

CHARCOAL IN NORTH AMERICAN BOREAL FORESTS: IMPLICATIONS
FOR CARBON STORAGE AND MANAGEMENT

By

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Abstract

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Charcoal plays an important role in boreal soil function and carbon storage, and is present in most boreal forest soils as a result of naturally recurring wildfires. Charcoal management has been proposed as a potentially valuable tool for addressing long term issues of global carbon cycles and sustainability of forest management. However, a proper understanding of boreal charcoal stocks and their effect on boreal soil carbon balance is imperative for successful application. The objectives of this thesis were to 1) review the role of boreal charcoal carbon stocks on boreal soil carbon balance; 2) determine naturally occurring wildfire derived charcoal stocks in North American boreal forests and compare these to laboratory produced charcoal; and 3) determine the risk of charcoal additions priming the decomposition of boreal soil organic matter.

A review of the literature of boreal soil charcoal studies found wildfires convert 0.7-2% of biomass to charcoal, with charcoal in boreal soils accounting for 1 Pg of carbon globally. Charcoal is highly aromatized and represents a form recalcitrant carbon, with half-lives one to two orders of magnitude greater than other soil organic matter, being able to remain onsite for millennia. However, due to a lack of soil mixing processes, charcoal in boreal soils is vulnerable to re-combustion in recurring fires, inhibiting the accumulation of charcoal over time, unlike in other fire prone ecosystems. Boreal charcoal stocks appear to be highly variable, depending on the intensity of fire. Increased fire intensity results in greater charcoal formation. Charcoal stocks in this thesis were 2-3 times greater than those reported for other boreal ecosystems where non-stand replacing fires are the predominant disturbance; suggesting global estimates of boreal charcoal carbon stocks may need to be revised upwards to account for greater wildfire intensity in North American boreal forests. Within boreal forests, charcoal is an important driver of soil function, stimulating microbial activity and nitrogen mineralization and decreasing phenolic concentrations. High productivity in post-fire stands has been attributed in part to the presence of active, newly produced charcoal that helps to reverse long term declines in productivity with increasing time since fire. Changes in carbon content and chemical composition, however, occur over time, especially in the first ~100 years.

The charcoal content of 75 soil cores 10 cm in diameter was measured to a depth of 10 cm along a chronosequence of five post-fire ages from boreal forests ~ 150 km north of Thunder Bay, Ontario. Charcoal particles > 0.25 mm were counted manually from each soil core. Charcoal stocks ranged from 2.30 to 5.20 Mg ha⁻¹, with an average carbon content of 53%. Charcoal carbon stocks ranged between 1.11 and 2.80 Mg C ha⁻¹ with a mean of 2.19 Mg C ha⁻¹. Young wildfire charcoal was found to be primarily aryl carbon with smaller amounts of alkyl-C, O-Alkyl, and methoxyl groups. Over the course of a 208 year chronosequence carbon density declined from 56 to 46%, with charcoal greater than 140 years old almost entirely aryl carbon. In the absence of fire, charcoal may lose many important properties and carbon content,

contributing to declining productivity with increasing time since fire. Laboratory produced charcoal between 300 and 350 °C was comparable to wildfire charcoal, suggesting that it may be possible to replicate wildfire charcoal properties. In the absence of fire, management of boreal charcoal stocks may be required to maintain ecosystem function and carbon balance.

Boreal forests soils are a globally significant carbon stock. By increasing soil microbial activity, charcoal additions to boreal soils may increase mineralization of soil organic matter, potentially releasing large amounts of CO₂, and offsetting soil carbon additions from charcoal. A soil microcosm experiment was used to investigate the effects of soluble and non-soluble charcoal components on soil respiration for soils with high and low organic matter. Charcoal was not found to increase the decomposition of soil organic matter. Increases in soil respiration were short lived and detected at only the highest amendment levels, likely the result of the breakdown of labile charcoal components and not organic matter. Application rates similar to those resulting from wildfires were not found to result in increased respiration. Soluble components of charcoal increased soil respiration in the presence of organic matter, but the effect was mitigated by the presence of charcoal in the soil.

Charcoal in boreal soils contributes significantly to soil carbon balance, acting as an important carbon stock. Charcoal stocks in this thesis were found to be sufficient to have a meaningful effect on soil and ecosystem processes. At these levels charcoal does not appear to present a risk to increased mineralization of existing soil organic matter. As a result charcoal additions similar to those occurring from wildfires are recommended as a starting point in boreal charcoal management. Incorporation of charcoal into ecosystem management using prescribed burns may contribute to sustainable management of boreal forests and maintaining global carbon cycles.

Keywords: charcoal, boreal forest, climate change, forest management, prescribed burn, soil carbon, wildfire

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Note to the Reader

Chapters 2, 3, and 4 have been submitted for publications as separate manuscripts. As a result, some overlap in context and methods can be expected. Chapter 2 is in press in the *Journal of Applied Ecology*, Chapter 3 has been submitted to the journal *Ecosphere*, and Chapter 4 has been submitted to the journal *Soil Biology and Biochemistry*.

Chapter 2:

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1 General introduction

Fire is a major driver of ecosystem processes, initiating stand succession and driving carbon and nutrient cycling through the mineralization of living and dead organic matter (Brais *et al.* 2000; Weir *et al.* 2000; Stocks *et al.* 2003). Between 0.7-2% of consumed biomass, however, is converted to charcoal (Czimczik *et al.* 2003; Lynch *et al.* 2004). Charcoal is carbon rich, composed primarily of aromatic carbon (Figure 1.1), with a high C:N ratio, and is highly resistant to decay. Charcoal, also known as biochar, is part of the black C continuum, which includes all carbon rich residues from fire or heat, including carbonaceous residues and condensates such as soot (Figure 1.2). Charcoal generally refers to particulate carbonaceous residues, while more soluble components are referred to as black carbon (Figure 1.2). Like most forms of black carbon charcoal is highly recalcitrant with mean residence times of thousands of years (Kuhlbusch & Crutzen 1995; Lehmann *et al.* 2008). Because of this, charcoal production and sequestration in soils has been promoted as an important management tool for carbon sequestration and ecosystem sustainability (Read & Lermitt 2005; Lehmann 2007; DeLuca & Aplet 2008).

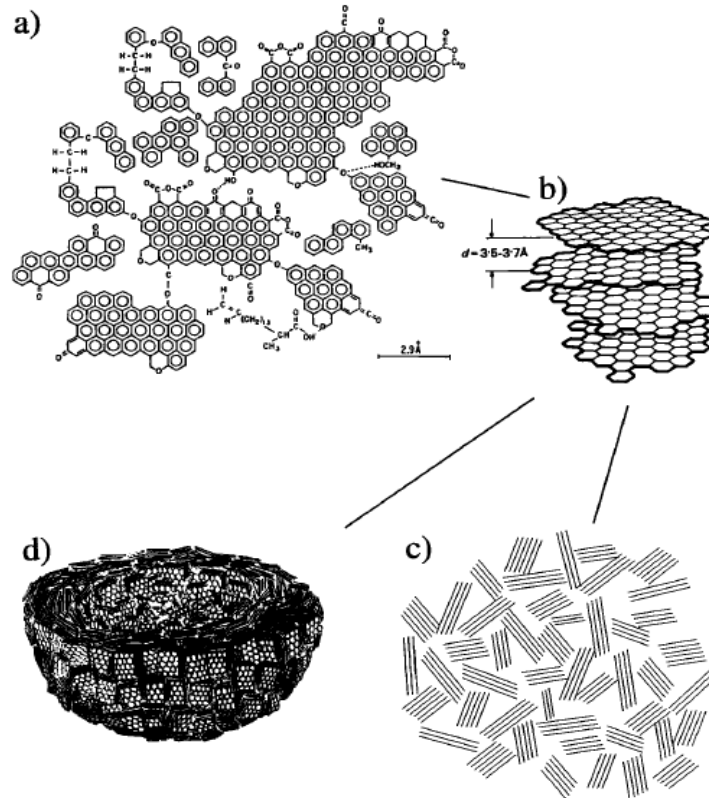


Figure 1.1 Basic structural units of charcoal (Schmidt & Noack 2000).

	slightly charred biomass	char	charcoal	GBC
formation T	low			high
size	mm and larger		mm to submicron	submicron
plant structures	abundant	significant presence	few	none
reactivity	high			low
initial reservoir	soils		soils and atmosphere	
paleotracer range	short (meters)	short (m to km)	short (m to km)	long (up to 1000s of km)

Figure 1.2 Black carbon combustion continuum (Masiello 2004).

Charcoal is present in all soils where fire is a common feature of the landscape (Kuhlbusch *et al.* 1996; Fearnside *et al.* 2001; Ohlson *et al.* 2009). Use of charcoal as a soil amendment in Amazonian dark earth dates back thousands of years (Lima *et al.* 2002). Nevertheless, despite its ubiquity, the role of charcoal in soil and ecosystem processes has only recently received increased attention with a number of studies finding increases in nutrient availability and productivity, reduced nutrient leaching, increased soil carbon content, and increased organic matter stability from charcoal additions (Liang *et al.* 2006; Chan *et al.* 2007; Van Zwieten *et al.* 2010).

Within the boreal forest charcoal represents an important carbon stock making up 1PG of soil carbon globally, equivalent to 8-10% of soil carbon, in the forest floor and upper mineral horizons (Ohlson *et al.* 2009). Charcoal also plays an important role in soil function by stimulating microbial activity and nitrogen mineralization and decreasing phenolic concentrations (Zackrisson *et al.* 1996; Wardle *et al.* 1998; Pietikäinen *et al.* 2000). Increased nutrient availability in post-fire stands compared to post-logged stands has been attributed to the presence of active charcoal stocks adsorbing base cations, inhibiting leaching from the forest floor (Thiffault *et al.* 2008). High productivity in post-fire stands has been attributed in part to the presence of active, newly produced charcoal, helping to reverse long term declines in productivity with increasing time since fire (DeLuca *et al.* 2002; Wardle *et al.* 2004). Charcoal also likely affects species composition as species differ in their response to charcoal, with some species exhibiting greater growth responses (Wardle *et al.* 1998; Thiffault *et al.* 2007).

Boreal carbon stocks are globally significant, accounting for roughly 50% of global carbon stocks, the majority of which is found in the soil (Bradshaw *et al.* 2009; Malhi *et al.* 1999). Increased temperatures resulting from climate change are expected to increase

decomposition of boreal soil carbon. As a result, boreal soils may become net carbon sources as decomposition of labile carbon stocks increases due to warmer soil temperatures, potentially releasing 30-60 PG of carbon by 2040 (Goulden *et al.* 1998; DeLuca & Boisvenue 2012). By maintaining a recalcitrant carbon stock in the form of charcoal, some soil carbon may be less vulnerable to increased decomposition with increased soil warming. In Australia, soil carbon models have been found to overestimate the response to soil warming by up to 15% when charcoal stocks were not included (Lehmann *et al.* 2008).

Fire frequency in managed boreal forests has decreased due to fire suppression and forest fragmentation (Weir *et al.* 2000; Bergeron *et al.* 2004; Lefort *et al.* 2004; Senici *et al.* 2010) leading to declining productivity in many forest stands, and preventing the renewal of active charcoal stocks (Wardle *et al.* 1998; DeLuca *et al.* 2002). Increased interest in biofuels has further increased the risk of excessive nutrient removals from boreal forests (Thiffault *et al.* 2010). Charcoal management has been proposed as a measure to mitigate negative effects of fire suppression, biomass removal and climate change on ecosystem productivity. Maintenance or addition of active charcoal to the forest soils could potentially increase the resistance of soil organic matter to soil warming, while decreasing the risk of nutrient removal (Zackrisson *et al.* 1996; Thiffault *et al.* 2008). Hence, charcoal management could be used to improve the sustainability of boreal forest management, while also potentially sequestering carbon in a highly stable form.

Nevertheless, concerns have been raised over risks to boreal SOC from the stimulating effects of charcoal additions. Wardle *et al.* (2008) found charcoal additions to Scandinavian boreal soils enhanced soil organic matter decomposition by improving nutrient availability, increasing pH and promoting microbial activity. However, humus loss may be the result of short

lived labile-carbon and soluble mineral fractions present in charcoal that may prime the decomposition of neighbouring organic matter as well as contribute to mass loss themselves (Lehmann & Sohi 2008). A number of studies actually report negative priming of soil organic matter by charcoal (Liang *et al.* 2010; Kimetu & Lehmann 2010), with increases in respiration attributed to short term mineralization of labile charcoal fractions (Liang *et al.* 2010, Zimmerman *et al.* 2011). Glucose additions are a known cause of substrate induced priming of organic matter decomposition, as well as that of charcoal (Hamer *et al.* 2004; Blagodatskaya & Kuzyakov 2008). As well, newly produced charcoal undergoes short term mass loss as labile compounds are mineralized; removal of these soluble components, by leaching charcoal, has been found to result in a 50% reduction of CO₂ evolution from soils amended with the leached charcoal (Jones *et al.* 2011), suggesting that these effects may be very short lived. As a result, a better understanding of interactions of soluble and insoluble charcoal components with boreal soil organic matter is imperative in order to minimize risks to other soil organic matter stocks.

Maintaining productivity and carbon balance is critical to sustainable management of boreal forests. Boreal charcoal management is a potentially valuable tool for addressing long term issues of global carbon cycles and sustainability of forest management. However, a proper understanding of boreal charcoal stocks is imperative for successful application. The objectives of this thesis were to 1) review the state of knowledge of charcoal in boreal ecosystems with an emphasis on charcoal stocks across all boreal ecosystems, and charcoal stability over time; 2) determine wildfire charcoal stocks in North American boreal forests in order to estimate landscape charcoal stocks, how charcoal properties and carbon content change with increasing time since fire, and how wildfire charcoal compares to laboratory produced charcoal; and 3)

examine the interactions of charcoal with boreal soil to determine if charcoal additions present a risk of priming the decomposition of boreal soil organic matter.

2 Charcoal function and management in boreal ecosystems

2.1 Introduction

Fire is the dominant disturbance force in most boreal forests. Fire return intervals of 100-700 years drive successional processes and nutrient cycling through rapid mineralization of living and dead organic matter (Bergeron *et al.* 2001; Stocks *et al.* 2003; Weir *et al.* 2000; Zackrisson 1977). Although most carbon is mineralized as CO₂, a small portion is pyrolyzed into charcoal (Lynch *et al.* 2004).

Charcoal in boreal forest soils has long been used as evidence of stand origin and historical disturbance patterns (Carcaillet & Talon 2001; Cyr *et al.* 2005). High recalcitrance of charcoal allows carbon dating of stand disturbances over millennia (Couillard *et al.* 2013; Cyr *et al.* 2005; Gavin 2003). Despite the ubiquity of charcoal in boreal soils, however, it has rarely been included as a meaningful component of soil function and carbon storage, leading to questionable assessments of the susceptibility of boreal carbon stocks to climate change (Kuhlbusch & Crutzen 1995; Lehmann *et al.* 2008), and omitting a meaningful component of boreal soil function (Wardle *et al.* 1998).

Charcoal production via pyrolysis of waste biomass has been promoted as a carbon negative biofuel based on its origin, soil amendment properties, and resistance to decay (Lehmann 2007b; Read & Lermitt 2005). Increased interest in biofuels, maintaining stand productivity and natural ecosystem processes make management of boreal charcoal stocks a potentially valuable component of boreal ecosystem management.

The role of charcoal in boreal soils has received increased attention in recent years with studies showing charcoal increases microbial biomass (Pietikäinen *et al.* 2000; Zackrisson *et al.*

1996), nitrification (DeLuca *et al.* 2006; DeLuca, Nilsson and Zackrisson 2002), phenolic adsorption (Berglund, DeLuca & Zackrisson 2004), and tree growth (Wardle, Zackrisson & Nilsson 1998). While charcoal quantity varies across boreal landscapes, it remains a meaningful fraction of the carbon pool (Ohlson *et al.* 2009). In this paper we review the role of wildfire charcoal in boreal ecosystems with an emphasis on boreal carbon budgets, ecosystem productivity, and implications for forest management.

2.2 Properties and role of charcoal in boreal soil function

Charcoal has a high initial carbon density (70-85%) relative to typical woody biomass (<50%), and is primarily made up of irregularly arranged aromatic rings, with a highly porous structure (Amonette & Joseph 2009; Boateng 2007). Aromatic structures are very stable and are responsible for the recalcitrance of charcoal (Glaser & Haumaier 2001; Schmidt & Noack 2000). Surface oxidation of aromatic rings results in carboxylation, creating large numbers of negative charged sites (Hockaday *et al.* 2006; Liang *et al.* 2006). Negative surface charges increase cation exchange capacity (Liang *et al.* 2006; Qiu *et al.* 2008); increasing adsorption of cations and phosphorus, and reduces nutrient leaching from the forest floor (Laird *et al.* 2010). Retention of nutrients by weak adsorption to charcoal surfaces and high fungal penetration of charcoal pores readily allows subsequent uptake by plants and fungi (Prendergast-Miller *et al.* 2011), increasing biomass production and ecosystem nutrient retention (Kolb *et al.* 2009). Organic compounds are also readily adsorbed by charcoal (Yu *et al.* 2006), creating ideal sites for fungi and bacteria to access desired substrates (Pietikäinen *et al.* 2000).

