Organic Geochemistry 82 (2015) 1–11

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Total and pyrogenic carbon stocks in black spruce forest floors from eastern Canada

Laure N. Soucémarianadin[a,*,1], Sylvie A. Quideau[a], M. Derek MacKenzie[a], Alison D. Munson[b], Juliette Boiffin[b,2], Guy M. Bernard[c], Roderick E. Wasylishen[c]

[a] Department of Renewable Resources – University of Alberta, 442 Earth Sciences Building, Edmonton, AB T6G 2E3, Canada
[b] Département des sciences du bois et de la forêt – 2405, rue de la Terrasse Pavillon Abitibi-Price – Université Laval, Québec, QC G1V 0A6, Canada
[c] Department of Chemistry – E3-24, Chemistry Centre – University of Alberta, Edmonton, AB T6G 2G2, Canada

ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form 28 January 2015
Accepted 5 February 2015
Available online 14 February 2015

Keywords:
Pyrogenic carbon
Boreal forest
Wildfire
Forest floor
^{13}C NMR
Molecular mixing model

ABSTRACT

Pyrogenic carbon (PyC), a by-product of recurrent boreal wildfires, is an important component of the global soil C pool, although precise assessment of boreal PyC stock is scarce. The overall objective of this study was to estimate total C stock and PyC stock in forest floors of Eastern Canada boreal forests. We also investigated the environmental conditions controlling the stocks and characterized the composition of the forest floor layers. Forest floor samples were collected from mesic black spruce sites recently affected by fire (3–5 yr) and analyzed using elemental analysis and solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. PyC content was further estimated using a molecular mixing model. Total C stock in forest floors averaged 5.7 ± 2.9 kg C/m^2 and PyC stock 0.6 ± 0.3 kg C/m^2. Total stock varied with position in the landscape, with a greater accumulation of organic material on northern aspects and lower slope positions. In addition, total stock was significantly higher in spruce-dominated forest floors than stands where jack pine was present. The PyC stock was significantly related to the atomic H/C ratio (R^2 0.84) of the different organic layers. ^{13}C NMR spectroscopy revealed a large increase in aromatic carbon in the deepest forest floor layer (humified H horizon) at the organic-mineral soil interface. The majority of the PyC stock was located in this horizon and had been formed during past high severity fires rather than during the most recent fire event.

1. Introduction

Surficial accumulation of organic material is one of the most distinctive features of boreal forests; large amounts of C are stored in thick forest floors overlying mineral soil. Although the boreal zone covers < 17% of the Earth's land surface, boreal ecosystems contain > 30% of the C stored in terrestrial ecosystems. Boreal forest soils alone contain two thirds of the soil organic C (OC) stored in forest soil (227×10^{12} kg; Kasischke, 2000). Increasing concern about climate change has brought global attention to boreal ecosystems, including Canada's forest, which represents 21% of the world's boreal forest (Natural Resources Canada, 2013). Recurring wildfire is a main driver of the C cycle in these forests (Bond-Lamberty et al., 2007; Hatten and Zabowski, 2009). On boreal forest sites where forest floor accumulation is much lower, such as pine-lichen or mixed wood forests, wildfire tends to consume most of the forest floor (e.g. Kasischke et al., 2000; Shvidenko and Nilsson, 2000; Czimczik et al., 2005). However, in boreal black spruce forests, such as those in Quebec, combustion of the thick forest floor layers by wildfire is often incomplete; PyC is a major product and may be a significant component of the overall soil C pool. While PyC exists as a continuum of thermally altered organic material (e.g. Hammes et al., 2007), both its amount and composition may vary as a function of fire severity. For instance, it has been shown that the PyC aromatic content increases with increasing fire severity (Schneider et al., 2013; Wolf et al., 2013; Soucémarianadin et al., 2014).

