quebec boreal black spruce forests are quite different from the characteristics of PyC produced by wildfires in other ecosystems. For example, a moderate intensity Mediterranean wildfire that affected a stone pine (*Pinus pinea* L.) forest produced PyC that was much more condensed and contained more aromatic C (Nocentini et al. 2010) than even the PyC from our highest fire severity class. In a more comparable boreal ecosystem; i.e., a Siberian Scots pine forest (*Pinus sylvestris* ssp. *sibirica* Lebed) affected by a surface fire (Czimczik et al. 2003), the $^{13}$C NMR spectra obtained were more similar to the spectra of class 5 fire severity from the present study.

**PyC properties and implications for their function in black spruce forests**

NMR spectroscopy and elemental analyses indicate that PyC produced in the Quebec black spruce forests by 2005–2007 wildfires was not composed of carbon moieties with intrinsic chemical properties (molecular structures) known to resist microbial degradation. Indeed, the PyC produced by these wildfires appeared to be composed of transition and amorphous chars; i.e., low in aromatic structures. One important consideration is that all fires in our study occurred early in the fire season; relatively low fire severity was observed at the soil level, validated by low organic matter consumption (Boilin and Munson 2013). Nonetheless, PyC properties varied predictably according to changes in fire severity observed at the microplot level.

Pyrogenic carbon porosity may play an important role in ecosystem successional processes through adsorption of phenolic compounds that otherwise may inhibit natural regeneration of black spruce trees. Zackrisson et al. (1996) showed that young (<100 yr) charcoals were able to adsorb phenolic compounds produced by ericaceous shrubs in boreal forests of northern Sweden. They linked the presence of these active charcoals to enhanced microbial biomass in the litter and higher stand productivity. As shown by Joanisse et al. (2007), condensed tannins typically found in high concentrations in *Kalmia* litter inhibit microbial enzyme activity and decrease nitrogen mineralization. As nitrogen is a main limiting nutrient in boreal forests, PyC porosity could thus play a critical part in post-fire tree reestablishment. Addition of PyC to forest floors resulted in the reduction of free polyphenols content (DeLuca et al. 2002), an increase in nitrogen availability (DeLuca et al. 2006, MacKenzie and DeLuca 2006), and a stimulation of boreal tree seedlings growth in a greenhouse experiment (Pluchon et al. 2014). Similarly, Keech et al. (2005) showed that PyC physical properties played a major role in determining its sorptive capacity. As shown for the reference set, the increase in PyC porosity is related to the temperature of formation (Fig. 4), although thermal ramping rate and charring duration are important factors (e.g., Brown et al. 2006). Unlike the laboratory-produced PyC or natural PyC formed at high temperatures used in the above studies, the potential for tannin adsorption (i.e., average measured specific surface area) was relatively low for our field PyC. This suggests that the adsorptive capacity
of wildfire-produced PyC cannot be taken for granted. However, these PyC samples were collected 4–5 years after wildfire; hence it is possible that the original porosity was higher but decreased over time. Indeed, phenols interacting with activated carbon may undergo an irreversible adsorption (Grant and King 1990). While the importance of PyC in ecosystem functioning, e.g., as a habitat for microorganisms involved in nutrient cycling (e.g., Saito 1990, Pietikäinen et al. 2000), should not be dismissed, our results indicate that its adsorptive role is either limited or at best short-lived in these boreal black spruce forests. Although a definitive causal relationship is difficult to establish, the presence at our study sites of a partially burnt forest floor covered by a slightly charred layer was linked to critically low black spruce regeneration (black spruce to jack pine [Boiffin and Munson 2013]).

The production of PyC during forest fires, and its successive accumulation as a recalcitrant carbon pool over several fire cycles, could partially offset the huge C losses taking place during the combustion events. In boreal forest soils, PyC comprises 1–50% of the total carbon present in surface mineral horizons (Deluca and Boisvenue 2012). Similarly, we previously showed that many Quebec boreal forest floors include a PyC-rich layer close to their interface with the underlying mineral soils, and that PyC represents, on average, 7–8% of the total carbon present in the mineral soils (Soucémariناند et al. 2014). PyC produced by wildfire is generally considered to have very slow turnover, and as such, to be an important sink in the global carbon cycle (e.g., Forbes et al. 2006, Lehmann et al. 2008). However, the surficial PyC layers we studied contained little aromatic carbon, and are unlikely to persist in these boreal forest ecosystems for very long. Consequently, we would like to warn against hasty generalizations, and further emphasize that it is crucial to consider both the PyC properties (low vs. high aromatic content) and the environment within which it will interact (e.g., thick forest floor vs. mineral soil) before inferring that the PyC will contribute substantially to the inert carbon pool.

The 3–5°C mean annual increase in temperature projected for the end of the century (Lempière et al. 2008) is predicted to result in an increase in fire frequency throughout the boreal forest zone, although with regional differences. By 2090, the black spruce–feathermoss domain is expected to experience a 4–5°C increase in summer temperature, and an increase in summer precipitation, although in the southern sector the precipitation increase (0–10%) should be less than in the northern sector (25–50%). Overall, fire seasons are expected to be longer (averaging +30 days), fires to be more severe (Wotton et al. 2010), and the southern sectors to be more prone to an increase in fire frequency and severity. On the other hand, fire seasonality is expected to shift toward an earlier fire season, which would favor lower fire severity at the soil level, producing the same low condensed PyC as reported here for the 2005–2007 fires. Under these conditions, PyC should not be expected to be much more recalcitrant than unburnt forest floor. Hence, our study reveals how a change in fire regime toward lower severity could potentially reduce the relative stability of PyC produced and its contribution to longer-term stable carbon pools in boreal forest soils. Tannin adsorption by PyC and its positive effects on ecosystem function and tree growth could also be hampered by this shift in fire regime.

**Conclusion**

In Quebec black spruce forests, 2005–2007 early-season wildfires produced forest floor PyC that displayed a relatively low degree of aromatization and condensation. The PyC chemical properties were related to fire severity, with an increase in fire severity inducing an increase in aromatization. However, the aromatic content of all field PyC samples was low when compared to the range of known values along the PyC continuum, which suggests a low intrinsic potential for recalcitrance. The porosity of the analyzed samples, hence their adsorptive capacity for tannins, was also low, suggesting that PyC was unlikely to significantly influence nitrogen mineralization in these boreal forests. Overall, these results are representative of PyC produced during early-season wildfires, and they provide insight into the most common type of PyC that would be produced in the scenario where early-season fires increase in frequency. Finally, these results can inform modeling of carbon cycles in boreal forests, by providing key information on the potential longevity of PyC pools.

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SUPPLEMENTAL MATERIAL

Ecological Archives

Appendices A–C are available online: http://dx.doi.org/10.1890/14-1196.1.sm