High porosity results in large surface areas up to $2500 \text{ m}^2 \cdot \text{g}^{-1}$ (Cherimisinoff & Ellerbusch 1978) or $3.6 \times 10^9 \text{ m}^2 \cdot \text{ha}^{-1}$ (Zackrisson *et al.* 1996), large numbers of reactive sites and high penetration by fungal hyphae (Figure 2.1). High porosity also helps to increase water retention in

coarse soils while decreasing bulk density in fine textured and compacted soils (Busscher et al. 2009).

In boreal soils, charcoal helps to maintain stand productivity and nutrient cycling. Increased retention of Ca and Mg in post-fire stands has been attributed to adsorption by charcoal (Brais *et al.* 2000). Schulze *et al.* (1999) observed tree roots growing in a solid mat in charcoal layers in Siberian boreal forests. Experimental additions of charcoal to boreal soils have found increased rates of nitrogen mineralization and nitrification (DeLuca *et al.* 2006; DeLuca, *et al.* 2002), adsorption of phenolic compounds (Wardle *et al.* 1998), and increased rates of microbial activity, leading to greater dissolved carbon uptake (Pietikäinen *et al.* 2000).

Increases in phenolic compounds and decreases in nitrogen mineralization in older forest stands are associated with decreased stand productivity and lower growth rates in forests regenerating after harvest than those after fire (Zackrisson *et al.* 1996). Charcoal additions to boreal soils can also have pronounced effects on vegetation communities and tree growth. In an experimental addition of charcoal to ericaceous dominated boreal soils Wardle *et al.* (1998) found little response in the growth of *Pinus sylvestris*, but growth and nitrogen uptake in birch were significantly greater. Changes in understory plant populations were also noted, with many species absent from ericaceous sites establishing and growing well following charcoal addition. Changes in vegetation communities owing to absence of fire derived charcoal may have long term consequences for species composition and ecosystem productivity as well as carbon cycling, by shifting vegetation communities to late successional communities lower in productivity and nutrient cycling (Wardle *et al.* 2004; Wardle *et al.* 1998).

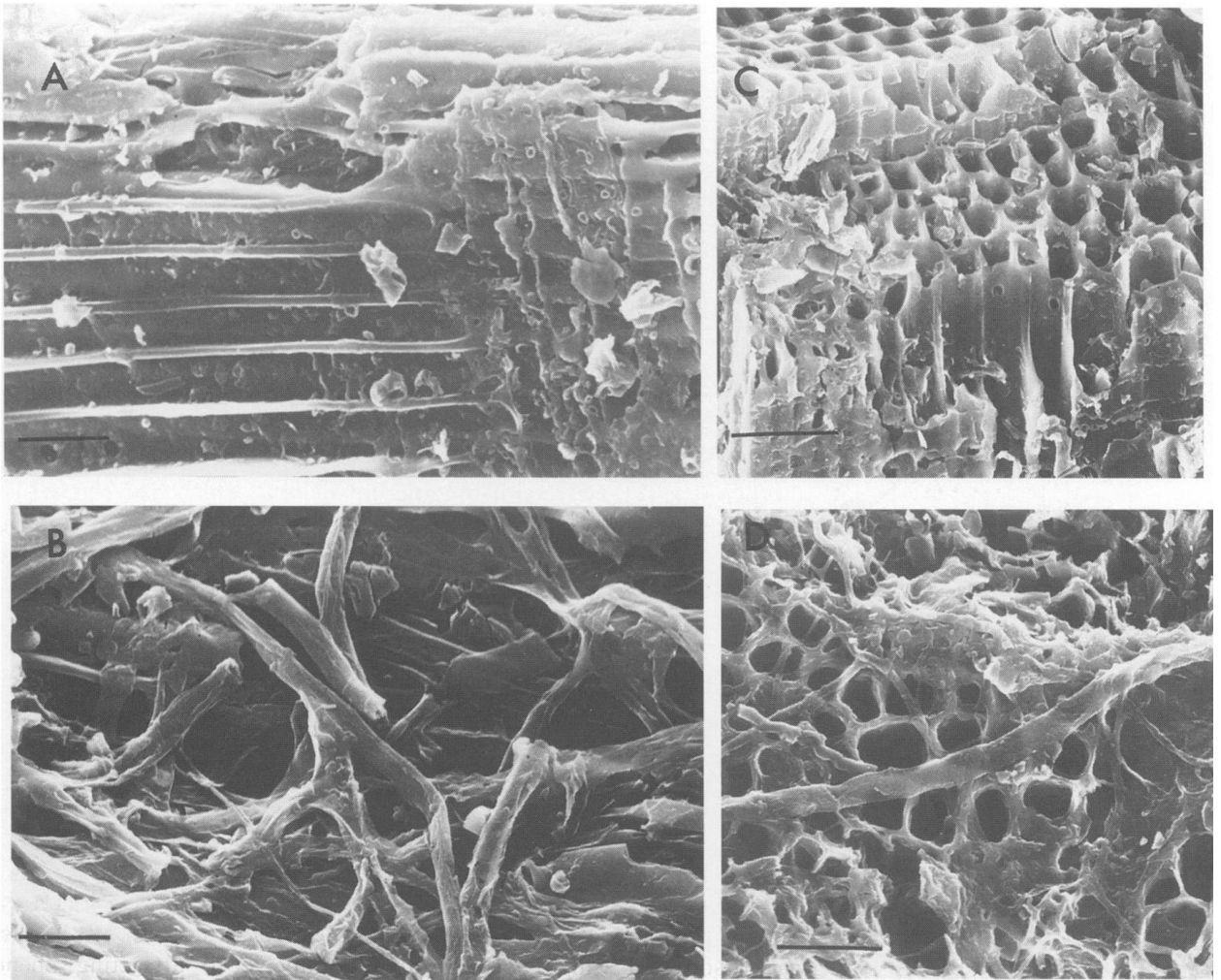


Figure 2.1. Wildfire charcoal originating from fires in 1987 (A + C), 1966 (B), and 1647 (B). Note high level of fungal hyphae colonisation in oldest charcoal (B). Scale bars 10 μ m (Zackrisson, Nilsson & Wardle 1996).

2.3 Charcoal formation

In boreal forest fires, the majority of burned organic matter is consumed, with only 0.7-2.0% of initial organic matter converted to charcoal. Similar conversion rates are reported in other ecosystems (0.6 – 2.7%) (Table 2.1). Variation in charcoal conversion rates is influenced by fire temperature, burn time, and the type and size of fuels (Czimczik *et al.* 2005; Demirbas 2004;

Demirbas 2006). Charcoal is formed by the incomplete oxidation of organic matter heated to temperatures that drive off volatile elements such as N, S, and O, resulting in increased carbon density of the remaining organic matter (Demirbas 2008). Comparison of laboratory produced charcoal with charcoal from vegetation fires in Australia found similar properties for charcoal produced at 450 °C (Fernandes *et al.* 2003) lower than typical wildfire temperatures, reflecting pyrolysis temperature, not actual wildfire temperatures.

Heating organic matter under limited oxygen exposure increases rates of charcoal formation. Therefore, it is possible that rapidly moving, high temperature fires may increase charcoal formation rates by reducing the overall time during which organic matter can fully combust (Butler *et al.* 2004). This is especially true for large tree limbs, boles, and downed woody debris, which have large volumes with less exposure to oxygen. Tinker and Knight (2000) found 8% of coarse woody debris (diameter > 7.5cm) was converted into charcoal, compared to typical rates of 0.6-2.7% for all organic matter (Table 2.1). Fuel stocks with higher carbon densities and complex carbon structures will result in greater charcoal conversion rates. For example, conifer wood, which has high lignin content, would have greater charcoal conversion rates than other forms of organic matter such as grasses (Demirbas 2001a; Demirbas 2001b). High lignin composition also increases the aromaticity of charcoal, potentially increasing long term stability of boreal charcoal (Bruun *et al.* 2008).

Table 2.1. Charcoal (char) or black carbon (BC) formation and storage in different fire prone ecosystems. Numbers in bold denote calculated stocks using a carbon density of 53% (Ohlson *et al.* 2009).

Ecosystem	Method	% Char or BC of fuel	Char or BC from fire (Mg·C·ha ⁻¹)	Char or BC from fire (Mg·ha ⁻¹)	Reference
Boreal		2	0.58	1.10	Lynch <i>et al.</i> 2004
Boreal	Charcoal	-	0.77 (0 – 2.22)	1.45 4.19	Ohlson <i>et al.</i> 2009
Boreal	BC	0.7	-	-	Czimczik <i>et al.</i> 2003
Boreal	BC	-	≤0.72	≤ 1.36	Czimczik <i>et al.</i> 2005
Boreal	Charcoal	-	0.13	0.24	Ohlson & Tryterud 2000
Boreal			1.32	2.49	
Boreal	Charcoal	-	0.45-2.86	(0.85-5.40)	Rosengren 2000
Boreal	BC	-	1.70-3.40	3.21-6.42	Kane <i>et al.</i> 2010
Boreal	Charcoal	-	0.52-1.10	0.98-2.07	Zackrisson <i>et al.</i> 1996
Tropical savannah	BC	0.6-1.5	0.28	-	Kuhlbusch 1996
Tropical slash and burn	BC	-	2.57	-	Rumpel <i>et al.</i> 2006
Tropical slash and burn	BC	1.8	4.30	-	Fearnside <i>et al.</i> 2001
Tropical slash and burn	BC	2.7	3.50	-	Fearnside <i>et al.</i> 1993
Temperate savannah	BC	-	1.0-15.0	-	Glaser & Amelung 2003

*All charcoal quantified visually from particles > 0.5mm; BC quantified using a variety of oxidation and NMR techniques.

2.4 Charcoal stability

Fire acts as a driver of long-term carbon sequestration in forest ecosystems (DeLuca & Aplet 2008). Stand replacing fires, acting on large amounts of biomass, increase charcoal formation, though, not necessarily conversion rates (Rosengren 2000). However, non-stand replacing fires, often occurring at shorter intervals and combusting less material, may result in similar amounts of charcoal accumulation over long time periods due to short fire return intervals (DeLuca & Aplet 2008). Evidence of the interaction of time, repeated fires and relatively small amounts of combustible material resulting in significant charcoal accumulations can be found in grasslands where charcoal amounts are similar to those reported for forest ecosystems, despite much smaller above ground biomass (Table 2.1). A similar tendency to accumulate charcoal over time, however, does not appear to occur in boreal forests, where charcoal levels are less than expected, given fire frequency and fuel loads (Ohlson & Tryterud 2000; Preston & Schmidt 2006).

Anthropogenic charcoal in Amazonian black earths has been found to be thousands of years old; also true of charcoal in European chernozemic soils (1160-5040 years) (Schmidt 2002) and coastal temperate rain forests (up to 12 000 years) (Gavin 2003). Most charcoal in boreal soils, however, has been dated to only a few hundred years, suggesting it may be less stable than in other ecosystems (Ohlson *et al.* 2009; Preston & Schmidt 2006). Charcoal conversion rates reported for boreal forests are similar to those of other ecosystems (Table 2.1). Despite very different fuels (wood, grass, mosses, lichens, herbs, etc.), the proportion of biomass converted to charcoal appears to be independent of the ecosystem. Given the relative frequency of fire in the boreal forest and reported conversion rates of 0.7-2.0% of biomass consumed (Lynch *et al.* 2004), large amounts of charcoal would be expected.

Boreal soils contain comparable amounts of charcoal to other fire prone ecosystems. Charcoal amounts of 0.13-3.40 Mg C·ha⁻¹ are reported for boreal ecosystems compared to 0.28-4.30 for other ecosystems (Table 2.1). One possible exception may be temperate grasslands where levels can be as high as 15.0 Mg C·ha⁻¹, possibly owing to high fire frequency and high rates of soil turnover from burrowing mammals, protecting charcoal for combustion in subsequent fires (Glaser & Amelung 2003).

It has been suggested that boreal fuels may be less suited to charcoal formation, or that charcoal produced in boreal forests is inherently less stable or more readily degraded by soil micro-organisms (Ohlson & Tryterud 2000; Preston & Schmidt 2006). This implies a lower potential for application to boreal forest soils for the purpose of carbon sequestration, since charcoal carbon would not remain sequestered as long as in other ecosystems, thereby limiting the benefits of improved soil properties, and reducing the impact of charcoal on boreal soil carbon stocks. Using charcoal data from natural forest stands provides the opportunity to assess the stability of charcoal in boreal soils. Examination of charcoal stocks reported by Zackrisson *et al.* (1996) and Ohlson (2009) in stands ranging from 2 to 347 years since fire in Scandinavia did not indicate a decline in charcoal quantities over time, while Gavin *et al.* (2003) reported only a weak relationship between charcoal abundance and time since fire.

Stand specific factors (fire intensity, vegetation type, and burning efficiency) probably play a much larger role in determining charcoal levels than do time since formation. Rosengren (2000) found higher charcoal quantities in Scandinavian forest stands subject to more intense fires, the result of more biomass on more productive sites, where more biomass was consumed, compared with stands of low intensity ground fires, consuming smaller amounts of biomass. Similar results have been found in grassland soils where wetter sites have higher charcoal stocks

than dry sites owing to greater biomass and therefore more charcoal produced from fire (Glaser & Amelung 2003).

In North American boreal forests, where crown fires predominate (de Groot 2013), charcoal levels may be greater than typical values reported for Eurasian boreal forests, potentially resulting in underestimates of charcoal carbon from Ohlson *et al.* (2009), who projected a landscape average of $0.77 \text{ Mg C}\cdot\text{ha}^{-1}$ from Scandinavian boreal forests, where ground fires predominate (de Groot 2013). Rosengren (2000), who sampled areas subject to both high and low intensity fires, found average charcoal stocks of $2.49 \text{ Mg C}\cdot\text{ha}^{-1}$. If North American boreal charcoal stocks are more representative of those resulting from crown fires, global boreal charcoal stocks may have to be revised upwards significantly, possibly by as much as a factor of 2-3. Discrepancies between these studies suggest large landscape variation and the need for further studies of all boreal regions and stand types to properly quantify boreal charcoal stocks.

2.5 Mechanisms for Charcoal Degradation

2.5.1 Decomposition

Laboratory studies report a range of charcoal recalcitrance under controlled conditions, with half-lives estimated from 10^2 to 10^7 years (Zimmermann 2010; Zimmermann *et al.* 2012). Such studies, however, have not addressed the range of ecosystem properties that may influence rates and modes of decomposition (e.g. texture, soil organic matter, moisture regime, seasonality, soil chemistry and biology). Decomposition is highly variable depending on initial feedstock and pyrolysis temperature, with recalcitrance increasing with pyrolysis temperature (Bruun *et al.* 2008; Nguyen & Lehmann 2009).

Abiotic decomposition is primarily caused by surface oxidation, resulting in the formation of carboxylic and hydroxyl groups, leading to large numbers of negatively charged surface sites, and a decrease in aliphatic groups (Bruun & Luxhøi 2008). This process takes place over the lifetime of the charcoal, but is the dominant mechanism initially. It is driven by rapid oxidation of carbonate groups (Jones *et al.* 2011), occurring more rapidly under well aerated conditions promoting surface oxidation (Nguyen & Lehmann 2009).

Biotic decomposition occurs by microbial mineralization, particularly by fungi, over much longer time periods, typically centuries (Hockaday *et al.* 2006). White rot fungi may be capable of decomposing charcoal as they utilize lignicolous substrates and are often found to infiltrate charcoal particles in soils (Hockaday *et al.* 2006; Preston & Schmidt 2006). High C:N ratios and aromaticity of charcoal, however, make it difficult for microbes to utilize charcoal as a carbon source. Incorporation of charcoal particles into stable soil aggregates, particularly in combination with clay particles and oxides, inhibits microbial decomposition (Baldock & Skjemstad 2000; Brodowski *et al.* 2006; Vasilyeva *et al.* 2011). Over time, however, microbial action results in an increase in carboxyl groups and declining aromaticity (Hockaday *et al.* 2007). As with other forms of recalcitrant organic matter, charcoal mineralization rates are increased somewhat by soil disturbances typical of agriculture and forest harvesting activities, which increase soil temperature and oxygen exposure (Glaser & Amelung 2003; Nguyen & Lehmann 2009).

Due to colder temperatures, degradation rates within boreal regions are likely to be somewhat slower than those of more tropical regions. There is also likely to be high landscape variation owing to site factors such as lowlands and permafrost. Charcoal buried in sphagnum dominated lowlands has been dated to over 5000 years, probably due in part to the anoxic environment, inhibiting decomposition, as well as protection from surface fires (Cyr *et al.* 2005).

Also, permafrost soils have been found to contain large black carbon stocks, which are likely to be protected from most forms of microbial and oxidative degradation (Guggenberger *et al.* 2008; Kane *et al.* 2010). While charcoal typically remains at the organic-mineral soil interface in most upland boreal forests, the generally less fire prone sphagnum and permafrost dominated stands may have much slower degradation rates and better protect charcoal from combustion.

2.5.2 Particle size and carbon content

While decomposition of charcoal in boreal soils occurs over extremely long time periods, mechanical degradation of charcoal occurs over much shorter periods. Zackrisson *et al.* (1996) measured particle sizes of samples from 12 *Pinus sylvestris* sites in northern Sweden. Over the first few hundred years after fire, the proportion of particles > 1.6 mm declined from just over 40% to approximately 20% while the proportion of particles < 0.5 mm and 0.5-1.6 mm increased by almost the same amount (Figure 2.2). Charcoal particle sizes in boreal soils, however, remain much larger than in other fire prone ecosystems. Rosengren (2000) found over 94% of particles were greater than 2 mm in size whereas in other fire prone ecosystems particles are typically < 53 μm (Glaser *et al.* 2000; Skjemstad *et al.* 1996); likely a reflection of the type of organic matter undergoing pyrolysis (e.g. Wood vs. grasses) as well as the result of greater pedoturbation and residence times, owing to protection from re-combustion.