A review by Preston and Schmidt (2006) reported a PyC stock in boreal forest floors of the order of 1000–2000 kg/ha. Significant PyC accumulation was observed in certain North American boreal forests (e.g. Harden et al., 2000; Bélanger and Pinno, 2008), but PyC stock appears to vary greatly among boreal ecosystems (Czimczik et al., 2005; Preston and Schmidt, 2006; Kane et al.,

* Corresponding author. Tel.: +1 780 492 5397; fax: +1 780 492 1767.
E-mail address: soucmari@ualberta.ca (L.N. Soucémarianadin).
[1] Present address: Department of Medical Biochemistry and Biophysics, Umeå University, SE-901 87 Umeå, Sweden.
[2] Present address: UMR 1137 Écologie et Écophysiologie Forestières – Centre Inra de Nancy-LorraineRue d'Amance, 54280 Champenou, France.

http://dx.doi.org/10.1016/j.orggeochem.2015.02.004
0146-6380/

2007, 2010). To correctly introduce soil PyC into C models and test its response to future climate conditions, there is a strong need to obtain additional and better estimates of PyC stock in boreal forest floors under different conditions on the landscape.

Most analytical methods are better adapted to quantify PyC in mineral soil than in organic soil. Indeed, the abundance and diversity of C structures in a well developed boreal forest floor constitute a challenge in terms of PyC quantification. The commonly used oxidation methods, such as thermal digestion (Kuhlbusch and Crutzen, 1995), nitric acid and peroxide (Kurth et al., 2006), oxidation with sodium hypochlorite or acid dichromate (Hammes et al., 2007) may not be able to degrade all the non-pyrogenic carbon, leading to an overestimate of PyC stock. Another issue common to protocols used for PyC quantitation, such as the benzene polycarboxylic acid (BPCA) method (Brodowski et al., 2005; Czimczik et al., 2005), is that only the condensed PyC is detected (Hammes et al., 2007). Advanced methods such as thermogravimetry–differential scanning calorimetry–quadrupole mass spectrometry–isotope ratio mass spectrometry (Lopez Capel et al., 2006; De la Rosa et al., 2011) are also available. In particular, chemical oxidation has been coupled to nuclear magnetic resonance (NMR) spectroscopy to quantify PyC in natural organic matter (Simpson and Hatcher, 2004). Nuclear magnetic resonance (NMR) spectroscopy is a direct non-destructive method that can allow adequate estimation of PyC in organic horizons, assuming that precautions against risks of over- and under-quantification are taken; this may be accomplished independently of the degree of condensation of the material.

The present study had three main objectives: (i) Estimation of forest floor C stock in a range of fire-affected upland black spruce forests representative of eastern Canada, (ii) quantification of the PyC stock in the distinct forest floor layers using solid state ^{13}C NMR spectroscopy and a molecular mixing model (Baldock et al., 2004; Rodríguez-Murillo et al., 2011) and (iii) investigation of the influence of regional variation in fire frequency and climate and local variation in topography and stand type, on the stock. This is the first quantitative investigation of PyC stock and wildfire effects on it, in eastern Canada, which represents a large proportion of the boreal forest of North America.

2. Material and methods

2.1. Site characteristics

The province of Quebec is divided into ten bioclimatic domains characterized by distinct vegetation and climatic conditions (Saucier et al., 2001). The black spruce-feather moss bioclimatic domain represents a third of the provincial territory and is divided into eastern and western subdomains, characterized by different precipitation regimes. The west subdomain receives an average precipitation of 850 mm/yr in its northern range and 900 mm/yr in its southern range, whereas the eastern subdomain receives 1020 mm evenly distributed throughout the year (Bergeron et al., 2004; Cyr et al., 2007). Mean annual temperature (Carrier, 1996) ranges from −2 °C in the north to just above 0 °C in the south. The western sector of the domain forms a transition zone between a continental climate (southern range) and a subpolar continental climate (northern range), while the eastern subdomain experiences a cooler, more humid maritime climate, at least in its southern range.