Carbon content of charcoal declines somewhat over time as more labile carbon fractions are oxidized. This process lasts approximately 100 years until charcoal approaches equilibrium with C:H ratios of surrounding organic matter (Ohlson *et al.* 2009); after this, remaining charcoal compounds are likely more recalcitrant and decomposition slows considerably (Bruun, Jensen & Jensen 2008).

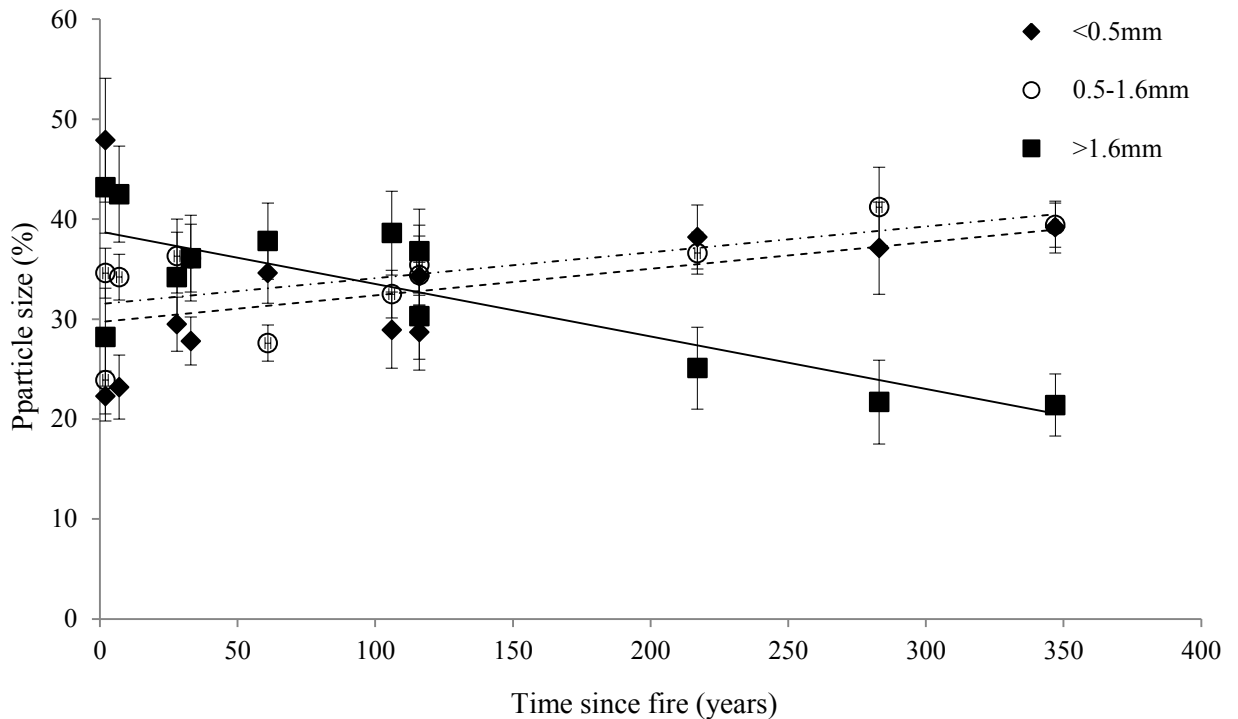


Figure 2.2 Change in proportion of charcoal particle size distribution over time. Developed from Zackrisson *et al.* (1996).

2.6 Location and Transport

Substantial amounts of aerosol black carbon, from vegetation fires and fossil fuel burning, move from terrestrial to aquatic pools (Kuhlbusch 1998). In the humid tropics, transport of charcoal offsite can occur from surface water runoff, especially on steep slopes (Rumpel *et al.* 2006). In many boreal regions, however, precipitation is low and run-off following wildfire is minimal, with the possible exception of some steep slopes. Furthermore, rapid development of thick vegetation and organic matter cover, typical after disturbances, would inhibit charcoal movement, making it unlikely significant quantities of charcoal are transported offsite.

Guggenberger *et al.* (2008), however, report a yearly export of 0.10 g BPCA-BC m⁻² from permafrost soils at the forest tundra ecotone in Northern Siberia, most of which occurred during spring runoff when surface flow was dominant, equivalent to only 0.455-0.003% of BC.

Immediately following wildfire, Lynch *et al.* (2004), found only 1% of charcoal was deposited more than 20 m from the fire edge, while Ohlson and Tryterud (2000) reported 45% of all charcoal particles found away from an experimental fire were within 1 m of the fire edge.

Downward movement of Charcoal through the soil column appears to be minimal.

Charcoal readily aggregates with mineral soil particles, stimulating the formation of soil micro-aggregates (Brodowski *et al.* 2006). Major *et al.* (2009) reported only 1% of charcoal had any downward movement in a soil in the humid tropics. This amount is similar to amounts of BC (Czimczik *et al.* 2005) and charcoal (Ohlson *et al.* 2009) found below the organic/mineral soil interface in boreal soils. Gavin (2003) found charcoal (> 0.5 mm in size) in mineral soils to depths of 30 cm but the majority of samples were within 10 cm of the organic/mineral soil interface, with the downward movement attributed to pedoturbation rather than translocation.

Boreal forest soils lack appropriate soil fauna, large numbers of burrowing mammals, and bio-mechanical properties required for extensive pedoturbation. In north temperate soils, sites with earthworms have organic matter incorporated much deeper into the mineral soil (Langmaid 1964). Soil disturbance by native burrowing mammals, ungulates, and frost heaving is limited compared to other ecosystems, where soil mixing is often the result of tree up-rooting (Šamonil *et al.* 2010; Schaetzl 1986). While blow-down events are common in boreal forests, stem snapping is more prevalent than tree uprooting due to winter conditions such as snow load, reducing the role of uprooting in soil turnover in boreal environments (Bergeron *et al.* 2009; McCarthy 2001; Peltola *et al.* 2000; Pham *et al.* 2004).

Studies of boreal charcoal and black carbon report 99% occurs at the organic/mineral soil interface, with only 1% recovered from within the mineral soil (Czimczik *et al.* 2005; Ohlson *et al.* 2009) (Figure 2.3). Factors inhibiting mixing of organic matter in the upper soil horizons inhibit incorporation of charcoal into mineral soil layers (Carcaillet & Talon 2001), possibly leaving charcoal vulnerable to re-combustion in subsequent fires. In all but the least severe and fast moving fires, the organic layer is prone to combustion, potentially removing the majority of the charcoal legacy, replacing it with charcoal from the most recent fire. This prevents charcoal accumulation typical of other fire prone ecosystems with more extensive pedoturbation mechanisms (grasslands, temperate forests, and tropical anthrosols), where charcoal is moved to deeper soil horizons and protected from combustion (DeLuca & Aplet 2008; Glaser & Amelung 2003; Lehmann *et al.* 2003). Soil mixing processes, more prevalent in other fire prone ecosystems, result in fire acting as a driver of long-term carbon sequestration (DeLuca & Aplet 2008). This effect is less prevalent in boreal soils due to reduced soil mixing. Nevertheless, by converting a portion of ecosystem carbon into charcoal, of which a portion is highly recalcitrant black carbon, fire may influence boreal carbon storage by maintaining a highly recalcitrant carbon pool.



Figure 2.3 Typical occurrence of charcoal particles at the organic-mineral soil interface. Soil core collected 150 km north of Thunder Bay, Ontario, Canada, from a 90 year-old fire origin *Pinus banksiana* dominated forest.

2.7 Interaction with soil organic matter

Although recalcitrant, charcoal is chemically active and interacts with surrounding soil organic matter, influencing cycling of non-black carbon in soils. By increasing nutrient availability, nitrogen mineralization, and microbial activity, charcoal may prime organic matter decomposition, minimizing soil carbon gains from charcoal additions (Berglund *et al.* 2004; Lehmann *et al.* 2003; Pietikäinen *et al.* 2000). While charcoal is primarily carbon, partial combustion of some organic matter results in an ash fraction present with the charcoal (Glaser *et al.* 2002). Ash contains soluble macro- and micronutrients and is responsible for most of the pH

buffering of newly produced charcoal and the availability of base cations (Thiffault *et al.* 2008). Wardle *et al.* (2008) reported increased humus loss when charcoal amendments were applied; however, this effect may be short-lived, and it is not clear if the observed decomposition was driven by inherent charcoal properties or the soluble ash component (Lehmann & Sohi 2008). Laboratory studies have found short term increases in soil respiration after charcoal additions; but this is attributed to mineralization of labile fractions, with no reported soil organic matter loss (Cross & Sohi 2011). These effects are also short lived (Luo *et al.* 2011), with an overall positive interaction between charcoal and soil organic matter, leading to decreased soil organic matter losses over time (Zimmerman *et al.* 2011).

In many cases, however, charcoal inhibits organic matter decomposition by promoting soil aggregate formation (Brodowski *et al.* 2006). High porosity of charcoal, combined with large numbers of negatively charged surface sites, provides protected locations for hydrophobic organic matter, while also promoting micro-aggregate formation with positively charged soil particles, protecting organic matter from microbial oxidation (Baldock & Skjemstad 2000; Liang *et al.* 2010). Amazonian anthrosols, amended with charcoal, have greater soil organic matter, and support more microbial biomass (Liang *et al.* 2006). Laboratory experiments also report greater rates of organic matter integration in soils amended with charcoal (Liang *et al.* 2010). It has been shown that soil respiration in charcoal amended soils is lower, with any increase in respiration attributed to short lived mineralization of labile fractions (Zimmerman *et al.* 2011). Although effects vary somewhat over time, as well as with charcoal type, most studies report a slight negative priming effect of charcoal on soil organic matter, suggesting that charcoal may stabilize other soil organic matter stocks (Cross & Sohi 2011; Zimmerman *et al.* 2011).

2.8 Role in boreal carbon budget

Although a relatively small component of overall ecosystem carbon (~1%) charcoal can comprise up to 8-10% of soil carbon, the largest repository of ecosystem carbon (Ohlson *et al.* 2009). Based on boreal forest sites in Scandinavia, Ohlson *et al.* (2009) have estimated boreal forest charcoal to comprise 1 Pg of carbon. There are concerns over the vulnerability of boreal soil carbon stocks to climate change and increased fire frequency and intensity (Balshi *et al.* 2009); by acting as a highly stable carbon stock, charcoal plays an important role in maintaining boreal carbon stocks (DeLuca & Aplet 2008).

To date, however, charcoal is not included as a separate pool most soil carbon models. Given its recalcitrance over other carbon pools, omissions of soil charcoal may result in an overestimation of the vulnerability of forest soil carbon to climate change. Lehmann *et al.* (2008) found soil climate models may over estimate soil carbon climate feedback by up to 15% in Australian soils. Interactions with SOM may further decrease soil responses to warming, by protecting labile organic matter from microbial decomposition (Brodowski *et al.* 2006). Inclusion of charcoal in soil carbon models is imperative in order to accurately model soil carbon responses to changes in climate, fire regimes, and forest composition.

2.9 Charcoal management

Loss of active charcoal properties may contribute to declining stand productivity with increasing time since fire (DeLuca *et al.* 2002; Wardle *et al.* 1998). Wildfire renews charcoal stocks, helping to restore soil function (Zackrisson *et al.* 1996). Globally, there are over 14.4M km² of wooded boreal forest, of which almost 8.2M km² have been harvested at least once (Burton *et al.* 2003), creating a large area of industrially impacted forest. Within managed boreal forests, fire

frequency has been reduced over the past century due to forest fragmentation and fire suppression (Bergeron *et al.* 2004; Berglund *et al.* 2004; Weir *et al.* 2000). Replacement of fire with forest harvesting in many parts of the boreal forest may prevent the renewal of active charcoal stocks, and may increase mineralization of existing stocks through soil disturbance, as well as reducing negative priming effects of charcoal on other soil organic matter (Thiffault *et al.* 2008). Resulting reductions in forest productivity may further lead to a reduction in carbon sequestered in labile stocks (Akselsson *et al.* 2005). Management of boreal charcoal stocks may be required to maintain forest soil carbon, soil function, and stand productivity.

Increased interest in biomass harvesting for biofuels has raised concerns over excess organic matter and nutrient removals, potentially leading to a decline in soil carbon and long-term productivity (Thiffault *et al.* 2010). Combining bioenergy with charcoal production and application has been proposed as a means of maintaining soil function and carbon stocks while producing energy from a renewable source (Lehmann 2007a; Read & Lermitt 2005). Charcoal management could offset increased losses of more labile organic matter associated with climate warming (Davidson & Janssens 2006; Knorr *et al.* 2005). The ability to tailor charcoal properties offers the potential to manage specifically for phenolic adsorption, carbon sequestration or nutrient retention (Novak *et al.* 2009a).

Manual charcoal additions have been proposed in agricultural and agroforestry settings as a means of increasing productivity while also sequestering large amounts of carbon in soils (Lehmann 2007b; Read & Lermitt 2005). These approaches, involving incorporation of charcoal into soils are unlikely to be practical in most boreal settings. Intense soil disturbances would be highly disruptive to other ecosystem processes, negating the benefits of increased charcoal function and carbon storage. The vast scale and relative remoteness of most boreal forests are

also likely to make intense management practices cost-prohibitive in all but intensively managed plantations.

Incorporation of fire in boreal forest management may help to maintain active charcoal stocks. Large amounts of forest residues remain after forest harvesting. Prescribed burning of logging residues has the potential to renew charcoal stocks. Peltola *et al.* (2011) report an average of 33.1 Mg·ha⁻¹ of logging residues across a range of *Picea* dominated sites in Finland. Assuming a charcoal conversion rate of 0.7-2% and carbon density of 53% for charcoal, burning logging residues would produce 0.12-0.35 Mg C·ha⁻¹, roughly equivalent to levels recorded for ground fires in Scandinavian studies, although less than levels recorded for higher intensity crown fires (Table 2.1), reflecting lower amounts of consumed biomass in non-stand replacing fires. Charcoal from burning slash would nevertheless represent a significant long-term carbon stock and is of sufficient levels to contribute meaningfully to soil function.

In view of the important contribution of wildfire charcoal to carbon balance and ecosystem function it is imperative that fire be viewed as playing a critical role in long term ecosystem productivity. Incorporating wildfire into large scale boreal forest management may be of benefit in addressing the long term sustainability of boreal forest management.

2.10 Conclusions

Charcoal is an important component of boreal soils. Charcoal formation rates are similar to those of other ecosystems with 0.7-2% of overall biomass converted to charcoal. The vast majority of fire-derived charcoal remains onsite at the organic/mineral soil interface where it undergoes a series of important changes over the first few hundred years, until a relative equilibrium is reached with surrounding organic matter. A lack of soil mixing in boreal ecosystems makes charcoal vulnerable to combustion during fire, inhibiting a build-up of charcoal stocks over time.

In the absence of re-burning, however, portions of boreal charcoal can remain onsite for hundreds to thousands of years, making up a meaningful component of soil organic matter, contributing to soil function, and acting as a stable fraction of the soil carbon pool. Nevertheless, some important charcoal properties, which contribute to initial post-fire productivity, are relatively short lived, resulting in a loss of charcoal function with increasing time since fire—contributing to declining stand productivity over time. Maintaining active charcoal stocks is imperative for long term sustainability of boreal ecosystems.

Management of boreal forest charcoal stocks may be necessary and advantageous in the absence of fire and decreased organic matter inputs due to forest harvesting. Managing boreal soil charcoal stocks has the potential to maintain soil function and the soil carbon pool. Incorporating fire into boreal forest management through the use of prescribed burns and wildfire is imperative to maintain future carbon stocks, long term productivity, and ecosystem function. It is imperative that the role of charcoal in boreal ecosystem function be fully understood. Future research needs include quantifying charcoal stocks across all boreal regions, positive and negative priming effects of charcoal, effects on forest productivity, phenolic adsorption, charcoal formation rates from different biomass stocks, the proportion of charcoal that is recalcitrant, and methods to replicate wildfire charcoal properties. Maintaining active boreal forest soil carbon stocks is imperative in the face of intense forest harvesting, fire suppression and climate change.

3 Charcoal carbon pool in North American boreal forests

3.1 Introduction

Wildfire is the principal disturbance force in much of the boreal forest. Fire return intervals between 100 and 700 years drive boreal ecosystem function by initiating stand succession and releasing nutrients through rapid mineralization of organic matter (Brais *et al.* 2000; Weir *et al.* 2000; Bergeron *et al.* 2001; Stocks *et al.* 2003). While most organic matter consumed by wildfires is completely mineralized, substantial amounts of charcoal are also produced through incomplete oxidation (Kuhlbusch and Crutzen 1995; Ohlson & Tryterud 2000). With a high carbon to nitrogen ratio and primarily aromatic structure, charcoal is very resistant to decay, representing a long-lived carbon stock (Skjemstad *et al.* 1996). In fire prone ecosystems charcoal comprises by far the oldest carbon pool, contributing to long term carbon storage (Krull *et al.* 2006).