Humo-ferric podzols are found in the majority of the black spruce-feathermoss domain (Soil Classification Working Group, 1998). In the World Reference Base (IUSS Working Group WRB, 2007), these soils belong to the reference soil group of Podzols. With the exception of some of the drier sites, forest floors are thick, typically ranging from 10 to > 120 cm. These podzolic soils have developed on glacio-fluvial sediments/till deposits and therefore have a sandy texture and generally contain a high proportion of coarse fragments (> 2 mm). Clay deposits are occasionally present in the western sector of the domain, because of the proximity to the Clay Belt (Robitaille and Saucier, 1998). Both subdomains are largely dominated by black spruce [*Piceamariana* (Mill.) Britton, Sterns &Poggenb.], with ericaceous shrubs [*Rhododendron groenlandicum* (Oeder) Kron & Judd, *Kalmia angustifolia* L. and *Vaccinium angustifolium* Ait.], feathermoss [*Pleurozium schreberi* (Brid.) Mitt.] and/or *Sphagnum* moss (*Sphagnum* spp.) constituting most of the understory. Locally, lichens [*Cladina rangiferina* (L.) Weber] associated with fire moss [*Ceratodon purpureus* (Hedw.) Brid.] and haircap moss (*Polytrichum* spp.) are present. On well-drained sites, jack pine (*Pinus banksiana* Lamb.) is often associated with black spruce in mixed stands and becomes dominant under the driest conditions.

In 2005–2007, high fire activity in Northern Quebec caused 1.2 Mha to be burned. Large fires occurred even in regions that do not often experience fires, i.e. with long fire cycles. These fires provided potential study sites spread over a 600 km gradient, with decreasing fire frequency along a west–east axis. All sites were outside the permafrost zone and were sampled in the summer of 2010. Only those fire sites accessible by road and which presented a large enough non-salvaged area were considered. A total of 14 fire sites, ranging from 330 to 56,000 ha, were selected. During the 3 yr, most fires took place at the beginning of the fire season (Kasischke et al., 2008; Turetsky et al., 2011). In Quebec, fire regime has been regionalized via landscape units of relative homogeneous environmental conditions, including vegetation, temperature and precipitation (Lefort et al., 2004; Chabot et al., 2009), using two descriptors of fire frequency: fire occurrence and fire cycle. To test the influence of fire frequency on the soil OC (SOC) stock and PyC stock, we divided our study area into 5 zones of homogeneous fire cycle and similar climatic conditions using these landscape units (Fig. 1). Briefly, East James Bay has the shortest fire cycle (< 200 yr) followed by the sector of Chibougamau (200–500 yr). The fire cycle lengthens again (> 500 yr) in both eastern (Saguenay and Ashuapmushuan) and western (West James Bay) regions, where annual precipitation is 950 mm and 825 mm, respectively. The North-Shore zone has the longest fire cycle (> 1000 yr). Each zone included 2 to 4 fire sites. In addition, topographic features are not only important for drainage (Saucier et al., 1994), but may also be significant in terms of fire frequency and intensity (Ryan, 2002). Therefore, within each site, plots were set up along topographic gradients to take into account the potential influence of slope position on fire behavior. Lastly, the variation in topographic features also influenced vegetation, with the upper-slope/crest often characterized by a pine-dominated canopy (with some spruce trees), while an almost pure spruce canopy was present at the lower slope positions.

2.2. Sampling protocol

2.2.1. Topographic gradients and plots

As described in detail by Boiffin and Munson (2013), we positioned 2 to 4 topographic gradients within each fire site, for a total of 46 gradients. Plots (2–3.20 m × 20 m) were situated on each gradient, yielding 133 plots in total (Table 1). For each plot, we defined slope position (upper/crest, mid, lower/toe) and recorded aspect (N and E vs. S and W). The average slope (standard deviation in brackets) at the sites was 11% (± 9%). We numbered each tree (> 2 m height), recorded the diameter at breast height (DBH) and calculated the basal area of spruce vs. pine trees within each plot. We estimated the amount of biomass consumed during the last fire event following the methodology of Kasischke et al. (2008) and Boby et al. (2010). On 5 microplots, we measured the thickness of the residual organic matter (OMr) as the distance between the