Charcoal plays an important role in boreal soil processes, increasing cation exchange capacity, nutrient retention and nitrification, while mitigating the effects of phenolic compounds (Nilsson & Zackrisson 1992; Zackrisson *et al.* 1996; Wardle *et al.* 1998; Pietikäinen *et al.* 2000; DeLuca *et al.* 2002). In boreal Siberia tree roots have been reported growing within the charcoal layer (1999). Charcoal stocks in boreal forests range from 0 to 2.22 Mg·C·ha⁻¹, with a landscape average for Scandinavia of 0.77 Mg C·ha⁻¹ (Zackrisson *et al.* 1996; Ohlson *et al.* 2009), comprising 3-13% of soil organic matter (Dai *et al.* 2005; Rumpel *et al.* 2006). Ohlson *et al.* (2009) estimated boreal charcoal stocks globally of 1 Pg, equivalent to as much as 1% of all vegetation carbon in boreal forests. The majority of studies of boreal charcoal stocks, however, are from European and Eurasian boreal forests where wildfire tends to be non-stand replacing (Zackrisson 1977; Wirth *et al.* 1999). In North American boreal forests, where crown fires

predominate (Johnson 1992), charcoal levels may be much greater, as more biomass is consumed in stand replacing wildfires, likely producing greater amounts of charcoal, potentially resulting in underestimates of soil charcoal carbon to date.

By acting as a recalcitrant carbon stock, charcoal can impact soil carbon balance. Lehmann *et al.* (2008) found soil climate models overestimated climate feedback in Australian soils by 15% when failing to include charcoal stocks. Boreal soil carbon stocks are important for global carbon balance and there is concern that climatic warming may destabilize these stocks (Goulden *et al.* 1998). Incorporation of accurate charcoal stocks into boreal soil climate models would aid in properly modeling boreal soil carbon feedback (Krull *et al.* 2006; Lehmann *et al.* 2008, DeLuca & Boisvenue 2012).

Anthropogenic charcoal in Amazonian black earths can be thousands of years old, as can charcoal in European chernozemic soils (1160-5040 years) (Schmidt 2002) and coastal temperate rain forests (up to 12 000 years) (Gavin 2003). Most charcoal in boreal forests, however, has been dated to only a few hundred years, suggesting it may be less stable than in other ecosystems potential decreasing the relative impact on soil carbon balance (Preston & Schmidt 2006; Ohlson *et al.* 2009). Boreal forest soils lack appropriate soil fauna, large numbers of burrowing mammals, and bio-mechanical properties required for extensive pedoturbation and as a result have lower rates of soil turnover (Schaetzl 1986; Šamonil *et al.* 2010). While blow-down events are common in boreal forests, stem snapping is more prevalent than tree uprooting, further reducing the role of uprooting in soil turnover in boreal environments (Peltola *et al.* 2000; McCarthy 2001; Pham *et al.* 2004; Bergeron *et al.* 2009).

Studies of boreal charcoal report 99% of the charcoal occurs at the organic/mineral soil interface, with only 1% found within the mineral soil (Czimczik *et al.* 2005; Ohlson *et al.* 2009). Factors inhibiting mixing of organic matter in the upper soil horizons inhibit incorporation of charcoal into mineral soil layers (Carcaillet & Talon 2001), leaving charcoal vulnerable to re-combustion in the next wildfire (Gavin 2003), replacing it with charcoal from the most recent fire; preventing charcoal accumulation typical of other fire prone ecosystems (grasslands, temperate forests, and tropical anthrosols), where charcoal is moved to deeper soil horizons and protected from combustion (Lehmann *et al.* 2003; Glaser & Amelung 2003; DeLuca & Aplet 2008). Carcaillet (2001) reports similar lack of charcoal incorporation in high elevation soils in the Alps where appropriate fauna for pedoturbation are similarly lacking.

In recent years, charcoal resistance to decay and important soil conditioning properties has led to interest in managing soil charcoal content to increase carbon sequestration while improving soil properties (Read & Lermitt 2005; Lehmann 2007b). In many parts of the boreal forest increased fire suppression, forest fragmentation, and timber extraction have lengthened fire return intervals (Zackrisson 1977; Weir *et al.* 2000; Bergeron *et al.* 2004; Senici *et al.* 2010), inhibiting the creation of new charcoal stocks, while further decreasing carbon sequestration by reducing the amount of carbon stored in living biomass as well as reducing organic matter inputs from litter-fall (DeLuca *et al.* 2002; Akselsson *et al.* 2005). Additions of charcoal to boreal soils have been found to reverse retrogressive succession and improve stand productivity (Wardle *et al.* 1998). In the absence of wildfire as a dominant disturbance force, management of boreal soil charcoal stocks may be necessary to help maintain ecosystem processes and carbon balance.

Understanding boreal soil charcoal stocks and how they change over time is critical for accurate carbon accounting, climate feedback modeling, and forest management. In this study

charcoal stocks from North American boreal forest soils of known post-fire ages were studied to determine the role of charcoal in the boreal carbon budget as well as the potential of charcoal application. It was hypothesized that North American boreal charcoal stocks would (1) be greater than those in Eurasian boreal forests; (2) be relatively stable over time; (3) exhibit changes in properties over time; and (4) have similar properties to charcoal produced in the laboratory.

3.2 Methods

3.2.1 Soil charcoal stocks

Charcoal stocks were quantified from sites representing a post-fire gradient of time since fire. A chronosequence of sites with similar parent material and topographic conditions was used to study charcoal stocks over a period of 14-208 years. This method is suitable for studying characteristics more likely to be related in a predictable and temporally linear matter (e.g. accumulation of organic matter or species richness versus species abundance or composition) (Walker *et al.* 2010). Charcoal stocks are formed from wildfire events and, as a result, would be expected to degrade and decline, however slowly, with increasing time since formation (Zackrisson *et al.* 1996).

Soils were collected from sites of known fire history (see Hart & Chen 2008), approximately 150 km north of Thunder Bay, Ontario (48°22'56" N; 89°14'46" W). This region is typified by stand replacing wildfires with a fire frequency of roughly 100 years (Senici *et al.* 2010). The area lies within the central boreal shield ecozone. Coarse, glacially derived brunisolic soils of varying thickness overlie Precambrian bedrock. Overstory species composition includes *Pinus banksiana* and *Populus tremuloides* on younger sites and *Picea glauca*, *P. mariana*, *Abies balsamea* and *Betula papyrifera* on older sites. Understory species communities are relatively rich with a moderate herbaceous cover including *Maianthemum canadense*, *Cornus canadensis*,

Clintonia borealis. *Acer spicatum* is a dominant understory shrub, while feathermosses are dominant in conifer stands.

Three sites were sampled from each of five post-fire dates of 14, 32, 90, 144, and 208 years after stand replacing fire. Each site was sampled using a 20 x 20 m plot in which five soil cores 10 cm in diameter were taken at random from each site to a mineral soil depth of 10 cm. This depth was deemed sufficient, given that very little soil mixing occurs in boreal soils with the majority of charcoal reported from the organic-mineral soil interface and the top 1-2cm of mineral soil (Czimczik *et al.* 2003; Ohlson *et al.* 2009). From 15 sites, a total of 75 soil cores were sampled. The presence of charcoal at the mineral soil surface in boreal soils makes it vulnerable to combustion in subsequent fires (Rosengren 2000; Preston & Schmidt 2006). As a result, charcoal ages were assumed to be the same as a site's post-fire stand age.

Soils were air dried and passed through a 1 mm sieve. All macroscopic charcoal (> 1mm) was removed, while remaining soil was homogenized and a 2 cm³ sample passed through sieves of 0.5 mm and 0.25 mm to determine microscopic charcoal content. Sub-samples were placed in Petri dishes and charcoal removed manually under a dissecting microscope. The relative efficiency of this method was tested by adding known amounts of lightly crushed laboratory produced charcoal (a range of particle sizes up to 2 mm), to soils that did not contain any charcoal. This method yielded a recovery success greater than 90%. As a result, all charcoal recovered from study soils is likely to be a slight underestimation of actual charcoal stocks and any landscape scale projections can be considered conservative.

Charcoal samples were oven-dried and weighed. Fixed carbon, the thermally stable, non-volatile carbon fraction, content of charcoal was determined using a LECO CNS2000 (LECO

Corp., St Joseph, MI). Carbon, hydrogen and nitrogen content were determined using a CHNS Elementar vario EL (Elementar Analysensysteme GmbH, Hanau, Germany). Charcoal weights were converted to relative carbon weights in order to determine the amount of carbon represented by charcoal. The decay rate of charcoal was determined by modelling changes in charcoal weights, carbon concentration, H:C ratio and C:N ratio. Constrained nonlinear regression was used to fit curvilinear regression models to the empirical data. Model selection was based on the estimation of coefficient of determination (R^2) and pattern of residuals. If no pattern was observed on predicted values versus residuals, the highest R^2 model was accepted. Given the prevalence of fire across most of the North American boreal forest (Johnson 1992), converting charcoal amounts to a landscape scale, while approximate, is likely a reasonable estimate.

3.2.2 Structure of laboratory and wildfire charcoal

Charcoal was produced in a laboratory at a range of temperatures (300-400 °C) from *Larix laricina* (Du Roi) K. Koch (tamarack) wood chips packed in 500 cm³ metal canisters and heated at a rate of 10 °C/min in a muffle furnace to a maximum temperature and held for one hour. Although a common component of boreal forests, *L. laricina* was chosen because of availability. Charcoal samples from each post-fire age were analysed to determine changes in charcoal properties over time.

Solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy was used to characterise the basic chemical structures of charcoal from a range of stand ages, and from laboratory produced charcoal. One composite sample was made for each age class by homogenizing all samples from each post-fire age. Samples were sent to the University of Manitoba Chemistry NMR lab for analyses. Spectra were done using cross polarization (CP) using a Bruker Advance

400 spectrometer operated at a ^{13}C frequency of 128.8 MHz for all analyses. 7-9 mg of charcoal was packed into a 2.5 mm diameter cylindrical rotor and spun at 5000 Hz in a Doty Scientific magic angle spinning (MAS) probe with a contact time of 3 ms, and an acquisition time of 20.48 mS. Free induction decay was acquired using a sweep width of 50 kHz. Line broadening for FID processing was done at 200 Hz.

3.3 Results

3.3.1 Charcoal levels and carbon content

Large quantities of charcoal were present at all sites sampled. Charcoal stocks ranged from 2.30-5.20 $\text{Mg}\cdot\text{ha}^{-1}$ and averaged 4.09 $\text{Mg}\cdot\text{ha}^{-1}$ for all sites within the top 10 cm of the mineral horizon. Average carbon concentration for all charcoal was 51.9%. Adjusting for carbon concentration, mean charcoal carbon stocks were 2.19 $\text{Mg}\cdot\text{C}\cdot\text{ha}^{-1}$ (Table 3.1).

The relationship between time since fire and quantities of charcoal and charcoal C was described using a sigmoidal decay curve (Table 3.1). Charcoal quantities did not change within the first ~100 years, after which time they began to decrease. Carbon content of charcoal was found to have an exponential decay with increasing time since fire (Figure 3.1). Carbon concentration declined somewhat over time, from a high of 56.4% in 14 year old stands to 46.5% in 208 year-old stands (Figure 3.2).

Table 3.1 Results of constrained linear regressions. TSF – Time since fire, in years.

Variable	Type of curve	Regression MS	Regression df	Residual MS	Residual df	R ²	Function
Charcoal (Mg/ha)	Sigmoidal	88.1	3	3.9	12	0.22	$\text{Charcoal} \left(\frac{\text{Mg}}{\text{ha}}\right) = \frac{4.755}{1 + 0.002 * e^{0.032 * \text{TSF}}}$
C density (%)	Sigmoidal	25.6	3	1.24	12	0.25	$\text{BlackC} \left(\frac{\text{Mg}}{\text{ha}}\right) = \frac{2.634}{1 + 0.004 * e^{0.030 * \text{TSF}}}$
C (%)	Exponential	13542	3	26	12	0.32	$\text{C}(\%) = 40 + 16.488 * e^{-0.004 * \text{Age}}$
H:C	Linear	0.034	2	0	13	0.31	$\text{H:C} = 0.062 + 5.1\text{E-}5 * \text{TSF}$
C:N	Exponential	44884	3	718	12	0.27	$\text{C:N} = 85.765 + 165.228 * e^{-0.132 * \text{TSF}}$

Carbon content in boreal organic matter is typically between 40-45% (Li *et al.* 2012; Smith *et al.* 2000). The carbon content in charcoal is unlikely to fall below this level since it will be in equilibrium with surrounding organic matter. The model was, therefore, parameterised with a minimum value for carbon content of 40%. The resulting model demonstrated that carbon content approaches 40% approximately 500-600 years after wildfire, after which time it would be expected to decay at a much slower rate (Ohlson *et al.* 2009).

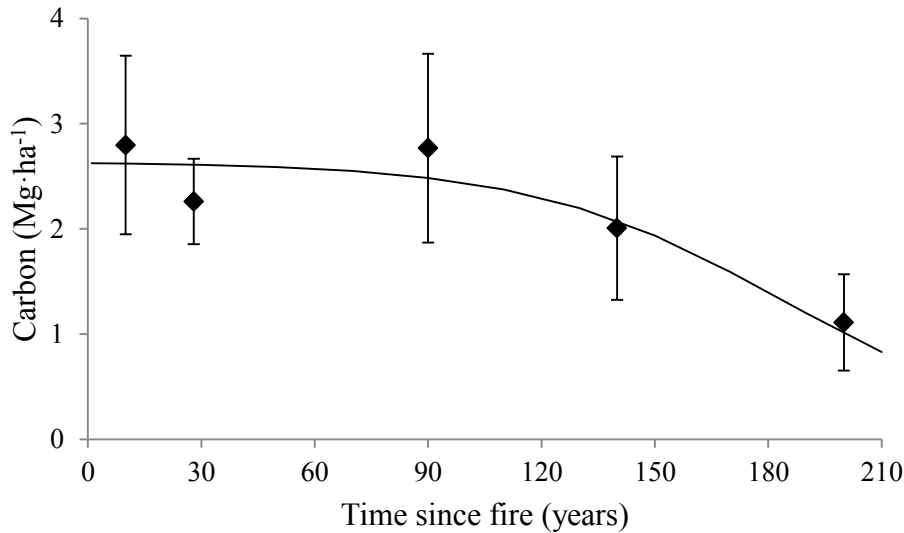


Figure 3.1 Charcoal carbon ($\text{Mg}\cdot\text{ha}^{-1}$) in relation to time since fire. Error bars are ± 1 SE. Black line is a sigmoidal decay curve fitted to the empirical data (see Table 3.1).

The H:C ratio of charcoal (Table 3.2) increased linearly with time since fire (Table 3.1). The increase was very moderate over the chronosequence with ratios increasing from 0.73 to 0.87 (Table 3.2). The C:N ratio, however, dropped significantly during the first few decades, more than 50% during the first 30 years, remaining unchanged over the following 200 year period, levelling out at a ratio of 86 (Table 3.2); much higher than the 40:1 typical for boreal forest organic matter (Smith *et al.* 2000).

Laboratory and wildfire charcoal had somewhat different elemental composition (Table 3.2). Nitrogen content was much lower for laboratory produced charcoal than wildfire charcoal, whereas hydrogen content was much greater.

Table 2.2. Elemental composition of wildfire and laboratory produced charcoal. Wildfire charcoal from five post-fire ages (time since fire - TSF). Numbers in brackets \pm 1 SE.

Charcoal type	N	C	H	S	H:C	C:N
	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹		
Wildfire						
TSF						
14	0.46 (0.03)	56.43 (2.27)	3.48 (0.18)	0.08 (0.010)	0.73 (0.01)	143.02 (10.47)
28	0.63 (0.09)	53.29 (1.99)	3.41 (0.20)	0.10 (0.027)	0.76 (0.02)	102.93 (13.53)
90	0.57 (0.09)	53.16 (1.73)	3.69 (0.26)	0.07 (0.001)	0.83 (0.07)	113.17 (16.90)
140	0.68 (0.12)	50.35 (5.41)	3.30 (0.28)	0.10 (0.018)	0.78 (0.04)	98.71 (32.37)
208	0.63 (0.06)	46.51 (2.90)	3.39 (0.03)	0.10 (0.011)	0.87 (0.05)	88.3 (13.15)
Laboratory						
300 °C	0.20	68.22	5.21	0.05	0.91	397.90
350 °C	0.27	71.43	4.40	0.04	0.73	308.61
400 °C	0.46	76.57	4.11	0.02	0.64	194.18

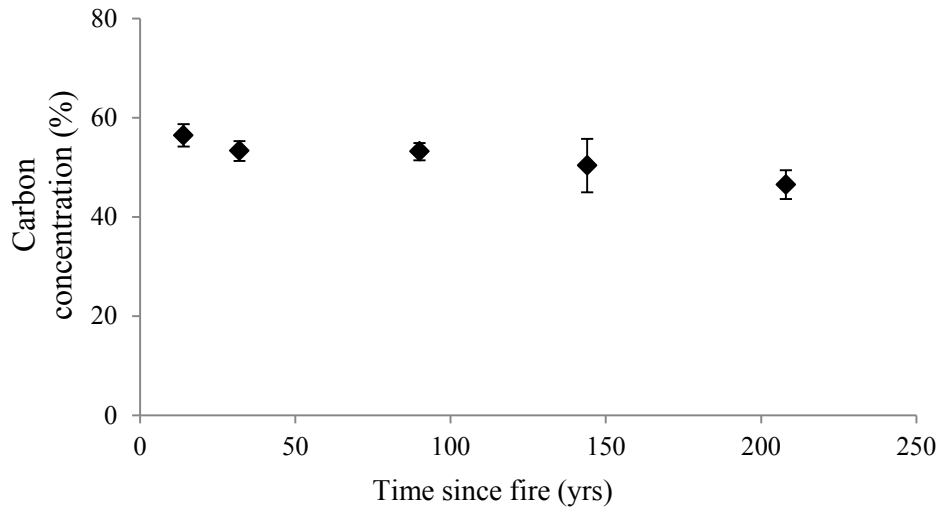


Figure 3.2 Carbon concentration (%) of charcoal from stands of increasing time since fire. Error bars are \pm 1 SE.

3.3.2 Cross polarization ^{13}C NMR

Solid state CP ^{13}C NMR spectra from charcoal of different post-fire stand ages revealed changes in carbon structures over time (Figure 3.3). All charcoal samples had high signal intensities for aryl C (129 ppm), revealing a high degree of thermal alteration typical of charcoal.

Charcoal from 14, 28, and 90 year-old stands was relatively complex. In addition to aryl C, charcoal from younger stands had moderate amounts of O-Aryl (143 ppm), O-Alkyl (73 ppm), methoxyl (55 ppm), and alkyl C (37 ppm), especially in 14 year old stands. In contrast, 140 and 200 year old stands were almost exclusively aryl C with only small amounts of O-alkyl C (Figure 3.3). Changes in charcoal structures between stand ages were characterized by the loss of more labile carbon groups, containing more single bonded C as opposed to double bonded aryl carbon.

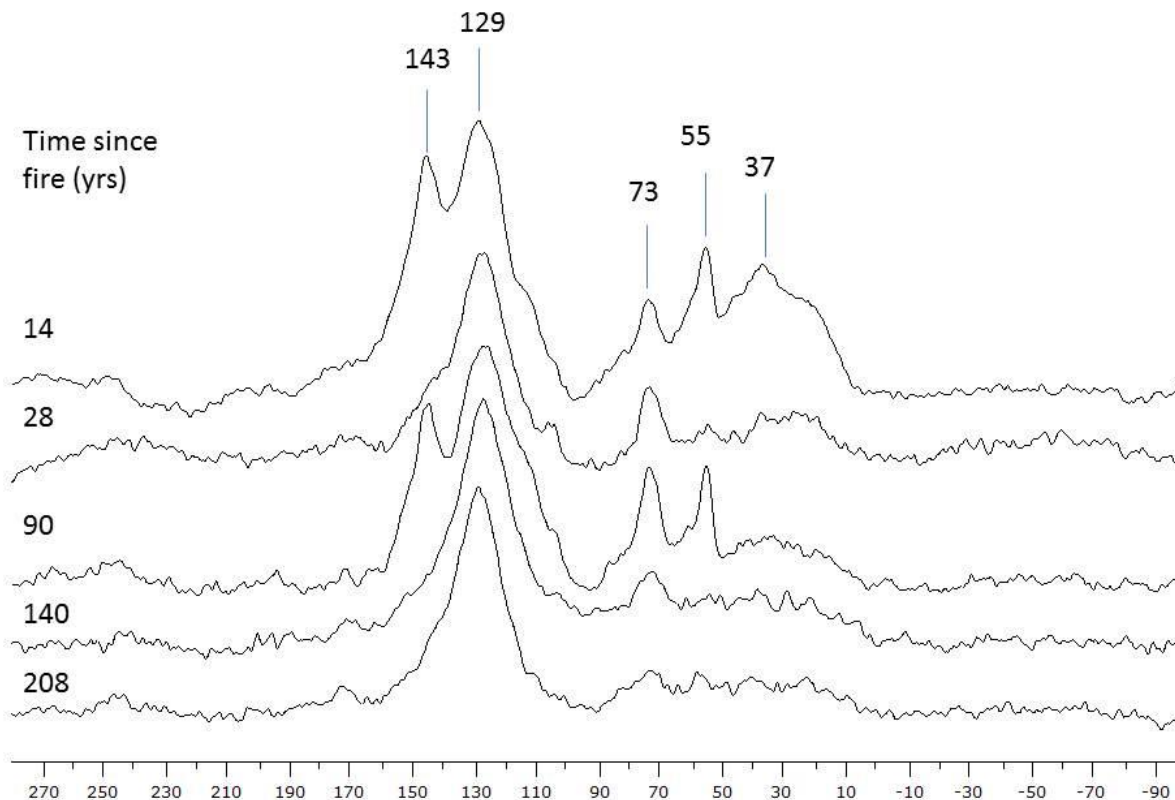


Figure 3.3 Nuclear Magnetic Resonance (NMR) Carbon-13 CPMAS-TOSS spectra of charcoal with increasing time since fire. Values above peaks are chemical shift positions (PPM).

3.3.3 Comparison to laboratory charcoal

Comparison of CP ^{13}C NMR between charcoal from 14 year-old stands and laboratory produced charcoal revealed similarities in charcoal produced between 300 and 350 °C (Figure 3.4). While all laboratory produced charcoals were dominated by aryl C (129 PPM), similar to wildfire charcoal, charcoals produced at 300 and 350 °C also had relatively large amounts of O-aryl (143 ppm), O-alkyl (73 ppm), methoxyl (55 ppm), and alkyl C (37 ppm). Charcoals produced at 400 °C and higher were dominated by aryl carbon, with only minimal contribution by non-aryl carbon groups (Figure 3.4).

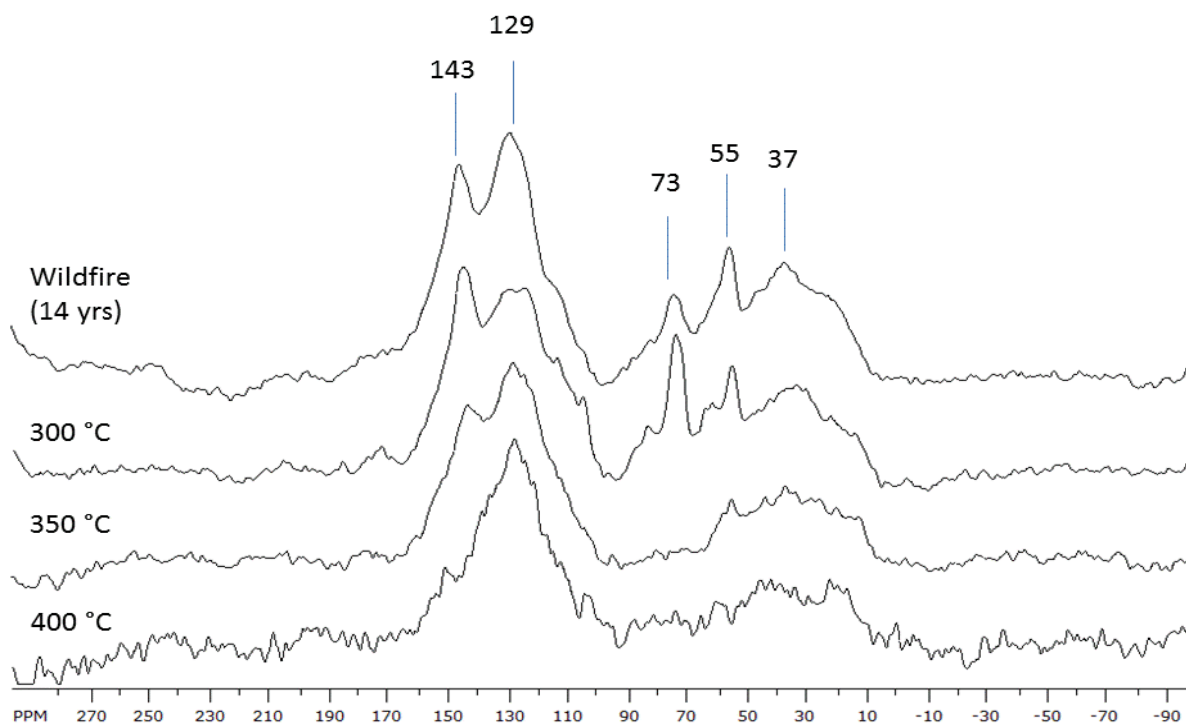


Figure 3.4 Nuclear Magnetic Resonance (NMR) Carbon-13 CPMAS-TOSS spectra of 14y wildfire charcoal and laboratory produced charcoal from a range of different temperatures. Values above peaks are chemical shift positions in PPM.

Charcoal produced at 300 °C differed somewhat from wildfire charcoal by having greater O-aryl (143 ppm) content than aryl (129 ppm) carbon, as well as a much greater contribution of O-alkyl (73 ppm) C than in wildfire charcoal, suggesting a temperature lower than that of wildfire charcoal, since there had been incomplete formation of aryl carbon and large amounts of polysaccharide derived O-alkyl C remained. Charcoal produced at 350 °C, appears to have been formed at a slightly higher temperature than wildfire charcoal due to the almost complete loss of O-alkyl C and the large reduction in methoxyl (55 ppm) C. As a result, it seems reasonable to assume boreal wildfire charcoal is likely formed at temperatures between 300 and 350 °C.

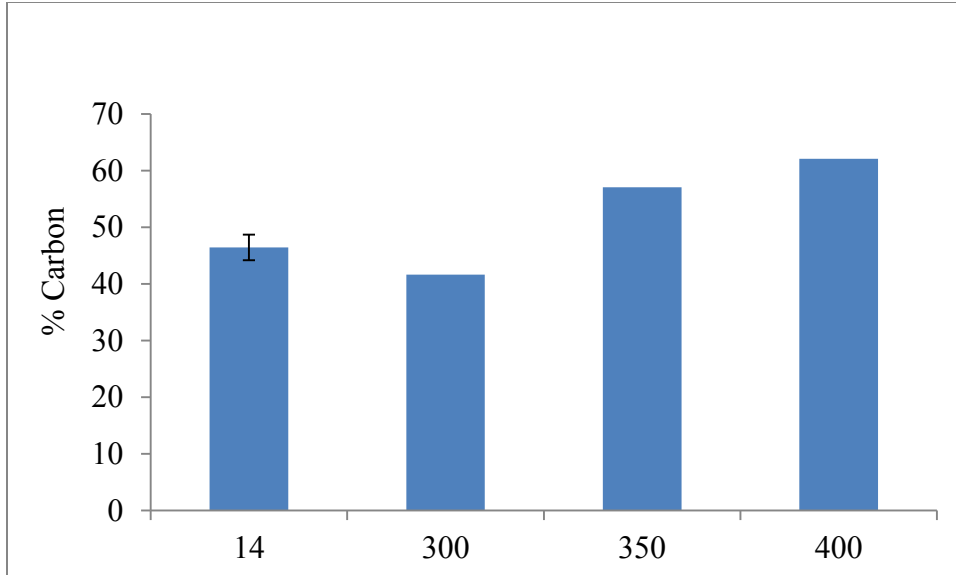


Figure 3.5 Fixed carbon concentration of 14 year-old wildfire origin charcoal and charcoal produced at 300-400 °C. Error bars for 14 year-old charcoal are ± 1 SE.

Fixed carbon amounts for 14 year old wildfire charcoal and laboratory produced (Figure 3.5) also suggest a formation temperature of 300 to 350 °C (Figure 3.4). Charcoal produced at 300 °C had somewhat lower fixed carbon content than wildfire charcoal, whereas charcoal produced at temperatures greater than 350 °C had much higher levels of fixed carbon.

3.4 Discussion

3.4.1 Charcoal carbon stocks

Charcoal stocks in this study ranged between 2.30 and 5.20 $\text{Mg}\cdot\text{ha}^{-1}$ with an average of 4.09 $\text{Mg}\cdot\text{ha}^{-1}$ within the top 10 cm of the mineral horizon. These quantities are considerably higher than those reported for many other boreal studies (Table 3.2). In this study, even the lowest recorded charcoal stocks were greater than the highest values from most studies conducted in Scandinavian boreal forests, suggesting, on average, greater charcoal stocks in North American boreal forests.

Greater charcoal stocks in North American boreal forests are likely the result of differing disturbance regimes. North American boreal forests are dominated by intense stand replacing crown fires (Johnson 1992), whereas Eurasian boreal forests are dominated by non-stand replacing ground fires. In a range of fire intensities in Scandinavia, Rosengren (2000) reported a range of charcoal stocks of 0.85 to 5.40 Mg·ha⁻¹, with the largest values from more productive stands subject to more intense fires, and lower quantities associated with lower volume stands subject to moderate and low intensity ground fires. Similar results have been reported in grassland ecosystems, where wetter sites with greater amounts of biomass have more intense fires, resulting in greater levels of soil charcoal than on dryer sites, with much lower biomass levels (Glaser & Amelung 2003). In general, charcoal quantities appear to be related to fire intensity, since more intense fires consume more biomass, producing greater amounts of charcoal (Ito 2005).

In the only attempt to date, Ohlson *et al.* (2009) used their findings from Scandinavian forests (average of 0.77 Mg C·ha⁻¹ with a range of 0-2.22 Mg C·ha⁻¹) to extrapolate a global boreal charcoal estimate of 1Pg of C. As overall charcoal stocks reported in this study are much greater than those used by Ohlson *et al.* (2009), estimates of global boreal charcoal carbon stocks may need to be revised upwards to account for larger charcoal quantities in boreal regions prone to more intense, stand replacing, wildfires. Charcoal levels recorded in this study represent between 2.7 and 3.1% of soil carbon and 2.5 and 5.6% of living biomass carbon (Paré & Bergeron 1995; Smith *et al.* 2000) and are comparable to those of other fire prone ecosystems where charcoal is considered to play an important role in carbon storage and ecosystem processes (Table 3.2) (Lehmann *et al.* 2003; DeLuca *et al.* 2006; Lehmann *et al.* 2008; Liang *et al.* 2010).

Table 3.3 Charcoal stocks from different fire prone ecosystems. Numbers in bold denote calculated stocks using a carbon density of 53% (Ohlson *et al.* 2009).

Ecosystem	Region	Charcoal from fire (Mg·C·ha ⁻¹)	Charcoal from fire (Mg·ha ⁻¹)	Reference
Boreal	North America	2.19 (1.11-2.80)	4.09 (2.30-5.20)	This study
Boreal	North America	0.58	1.10	Lynch <i>et al.</i> 2004
Boreal	Scandinavia	0.77 (0 – 2.22)	1.45 4.19	Ohlson <i>et al.</i> 2009
Boreal	Siberia	≤0.72	≤ 1.36	Czimczik <i>et al.</i> 2005
Boreal	Scandinavia	0.13	0.24	Ohlson & Tryterud 2000
Boreal	Scandinavia	1.32	2.49	Rosengren 2000
Boreal		0.45-2.86	(0.85-5.40)	
Boreal	North America	1.70-3.40	3.21-6.42	Kane <i>et al.</i> 2010
Boreal	Scandinavia	0.52-1.10	0.98-2.07	Zackrisson <i>et al.</i> 1996
Tropical savannah	-	0.28	-	Kuhlbusch 1996
Tropical slash and burn	-	2.57	-	Rumpel <i>et al.</i> 2006
Tropical slash and burn	-	4.30	-	Fearnside <i>et al.</i> 2001
Tropical slash and burn	-	3.50	-	Fearnside <i>et al.</i> 1993
Temperate savannah	-	1.0-15.0	-	Glaser & Amelung 2003

Wildfire charcoal carbon concentration reported here ($52\% \pm 1.49\text{SE}$) is similar to that reported by Ohlson *et al.* (2009). However, carbon concentration of laboratory charcoal was considerably higher than that of 14 year-old wildfire charcoal. Carbon concentration for 14 year-old charcoal was $56\% \pm 2.27\text{SE}$, whereas carbon concentration of newly produced charcoal is typically about 80% (Boateng 2007; Lehmann 2007; Ohlson *et al.* 2009). This study also found similar levels in laboratory produced charcoal as values reported for fresh wildfire charcoal. Fixed carbon content of 14-year old wildfire charcoal, however, was very similar to laboratory produced charcoal (Figure 3.5), suggesting that a portion of carbon in freshly produced charcoal is quite labile and can be oxidized fairly rapidly. A number of studies report initially high respiration rates in soils amended with charcoal to be the result of short lived breakdown of labile carbon compounds in charcoal (Smith *et al.* 2010; Jones *et al.* 2011).

Most studies assume charcoal carbon contents of 70-80% when inferring landscape level charcoal carbon stocks (Lynch *et al.* 2004; DeLuca & Aplet 2008). While these values are reflective of freshly produced charcoal, they are not representative of charcoal stocks more than a few years old. Based on this study, as well as Ohlson *et al.* (2009), charcoal carbon contents of 50-60% are much more likely to reflect actual charcoal carbon stocks. When accounting for long term charcoal carbon stocks, fixed carbon content may better represent long term carbon stocks of freshly produced charcoal than initial carbon content. As a result, carbon content values of 50-60% are likely to be better estimates of long term carbon concentration of soil charcoal.

3.4.2 Change in charcoal and carbon over time

Modelling decay rates of charcoal is important to ensure changes in carbon stocks over time can be properly accounted for. Regression models explained only 22% of variation in charcoal stocks

over time, 32% of variation in charcoal carbon content, and 25% of the variation of charcoal carbon. Relatively weak model performances are likely the result of variation between sites due to stand specific factors such as fire intensity and pre-wildfire stand volume, as well as variation in charcoal properties due to the wide range of fuels consumed in wildfires. Gavin *et al.* (2003) reported only a weak relationship between charcoal abundance and time since fire. Variation in boreal charcoal stocks has been attributed to landscape position, area burned, fire intensity, organic layer depth and soil bulk density (Rosengren 2000; Ohlson *et al.* 2009, Kane *et al.* 2010). In the short term (a few centuries), local stand level effects likely exert a greater influence over charcoal stocks than does decay.

Zackrisson *et al.* (1996) found no significant decline in charcoal levels over a 350 year post-fire chronosequence, while also recording large variability in charcoal stocks between sites. In this study, charcoal levels seemed to decline after 140 years. However, given the likely stability of charcoal in boreal soils and the natural variation in charcoal stocks, much longer chronosequences, likely >500 or even >1000 years, may be required to project decay rates of charcoal accurately in boreal soils. Nevertheless, more than 200 years after wildfire, 1.1 Mg C·ha⁻¹ remained in charcoal form, roughly 1.4-1.6% of soil organic carbon and between 1.3 and 2.8% of living biomass (Paré & Bergeron 1995; Smith *et al.* 2000), representing a significant carbon stock more stable than surrounding soil organic matter.

Increase in H:C ratios and declines in C:N ratios are consistent with the preferential loss of carbon in charcoal. Carbon content of fresh charcoal is much greater than that of surrounding organic matter and is likely to be mineralized preferentially until in relative equilibrium with surrounding organic matter. This process appears to be relatively short lived, as the C:N ratio appeared to have stabilized after only 30 years following wildfire, despite a decrease of 50% in

the first 30 years. It is also likely that much of the nitrogen in the charcoal is held in refractory compounds, such as pyridine-like structures, and not readily mineralized (Bagreev *et al.* 2001; Chan and Xu 2009). The relative stability of the C:N ratios after 30 years suggests that decomposition rates of charcoal are likely to slow over time as easily mineralized charcoal is lost and primarily refractory aryl carbon remains (Krull *et al.* 2006; Nguyen *et al.* 2008).

3.4.3 Wildfire charcoal NMR

Changes in NMR ^{13}C CP carbon groups reveal an overall trend of reduced complexity over time. Increased proportions of aryl carbon are expected as more labile alkyl, O-alkyl and methoxyl groups are mineralized, as they can be used as microbial substrate directly. Czimzik *et al.* (2003) found similar NMR results in freshly produced charcoal from Siberian boreal forests, with predominantly aryl C structure and moderate amounts of alkyl and O-alkyl carbon. Carboxyl signals were very weak in the wildfire charcoal. Czimzik *et al.* (2003) also reported weak carboxyl signals. Studies from other ecosystems have found moderate carboxyl/carbonyl content of charcoal (Fernandes *et al.* 2003), suggesting that fuel type and fire intensities may influence charcoal properties in other fire prone ecosystems.

Loss of more active labile charcoal groups over the first 100 years may explain observed reductions in the ability of charcoal to adsorb phenolic compounds after about 100 years. Zackrisson *et al.* (1996) found phenolic adsorption declined significantly after 100 years following fire for charcoal collected from Scandinavian boreal forests. Loss of more reactive, oxygen containing groups may reduce adsorptive capacity.

This study is the first to compare boreal charcoal of different ages using NMR. The results demonstrate that changes in charcoal carbon groups take place over time. While most carbon in

charcoal is highly recalcitrant, portions are more labile, with important changes occurring in the first few hundred years. As a result, not all charcoal is entirely passive. Charcoal is made up of a number of different components, some of which can undergo significant changes over time and are vulnerable to decay. Remaining charcoal is likely very stable since it is almost entirely aryl carbon, which is not readily accessible to microbial decay (Nguyen *et al.* 2008).

3.4.4 Comparison of wildfire and lab charcoal

The youngest wildfire charcoal available was from a 14 year-old fire, which is considerably older than the laboratory produced charcoal. Nevertheless, wildfire charcoal had very similar NMR ^{13}C CP spectra to charcoal produced between 300 and 350 °C. All charcoals had predominantly aryl and O-aryl structures, but also moderate amounts of Alkyl, O-alkyl, and methoxyl C structures, as well as similar levels of fixed carbon. As a result, it appears that laboratory charcoal produced between 300 and 350 °C can reproduce many of the properties of young wildfire charcoal. Our results are similar to those reported by Czimzik *et al.* (2003), who found fresh wildfire charcoal from Siberia to have large amounts of aryl C but also moderate amounts of O-alkyl and alkyl carbon.

In temperate and tropical ecosystems, however, charcoal may be formed at higher temperatures. Fernandes *et al.* (2003) found synthetic charcoal produced at 450 °C to be most similar to wildfire charcoals from Australia. Charcoals were almost entirely aryl C, as would be expected given the higher pyrolysis temperatures. It appears that boreal charcoal may be produced at somewhat lower temperatures than charcoal in other ecosystems. Interestingly, formation temperature of boreal charcoal appears to be much lower than actual fire temperature. Although highly variable, boreal stand replacing fires reach temperatures of roughly 800 °C with peaks recorded as high as 1330 °C (Butler *et al.* 2004).

Greater amounts of more labile carbon groups found in young boreal charcoal samples, compared to charcoal from other ecosystems may help to account for some of the perceived lower stability of boreal charcoal. Initial rapid reduction in C:N ratios and carbon content suggest that a portion of boreal charcoal is relatively labile. Charcoal produced at higher temperatures undergoes much greater condensation making it more resistant to decay (Boateng 2007).

This study is amongst the first to compare boreal wildfire and laboratory charcoal using ^{13}C NMR. As such, results should be seen as an initial attempt at understanding production of charcoal to emulate boreal wildfire charcoal. Nevertheless, boreal charcoal properties can be replicated, at least in part, in laboratory conditions, making possible management of a critical driver of ecosystem function.

3.4.5 Management implications

In fire prone ecosystems, charcoal has a significant impact on ecosystem function and carbon balance (Zackrisson *et al.* 1996; Wardle *et al.* 1998; Liang *et al.* 2006; DeLuca and Aplet 2008), recently this has led to advocacy for charcoal management where fires are suppressed (DeLuca & Aplet 2008). Berglund *et al.* (2004) reported increased nitrification rates in boreal soils following additions of $2 \text{ Mg}\cdot\text{ha}^{-1}$ of charcoal, while a number of studies have found decreased effects of allelopathy when charcoal has been added to soils in Scandinavia (Nilsson & Zackrisson 1992; Nilsson *et al.* 1993; Zackrisson *et al.* 1996). For example, Nilsson and Zackrisson (1992) reported reduced allelopathic effects of *Empetrum hermaphroditum* on seed germination and establishment of scots pine with additions of $5 \text{ Mg}\cdot\text{ha}^{-1}$ of charcoal, while Wardle *et al.* (1998) found increased growth rates of birch over scots pine following charcoal additions of $2 \text{ Mg}\cdot\text{ha}^{-1}$. Rates of charcoal additions reported in these studies are equal to or less than those reported in this study, suggesting that charcoal levels in North American boreal forest

soils are sufficient to have pronounced effects on soil function and productivity, as well as influence community composition.

Managing charcoal stocks may also help to buffer decreases in soil carbon levels due to climate change. Lehmann *et al.* (2008) found soil carbon models overestimated the response to global warming by 15% when black carbon was not included. With increased climate change boreal forests are expected to become net carbon sources, as decomposition rates of labile carbon increase due to warmer temperatures (Goulden *et al.* 1998). By maintaining a recalcitrant carbon stock, some soil carbon may be less vulnerable to increased decomposition with increased soil warming.

In the absence of fire, charcoal additions to soils may be required in order to maintain active charcoal stocks necessary for stand productivity and ecosystem function (Wardle *et al.* 1998; Wardle *et al.* 2004; DeLuca & Aplet 2008). Charcoal produced at 300-350 °C appears most likely to replicate boreal charcoal properties providing both active and recalcitrant black carbon components. Incorporation of charcoal into boreal forest management will help to emulate natural disturbance dynamics while increasing the sustainability of resource extraction and soil carbon stocks.

3.5 Conclusions

Charcoal stocks in North American boreal forests were found to be much greater than those reported in other boreal studies, most of which are from Scandinavia. As a result, estimates of global boreal charcoal carbon stocks may need to be revised upwards to account for larger charcoal quantities in boreal regions prone to stand replacing wildfires. Boreal charcoal stocks undergo important changes over time resulting in a loss of complexity and likely a reduction in

reactivity with surrounding soils, but nevertheless represent a refractory carbon stock equivalent to 3-5% of soil organic carbon. Significantly, laboratory produced charcoal can replicate many properties of wildfire charcoal. Most importantly, charcoal stocks quantified in this study are equal to or in excess of quantities identified in other ecosystems where charcoal has been found to have a significant impact on ecosystem processes including soil development, productivity, and carbon storage.

This study is the first to compare changes in boreal charcoal carbon structures over time as well as the first to compare boreal wildfire charcoal chemical structure to that produced in a laboratory. Future research needs include fuel characterization, the response of charcoal to soil warming, longer chronosequence studies, and broader landscape quantification of charcoal in North American boreal forests in order to properly account for differences in fire frequency and intensity across the boreal landscape. Inclusion of charcoal stocks into boreal carbon models is imperative for accurate carbon accounting. Incorporating charcoal into forest management may be an important tool in addressing natural disturbance emulation and maintaining ecosystem function and carbon balance, particularly in light of climate change and resource extraction.

4 Influence of charcoal on boreal soil carbon balance: does charcoal prime the decomposition of soil organic matter?

4.1 Introduction

Wildfire is the predominant natural disturbance in boreal forests influencing stand succession, and carbon and nutrient cycling (Brais *et al.* 2000; Weir *et al.* 2000; Bergeron *et al.* 2001; Stocks *et al.* 2003). Wildfires result in the formation of significant quantities of charcoal, converting 0.7-2% of biomass to charcoal (Zackrisson *et al.* 1996; Lynch *et al.* 2004; Ohlson *et al.* 2009). Charcoal is increasingly recognized as an important driver of boreal soil function by stimulating microbial activity and nitrogen mineralization and decreasing phenolic concentrations (Zackrisson *et al.* 1996; Wardle *et al.* 1998; Pietikäinen *et al.* 2000). High productivity in post-fire stands has been attributed in part to the presence of active, newly produced charcoal that helps to reverse long term declines in productivity with increasing time since fire (DeLuca *et al.* 2002; Wardle *et al.* 2004).

Increased interest in biofuels has increased the risk of excessive nutrient removals from boreal forests (Thiffault *et al.* 2010). At the same time, fire suppression and forest fragmentation in managed boreal forests has decreased fire frequency (Weir *et al.* 2000; Bergeron *et al.* 2004; Lefort *et al.* 2004; Senici *et al.* 2010) leading to declining productivity in many forest stands, and preventing the renewal of active charcoal stocks (Wardle *et al.* 1998; DeLuca *et al.* 2002). Charcoal is primarily composed of aromatic carbon, with a high C:N ratio, and as a result it is highly resistant to mineralization, with mean residence times of thousands of years, representing a recalcitrant carbon pool (Kuhlbusch & Crutzen 1995; Lehmann *et al.* 2008). Because of this charcoal production and sequestration in soils has been promoted as a carbon negative biofuel

(Read & Lermitt 2005; Lehmann 2007), while also increasing soil sustainability, stand productivity, and emulation of natural ecosystem processes through addition of active charcoal. According to Woolf *et al.* (2010), global emission of greenhouse gases could be reduced by up to 12% if charcoal from pyrolysis were sequestered in soils.

In contrast, Wardle *et al.* (2008) suggested that by increasing soil microbial activity, charcoal additions to boreal soils may increase mineralization of soil organic matter, potentially releasing large amounts of CO₂, and offsetting soil carbon additions from charcoal. In a 10-year litter bag study, Wardle *et al.* (2008) reported that freshly produced charcoal stimulated the decomposition of humus. These effects, however, appeared to be relatively short lived, with humus loss occurring in the first two years of the study with very little differences in later years. While charcoal has primarily a carbon dense, recalcitrant structure, a small ash fraction is also present (Glaser *et al.* 2002; Deenik *et al.* 2008). Ash contains soluble macro- and micronutrients, which increase pH and the availability of base cations such as Ca, K, and Mg (Thiffault *et al.* 2008). Increased nutrient availability, as well as reduced acidity, may prime the decomposition of soil organic matter by stimulating microbial activity (Hamer *et al.* 2004). Lehmann and Sohi (2008) suggested that the humus loss found by Wardle *et al.* (2008) might have happened in part due to short lived labile-carbon and soluble mineral fractions present in charcoal that may prime the decomposition of neighbouring organic matter as well as contribute to mass loss themselves. Laboratory experiments have found glucose additions to cause some substrate induced priming of organic matter decomposition, as well as that of charcoal (Hamer *et al.* 2004; Blagodatskaya & Kuzyakov 2008). Freshly produced charcoal has also been found to undergo some short term initial mass loss as labile compounds are mineralized, with observed effects declining quickly

over time (Jones *et al.* 2011). For example, Jones *et al.* (2011) reported a 50% reduction in CO₂ evolution from soils where charcoal had been washed of soluble components prior to addition.

Charcoal may actually inhibit organic matter decomposition by promoting soil aggregate formation and regulating nutrient availability (Brodowski *et al.* 2006). High internal pore spaces in charcoal, combined with a large number of negatively charged surface sites provide protected locations for hydrophobic organic matter, inhibiting exposure to oxygen and fungal enzymes (Baldock & Skjemstad 2000; Liang *et al.* 2008; Liang *et al.* 2010). Amazonian anthrosols amended with charcoal have been shown to have higher levels of organic matter, suggesting a positive interaction between charcoal and SOM (Steiner *et al.* 2007). This has been supported by studies reporting negative priming of SOM by charcoal (Liang *et al.* 2010; Kimetu & Lehmann 2010), with any increase in respiration attributed to short term mineralization of labile charcoal fractions (Liang *et al.* 2010; Zimmerman *et al.* 2011).

Understanding the interaction between charcoal and soil carbon dynamics is imperative in order to maximize the benefits of soil charcoal additions while avoiding the destabilization of soil carbon stocks. The objectives of this study were to test whether laboratory produced charcoal additions increase boreal soil respiration. It was hypothesized that soluble components of charcoal would increase soil respiration and that any increase in soil respiration from charcoal additions would be short lived. By separating charcoal components, it is hoped that a clearer understanding of short and longer term effects of charcoal additions on boreal soil carbon stocks will be gained.

4.2 Methods

4.2.1 Charcoal samples

Charcoal was produced in a laboratory from *Larix laricina* (Du Roi) K. Koch (tamarack) wood chips packed in 500 cm³ metal canisters and heated at a rate of 10 °C/min in a muffle furnace to a maximum temperature of 550 °C and held for one hour. This temperature was chosen based on other studies of charcoal production from woody biomass between 500-600 °C (Brown *et al.* 2006; Singh *et al.* 2010; van Zwieten *et al.* 2010). Volatile carbon, fixed carbon (the thermally stable, non-volatile carbon fraction, content of charcoal) and ash content were determined using a LECO TGA (LECO Corp., St Joseph, MI). Carbon, hydrogen and nitrogen content were determined using a CHNS Elementar vario EL (Elementar Analysensysteme GmbH, Hanau, Germany). Cation exchange capacity was determined using ammonium acetate at pH 7.0 (Hendershot *et al.* 2008a). A 2 to 1 slurry of double deionized water to charcoal was used to determine pH using a Corning pH meter (Acton, MA) (Hendershot *et al.* 2008b).

Solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy was used to characterise the basic chemical structures of the laboratory produced charcoal. Samples were sent to the University of Manitoba Chemistry NMR lab for analyses. Spectra were done using cross polarization (CP) using a Bruker Advance 400 spectrometer operated at a ¹³C frequency of 128.8 MHz for all analyses. 7-9 mg of charcoal was packed into a 2.5 mm diameter cylindrical rotor and spun at 5000 Hz in a Doty Scientific magic angle spinning (MAS) probe with a contact time of 3 ms, and an acquisition time of 20.48 ms. Free induction decay was acquired using a sweep width of 50 kHz. Line broadening for FID processing was done at 200 Hz.

4.2.2 Charcoal leaching

To isolate short term soluble components of charcoal from more long-lived effects of non-soluble, recalcitrant components, half the charcoal was leached of soluble components. Leached

charcoal was produced by passing distilled water through ground charcoal at a 30:1 ratio of distilled water to charcoal. To determine adequate leaching rates, a ground and sieved charcoal sample was progressively leached in batches of 3:1 distilled water to charcoal until the concentration of cations in the leachate stabilized (Figure 4.1). Leachate from the treatment was collected and homogenized, and used for the soluble nutrient treatment in place of distilled water. Nutrient content of the leachate was determined by ICP-AES using a Varian Vista Pro CCD Simultaneous ICP-OES (Varian Inc., Palo Alto, CA), while pH was determined using a Corning pH meter (Acton, MA) (Hendershot *et al.* 2008b).

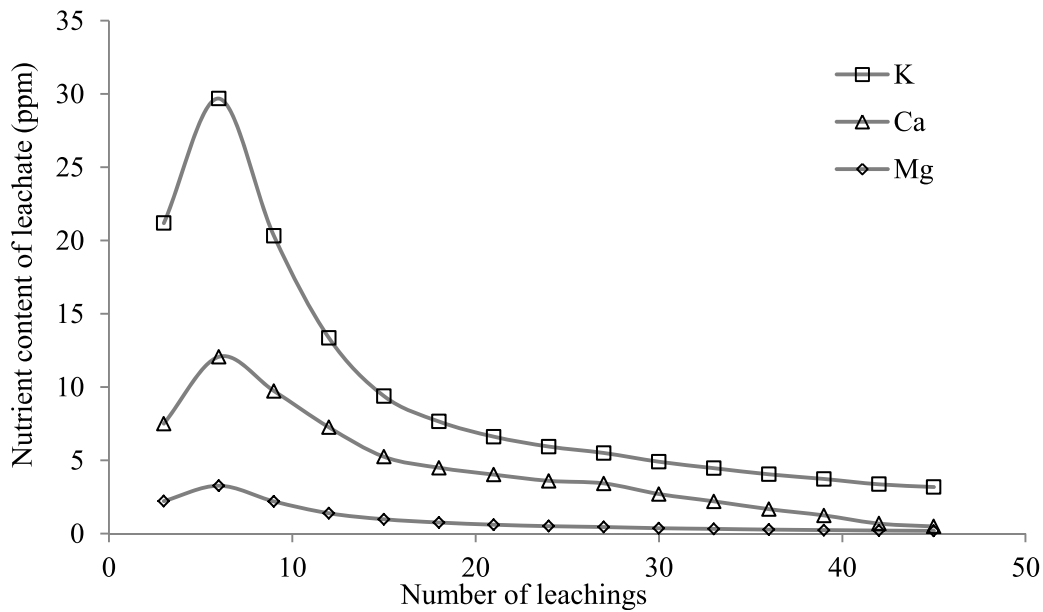


Figure 4.1 Nutrient content of leachate with successive leaching of ground charcoal with distilled water.

4.2.3 Soil incubations and carbon dioxide measurements

Soil respiration in response to charcoal applications was tested using soil microcosms. Mineral soil was collected from a *Pinus resinosa* plantation (48°21'20N, 89°23'25W) from a depth of 0-15 cm. The soil was a sandy regosol of ~98% sand and ~2% silt content, determined using the hydrometer method (Kroetsch & Wang 2008), and very low organic matter content (0.82%),

determined using loss on ignition. Soil was dried and sieved to 2 mm and homogenized to ensure uniform conditions. Forty-eight PVC tubes (10 cm diameter x 30 cm tall) were used for soil incubation. Columns were sealed at the base using nylon mesh fabric and fiberglass filters. Columns were attached to funnels at their base, which were supported by wooden frames. Columns were packed to a depth of 20 cm with soil mixtures containing leached and unleached laboratory created charcoal contents of 0, 1, 10, 100 Mg·ha⁻¹ equivalents (0, 0.81, 8.1, 81 g/column, respectively). Treatment rates were chosen to reflect potential applications rates. Boreal wildfire charcoal stocks typically range from 1-10 Mg·ha⁻¹ (Rosengren 2000; Lynch *et al.* 2004; Ohlson *et al.* 2009; Hart & Luckai 2013), while studies of charcoal applications to soils typically use treatments between 10-100 Mg·ha⁻¹ (Chan *et al.* 2007; Van Zwieten *et al.* 2010), with 100 Mg·ha⁻¹ representing the extreme high end of any potential treatment. Commercially obtained peat was used as a surrogate for soil organic matter and was added at a rate of 10 Mg·ha⁻¹ (8.1 g/column) to half the columns. All treatments were replicated in triplicate. To ensure uniform conditions, all treatments were homogenized in batches prior to packing in columns.

Columns were held at approximately 25 °C for the 10 week duration of the study. Columns were watered weekly with 200 ml of distilled water, with the exception of six tubes, three each of control and control with peat, which were watered with leachate. Soil respiration was measured weekly, prior to watering, using a Li-Cor 6400XT (LICOR Biosciences, Lincoln, NE).

Starting soil pH and electrical conductivity was determined by 2 to 1 slurry of distilled deionized water to soil using a Corning pH meter (Acton, MA) (Hendershot *et al.* 2008b). Soil nutrient content was determined by Mehlich 3-extractable elements (Ziadi & Tran 2008). Nitrate and exchangeable ammonium was measured using a 10:1 2.0M KCl solution to soil extraction

(Maynard *et al.* 2008) on a Technicon Autoanalyzer (SEAL Analytical, ltd.). Cation exchange capacity of soils was measured ammonium acetate extraction at pH 7.0 (Hendershot *et al.* 2008b).

4.2.4 Statistical analyses

Starting soil pH, nutrient content, cation exchange capacity and electrical conductivity were examined with using a general linear model (GLM). Two models were created for each dependent variable: 1) fixed effects of charcoal and peat and their 2-way interaction, and 2) fixed effects of leached charcoal and peat and their 2-way interaction. Pairwise comparisons between control and treatment levels were made with independent samples T-tests. Bonferroni corrections were used to adjust the significance level (α).

Repeated measures data were analysed using a general linear mixed model (MIXED, IBM SPSS Statistics 20). Compared to conventional repeated measures analysis methods (e.g. univariate or multivariate General Linear Modelling (GLM)), MIXED is a more robust and flexible procedure (Cnaan *et al.* 1997; SAS Institute, Inc.1999; Littell *et al.* 1998). For the current dataset MIXED had a number of advantages compared to GLM. MIXED uses generalized least squares to test fixed effects resulting in more powerful tests; assumptions of sphericity and compound symmetry can be relaxed and more appropriate covariance patterns can be adjusted. Akaike's Information Criterion was used to select covariance structure (Burnham and Anderson 1998). MIXED is also better at handling missing data. In GLM the deletion is done listwise, deleting a subject with a missing time point from the analysis, whereas in MIXED only the missing time point is dropped. Time can also be treated as a continuous variable making it possible to model regression for time points (as opposed to comparing means in GLM).

Three models were used to test changes in soil respiration rate compared to control soils: 1) fixed effects of charcoal, peat, time and their 2- and 3-way interactions; 2) fixed effects of leached charcoal, peat and time and their 2- and 3-way interactions, and 3) fixed effects of leachate, peat and time and their 2- and 3-way interactions. Measurement time was treated as a continuous variable and included to the fixed effects as a covariate. Different models with and without random effects intercept and/or slope and with different covariance structures were tested. The best fit was achieved by including random effect intercept and slope and by using heterogeneous first order autoregressive covariance structure.

To compare single treatments with control soils, or with each other, mixed model with time as covariate and treatment as fixed effect was created. Comparisons of treatment pairs including time effect were made using TEST subcommand.

4.3 Results

4.3.1 Charcoal and soil properties

Solid state CP ^{13}C NMR spectra of the charcoal showed high signal intensities for aryl C (129 ppm) as well as some O-Aryl C (143 ppm) (Figure 4.2). The predominantly aryl C content and small O-aryl C content are typical of a high degree of thermal alteration. Charcoal had significantly different physical and chemical properties to that of the forest soil. Electrical conductivity was a full order of magnitude greater for charcoal and peat. Study soils and peat were moderately acidic, while charcoal was relatively alkaline with a pH of 8.7 (Table 4.1).

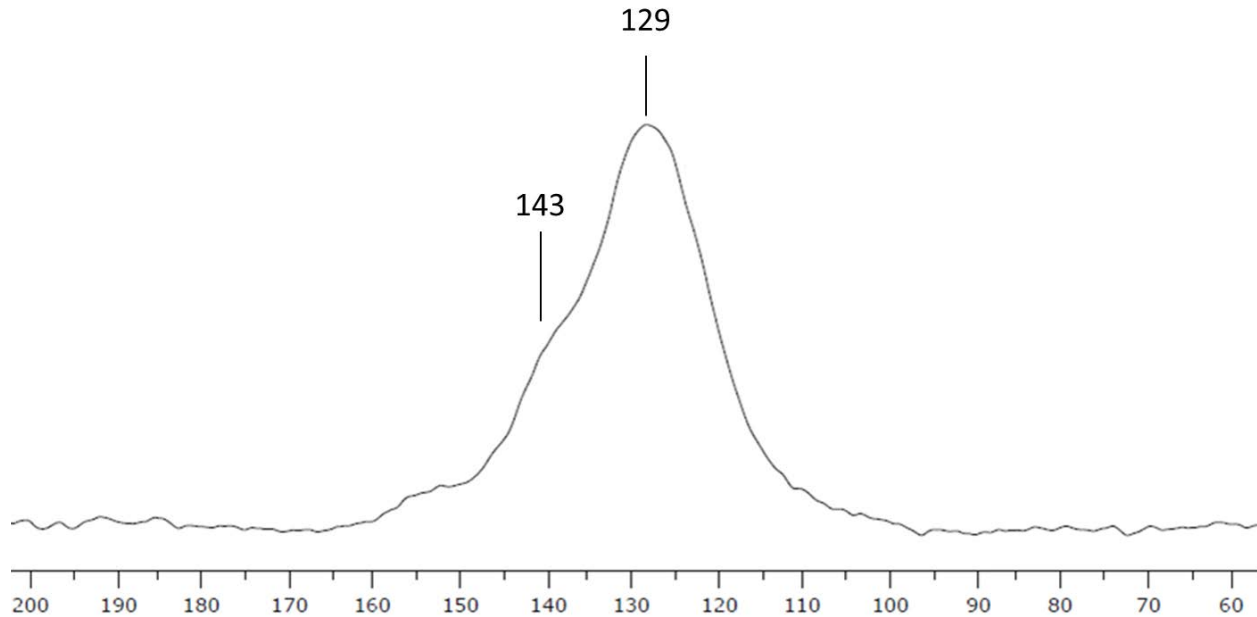


Figure 4.2 Nuclear Magnetic Resonance (NMR) spectroscopy of charcoal produced at 550 °C. Values above peaks are shift positions (PPM).

Table 4.1 Characteristics of charcoal, peat, and soil.

	Charcoal	Peat	Soil
pH (H ₂ O)	8.7	5.6	6.0
EC	142.5	163.0	14.6
Total Carbon (%)	84.8	48.5	0.8
Fixed Carbon (%)	74.3	23.6	nd
Volatile matter	24.9	74.4	nd
Ash (%)	0.88	2.0	nd
Nitrogen (%)	0.15	nd	nd

*nd = not determined

Both leached and unleached charcoal increased soil pH ($p < 0.0001$), whereas peat had an acidifying effect ($p < 0.0001$). The liming effect of charcoal was most pronounced for the highest charcoal additions ($100 \text{ Mg}\cdot\text{ha}^{-1}$), increasing pH from 6 to 6.7 and 6.5 for unleached and leached charcoal, respectively. The effect was more moderate for both $10 \text{ Mg}\cdot\text{ha}^{-1}$ treatments, increasing pH from 6 to 6.1.

Charcoal had no effect on electrical conductivity or cation exchange capacity.

Availability of Ca, K, and Zn increased with increasing additions of unleached charcoal ($p < 0.0001$ for Ca and K, and $p = 0.008$ for Zn), whereas increasing leached charcoal additions only resulted in increased availability of K and Zn ($p = 0.003$ and 0.017 , respectively). Availability of Mg decreased somewhat with increasing addition of unleached charcoal ($p = 0.002$). Availability of NH_4 and NO_3 increased for both unleached and leached charcoal additions, regardless of the quantity of charcoal added ($p < 0.0001$ and $p = 0.001$, and $p = 0.007$ and $p = 0.049$, respectively). Peat did not have an effect on nutrient availability, with the exception of Mg which increased somewhat ($p < 0.0001$). Leachate was a source of Ca and K, but was not a significant source of other nutrients (Table 4.3).

Table 4.2 Charcoal effects on soil available nutrients ($\text{mg}\cdot\text{kg}^{-1}$) and soil pH. ± 1 SE in brackets.

Treatment	pH	K	Mg	Ca	Zn	NH_4	NO_3
Control	6.01 (0.01)	51.7 (2.6)	78.6 (1.2)	401.9 (4.3)	0.45 (0.02)	14.9 (3.4)	0.3 (0.33)
C1	6.05 (0.03)	52.2 (3.6)	79.4 (6.0)	420.8 (2.8)	0.46 (0.03)	34.7 (5.1)	0.6 (0.15)
C10	6.13 (0.02)	61.2 (6.8)	80.0 (1.0)	428.3 (5.4)	0.49 (0.02)	38.3 (4.1)	1.0 (0.31)
C100	6.67 (0.02)	74.8 (4.3)	76.7 (9.0)	442.0 (6.3)	0.66 (0.04)	33.4 (2.0)	0.1 (0.20)
L1	6.03 (0.03)	58.0 (4.9)	81.0 (1.1)	428.4 (5.5)	0.50 (0.02)	32.1 (1.6)	1.2 (0.13)
L10	6.10 (0.03)	60.5 (1.8)	80.3 (1.0)	425.6 (6.1)	0.51 (0.02)	33.9 (1.7)	1.4 (0.60)
L100	6.53 (0.02)	70.0 (4.1)	77.6 (1.9)	426.3 (10.6)	0.57 (0.01)	29.9 (1.7)	1.0 (0.10)
P	5.59 (0.08)	64.8 (2.7)	85.8 (1.1)	416.3 (0.9)	0.50 (0.02)	13.1 (0.7)	0.2 (0.13)
C1+P	5.56 (0.03)	64.0 (6.1)	85.3 (8.0)	420.3 (4.1)	0.59 (0.08)	29.9 (1.0)	1.1 (0.16)
C10+P	5.71 (0.04)	50.7 (2.3)	84.9 (7.0)	428.2 (2.6)	0.51 (0.03)	30.6 (1.1)	1.0 (0.04)
C100+P	6.25 (0.02)	82.9 (1.8)	80.9 (9.0)	428.1 (1.7)	0.62 (0.06)	28.7 (1.1)	1.0 (0.09)
L1+P	5.67 (0.03)	47.9 (1.6)	83.6 (3.0)	417.5 (12.3)	0.45 (0.05)	11.2 (0.4)	0.02 (0.02)
L10+P	5.71 (0.01)	61.7 (4.6)	85.7 (2.7)	434.6 (15.3)	0.52 (0.04)	20.0 (7.0)	0.1 (0.09)
L100+P	6.09 (0.03)	65.7 (2.9)	80.8 (1.4)	426.9 (10.9)	0.56 (0.02)	26.4 (1.9)	1.1 (0.11)

Table 4.3 Nutrient content of leachate.

Nutrient	Concentration (mg·L ⁻¹) ± 1SE
Ca	1.32 ± 0.0098
K	10.57 ± 0.0176
Mg	0.16 ± 0.00058
Mn	0.01 ± 0.00012
Na	0.14 ± 0.00038
P	0.25 ± 0.0062
S	0.19 ± 0.0024
Zn	0.006 ± 0.00033

4.3.2 Effects of charcoal on soil respiration

Charcoal increased soil respiration, however, the effect was relatively short-lived and limited to the highest rate of application (Table 4.4, Figure 4.3). Although initially high, the respiration rate of the C100 treated soils decreased substantially by week five, remaining somewhat higher than other treatments for the remainder of the experiment. Soils high in organic matter (peat) did not have higher respiration rates than those with low organic matter content. For all treatments, respiration rate decreased somewhat over time.

Table 4.4 Results of three mixed models studying the main effects and interactions of a) charcoal (C), peat (P) and time; b) leached charcoal (L), peat (P) and time; and c) leachate (Leach), peat (P) and time. Time was included as a covariate.

Effects	Model I		Effects	Model II		Effects	Model III	
	F	Sig.		F	Sig.		F	Sig.
C	12.393	<.0001	L	2.085	0.119	L	169.33	<.0001
P	1.745	0.192	P	0.076	0.785	P	36.469	<.0001
C x P	0.058	0.981	L x P	2.005	0.131	L x P	11.28	0.005
Time	143.532	<.0001	Time	14.805	0.001	Time	163.67	<.0001
C x Time	5.735	0.002	L x Time	1.942	0.154	L x Time	57.603	<.0001
P x Time	0.848	0.362	P x Time	0.292	0.595	P x Time	5.392	0.04
C x P x Time	0.433	0.73	L x P x Time	0.922	0.447	L x P x Time	2.025	0.182

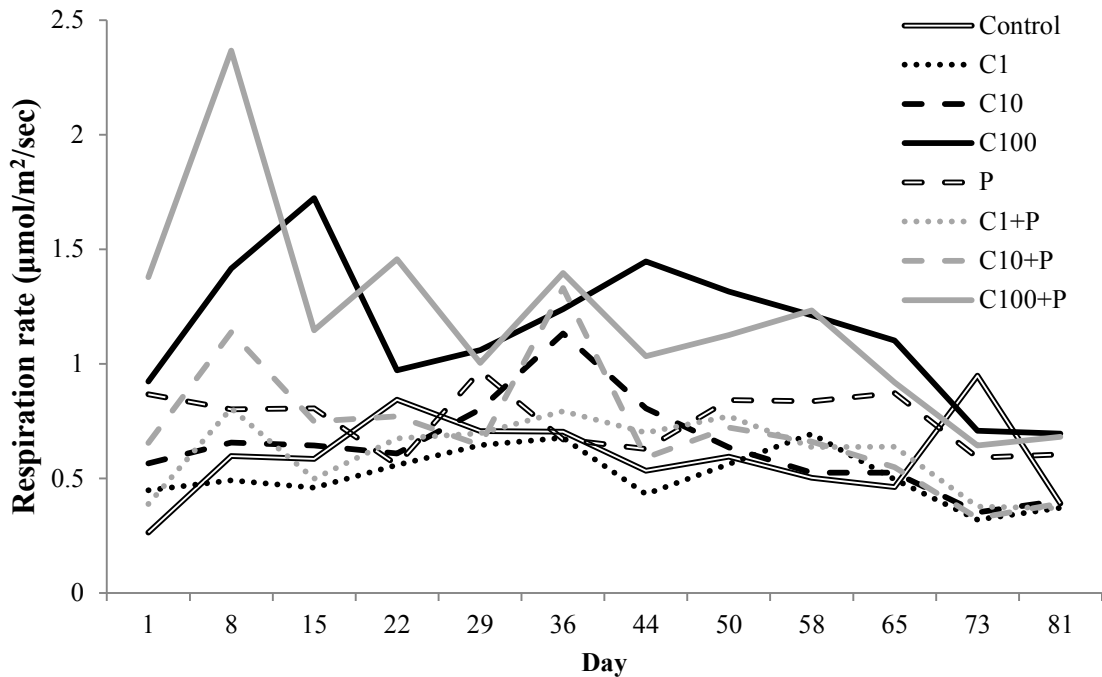


Figure 4.3 Respiration rates for soil columns containing organic matter (P) and/or treated with unleached charcoal (C) in amounts equivalent to 1, 10 and 100 $\text{Mg}\cdot\text{ha}^{-1}$.

Respiration of soils treated with leached charcoal did not have greater respiration rates than control soils (Table 4). Similarly to unleached charcoal, there was no interaction with organic matter treatments, with respiration decreasing somewhat over time for all treatments. Respiration rates were highest in soils with high organic matter content (peat) receiving leachate treatment compared to soils receiving only distilled water both with and without peat treatments (Table 4.4, Figure 4.4). Respiration rates were approximately 3.6 times greater for leachate treated soils containing organic matter compared to control soils, 2.9 times greater than peat only treated soils, and 1.6 times greater than leachate only treated soils. Time also had a significant effect on respiration, with respiration rates decreasing somewhat over the course of the experiment for soils treated with leachate and peat.

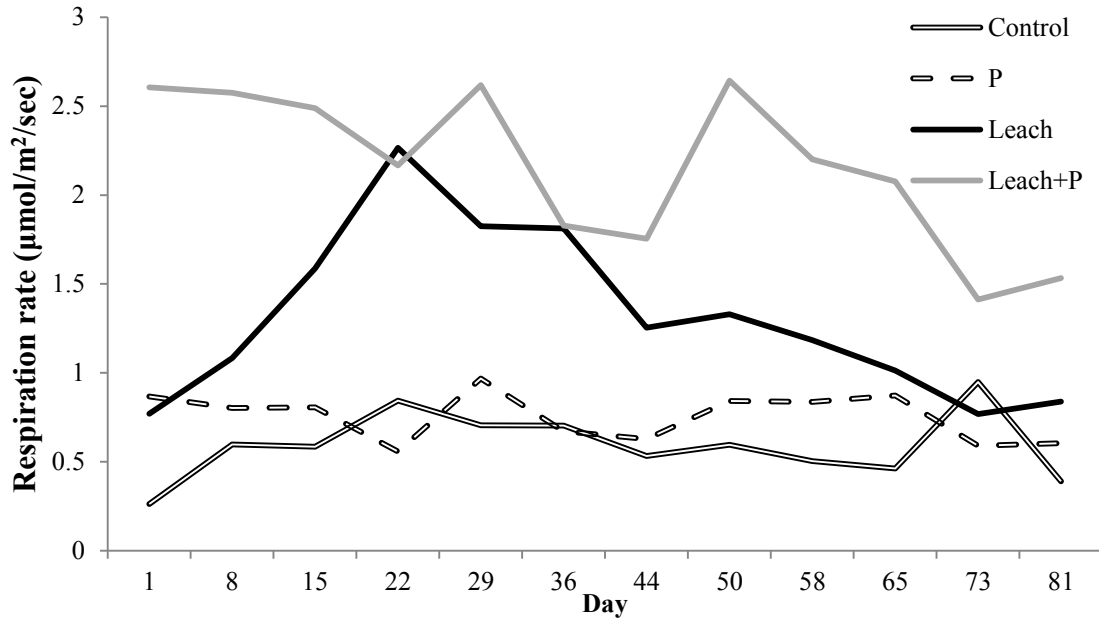


Figure 4.4 Respiration rates for soils treated with organic matter (P) and leachate (Leach).

4.4 Discussion

4.4.1 Charcoal and soil properties

The high Aryl carbon content of the charcoal is typical of most charcoals especially those produced at temperatures above 400 °C (Baldock & Smernik 2002; Novak *et al.* 2009a). The high aryl C content as well as very high fixed carbon content, suggest the charcoal is highly resistant to decay. High carbon density of the charcoal produced in this study (84.9%) is comparable to most freshly produced charcoals. Luo *et al.* (2011) reported 83.9% for charcoal produced at 700 °C, while Taghizadeh-Toodi *et al.* (2012) reported 82.6% C in charcoal produced at 500 °C from *Pinus radiata* wood. The carbon content also compares well with freshly produced boreal charcoal with Ohlsson *et al.* (2009) reporting a carbon content of ~80% from charcoal produced from an open fire of a mixture of Scandinavian boreal tress species.

Ash and nitrogen (N) content of charcoal in this study, however, was much lower than that in many other studies. This is likely the result of precursor material. Wood is a carbon dense material with low ash and nitrogen content, compared to other forms of vegetation. Studies using less carbon dense material such as agricultural by-products report ash contents of 5-9%, and nitrogen contents of 0.5-2.7 % (Novak *et al.* 2009a). The ash and nitrogen content, however is very typical of woody biomass, with charcoal derived from *Pinus resinosa* reported to be 0.8% ash and 0.25% N (Baldock & Smernik 2002). As a result, the charcoal used in this study can be considered to have low ash content and likely supplied fewer nutrients than charcoal derived from more nutrient rich precursor materials.

Addition of unleached charcoal had important effects on soil properties increasing pH and availability of Ca, K, and Mg in accordance with added charcoal quantity. The changes in pH and nutrient availability are consistent with properties that might be expected to facilitate microbial activity and possibly prime the decomposition of OM. Additions of leached charcoal increased pH somewhat less than unleached charcoal, as expected after the removal of base cations through leaching.

Leaching charcoal had the desired effect of reducing the soluble nutrient contribution of charcoal. No increase in availability of Ca occurred after additions of leached charcoal. Although availability of K and Zn were increased by increasing additions of leached charcoal, the effect was much lower than for additions of unleached charcoal. The small decrease in availability of Mg may be the result of adsorption by leached charcoal. As expected, the leachate contained important quantities of soluble nutrients consistent with those found in the unleached charcoal (Ca, K, and Mg). Only Zn was not found in meaningful quantities in the leachate. This is likely the result of a high affinity for charcoal, inhibiting leaching with distilled water.

As discussed above, charcoal nitrogen content was extremely low. Hence, the increased availability of NH_4 and NO_3 is not the direct result of charcoal additions. Charcoal has been found to increase availability of NH_4 and NO_3 by increasing nitrification rates and ammonia oxidizing bacteria in soils (Ball *et al.* 2010). Ammonia adsorbed to charcoal has also been found to be bioavailable (Taghizadeh-Toosi *et al.* 2012). Interestingly, the availability of NH_4 and NO_3 increased for all charcoal treatments, regardless of charcoal type or the amount added, with no significant difference between charcoal treatments. The lowest charcoal treatment in this study ($1 \text{ Mg}\cdot\text{ha}^{-1}$) is comparable to levels of wildfire derived charcoal in boreal soils which have been found to increase nitrification rates (Berglund *et al.* 2004). As a result, it appears that charcoal additions roughly comparable to those resulting from boreal wildfires are enough to increase the availability of nitrate and ammonia, with further additions offering no further benefit.

Despite the high cation exchange capacity (CEC) of the charcoal, charcoal additions did not increase cation exchange capacity of soils. This is consistent with a number of short term studies examining fresh charcoal additions to soils (Novak *et al.* 2009b). Steiner *et al.* (2007) suggested that this is due to reactions with Al and Fe, which can block exchange sites, inhibiting access to positively charged sites on the charcoal surface. Tars resulting from pyrolyzation can also block charcoal pores, preventing access to cation exchange sites (Pietkäinen *et al.* 2000). However, microbial degradation of tars has been found to increase charcoal CEC by increasing access to cation exchange sites. Singh *et al.* (2010) reported increased ability of biochar amended soils to reduce NH_4 leaching over time, attributing it to increased CEC. Amazonian anthrosols, where charcoal additions are hundreds to thousands of years old, have much higher CEC than surrounding soils, supporting the idea that CEC develops in situ over time (Liang *et al.* 2006).

4.4.2 Effects of charcoal on soil respiration

This study is the first to fully separate soluble and non-soluble components of charcoal. Jones *et al.* (2011) found a 50% reduction in respiration when charcoal was leached of soluble components. However, the leachate was not used to test the effects of soluble charcoal nutrients in the absence of charcoal.

The respiration rate was highest for the highest charcoal additions. However, the respiration rate decreased significantly over the study period. Higher respiration rates for high charcoal additions may be due to decomposition of labile charcoal components, and not due to increased decomposition of organic matter as a result of charcoal addition. For C100, the respiration rate decreased to the level of control soils by the end of the experiment. The peak increase in respiration rate of C100 in the beginning of experiment was likely caused by the decomposition of labile fractions in the charcoal, as it was not observed for leached charcoal, where soluble fractions were likely removed by leaching. Although in the case of the leached charcoal treatments, variability of respiration rates was very high. The gradual decrease in respiration found in all treatments over time may represent the absence of organic inputs during the experiment. As a result, easily mineralized substrate would be consumed leaving increasingly larger proportions of less easily mineralized substrate.

Increased respiration in leachate treated soils, as well as the positive interaction with SOM suggests soluble components of charcoal are capable of priming organic matter mineralization. However, in the presence of the black carbon fraction of charcoal, no positive interaction with SOM was found, with respiration rates of C100 and C100+P behaving roughly the same. These results suggest that charcoal can have a negative priming effect on SOM. A number of studies report moderate negative priming effects of charcoal. Particularly for charcoal

produced at higher temperatures, with lower labile fractions and ash content (Zimmerman *et al.* 2011). Negative priming is attributed to the formation of stable soil aggregates, protecting SOM from microbial attack, as well as moderation of nutrient availability by charcoal's affinity for cations. In contrast, positive priming is reported for charcoals produced at low temperatures where greater soluble components are present compared to charcoal produced at much greater temperatures, however even these effects are generally short lived (Luo *et al.* 2011). Given the short term nature of this study, it seems more likely that the moderation of a priming effect by charcoal is likely the result of moderation of nutrient availability. Over time, as soluble components of charcoal are leached out and more labile fractions mineralized, remaining recalcitrant charcoal may have a stabilizing effect on surrounding SOM.

Charcoal is a continuum of labile and refractory components (Zimmerman 2010). A number of studies report initially high respiration rates in charcoal amended soils followed by a rapid slowdown (Singh *et al.* 2010; Jones *et al.* 2011). Bruun *et al.* (2008) reported rapid mineralization of charcoal over the first 20 days, attributing it to abiotic decomposition because of the lack of a lag phase typical of biotic decomposition, followed by a rapid decline as labile components were consumed. This initial oxidation is responsible for the formation of carboxylic groups, resulting in increased CEC (Cheng *et al.* 2006) leading to a loss of carbon from charcoal. Major *et al.* (2010) reported a 2.2% loss of carbon from charcoal over a two year period while Zavalloni *et al.* (2011) found 2.8% of carbon was respired over the first 84 days from charcoal produced at 500⁰C. Ohlson *et al.* (2009) reported an average carbon content of boreal charcoal of 53% but ~80% for fresh wildfire charcoal, implying substantial loss of some carbon from charcoal over time.

The lower application rates of 1-10 Mg·ha⁻¹ in this study are very similar to levels reported for boreal wildfire charcoal stocks. Rosengren (2000) found 2.49 (0.85-5.40) Mg·ha⁻¹ while Zackrisson *et al.* (1996) report 0.98-2.07 Mg·ha⁻¹, and Kane *et al.* (2010) 3.21-6.42 Mg·ha⁻¹. No increase in respiration was observed at these applications levels, suggesting that virtually no risk of SOM priming exists for lower treatment levels. As a result, application rates typical of boreal wildfire derived stocks likely pose a minimal risk of SOM priming.

This study used charcoal produced from one species produced at one pyrolysis temperature. It is important to note that the charcoal used in this study was produced at a much higher temperature, and had a resulting higher aryl C content, than charcoal found to most closely resemble wildfire charcoal produced at 300-350 °C (Ch. 3). Charcoal properties are known to vary with pyrolysis conditions and substrate (Demirbas 2001). Porosity, affecting adsorptive ability, varies between species, especially between angiosperms and gymnosperms (Keech *et al.* 2005), while pyrolysis temperature can affect nutrient availability, with charcoal from lower pyrolysis temperatures generally having higher nutrient availability, and less aromatization (Makoto *et al.* 2010). Studies of a full range of charcoals from different substrates and pyrolysis conditions in a range of boreal soils types are needed to fully understand the effects of charcoal additions to boreal SOM. Long term *in situ* studies are particularly needed, in order to determine the long term effect on boreal soil carbon balance.

Low ash content of charcoal in this study may help explain the absence of a priming effect. Although base cation availability increased, amounts may not have been enough to prime the decomposition of organic matter. Adsorption by charcoal may have moderated the availability of nutrients, something absent in leachate treated columns. Soil pH was circumneutral and the liming effect of the charcoal may have been moderated, with pH only increasing from 6.0 to 6.7

for even the highest treatment. Sites used by Wardle *et al.* (2008), where some priming of SOM by charcoal additions was reported, were very acidic (pH 3.5-4.3 vs. 6.0 in this study), and possibly benefitted more by an liming from charcoal additions.

While charcoal was not found to prime the decomposition of SOM, charcoal does nevertheless appear to undergo short term mineralization in soils, contributing to soil respiration. This process will inevitably result in a decrease in carbon content of the charcoal over time, until labile fractions have been mineralized, after which the rate of carbon loss is likely to slow considerably. Carbon added as charcoal is likely to exceed any losses due to SOM decomposition, and result in a net increase in carbon sequestered in highly stable soil carbon stocks. However, it is nevertheless important that short term carbon losses be taken into account when assigning carbon sequestration values.

4.5 Conclusions

Charcoal does not appear to prime the decomposition of soil organic matter. Increased soil respiration is short lived and most likely the result of mineralization of labile components of the charcoal itself. Importantly, effects are only detectable at very high charcoal application rates. Application rates comparable to those found following wildfires appear to present very little risk of increased soil respiration and SOM loss. Although soluble components of charcoal can contribute to increased soil respiration, this effect appears to be mitigated somewhat by the presence of charcoal in the soil, suggesting charcoal may increase the stability of other SOM stocks by protection from microbial attack or by moderating nutrient availability. Although ephemeral, carbon accounting may require that estimates of charcoal carbon amendments be downgraded somewhat to account for initially high mineralization of charcoal following application.

5 Implications for soil carbon modelling

Models are important tools for simulating interactions in complex systems, allowing projections of future conditions, as well helping to identify important knowledge gaps in our understanding of ecosystem function. Models are especially effective in landscape and temporal projections where direct measurements are costly and impractical. Forests play an important role in global carbon cycling which occurs over large landscapes and time periods. Increasingly, modelling of forest soil carbon is recognized as an important component of effective forest management (Kurz *et al.* 2009). This is especially important in light of climate change. Historically, the boreal forest has acted as a carbon sink, continuing to sequester atmospheric carbon (Akselsson *et al.* 2005). Much of the carbon stored in boreal soils, however, is relatively labile. Mineralization of organic carbon increases with increasing temperatures (Davidson & Janssens 2006). As a result, soils high in soil organic carbon may become CO₂ sources, further contributing to climate warming in a positive feedback. Given the importance of boreal soils to global carbon balance, it is imperative that the response of soil carbon pools to increased temperatures be understood. To date, however, charcoal has not been included in most soil carbon models (DeLuca & Aplet 2008). Given its recalcitrance over other carbon pools, omissions of soil charcoal may result in an overestimation of the vulnerability of forest soil carbon to climate change.

Charcoal is found in most soils that are subjected to periodic burning, and is highly resistant to microbial decay (Czimczik *et al.* 2005, Dai *et al.* 2005, Cheng *et al.* 2006, Czimczik & Masiello 2007). Mean residence times of black carbon are estimated to be on centennial scales (Santos 2012, Singh 2012), with some between 1000-10 000 years (Couillard *et al.* 2013; Schmidt 2002), far longer than other non-black carbon pools. However, quantification of black carbon in boreal soils is a relatively recent phenomenon. Current soil organic matter models do

not treat black carbon as a separate soil carbon stock (eg. CENTURY, Roth-C, CBM-CFS3) and include it with non-black carbon soil carbon stocks, potentially overestimating the vulnerability of boreal soil carbon to climate warming.

Compared to non-black carbon forms of organic matter, charcoal has a unique decomposition pathway and represents a discrete soil carbon stock that is readily distinguished from other soil carbon stocks. Most soil carbon models include organic matter in three categories based on their rate of cycling (active, passive, slow) (Figure 5.1). However, charcoal behaves differently than other soil carbon stocks. Unlike non-charcoal soil organic matter stocks, charcoal mineralization increases minimally with increasing soil temperature (Bruun *et al.* 2008, Cheng *et al.* 2008, Novak *et al.* 2010). As well, where non-charcoal organic matter stocks typically increase with time since fire, charcoal stocks are greatest immediately after fire. Labile fractions of charcoal mineralize rapidly over a short period with the decomposition rate declining slowly over time (Figure 5.2). Charcoal also interacts with surrounding organic matter and can cause short-term priming of organic matter decomposition, but over the long term increasing organic matter stability, further contributing to soil carbon stocks (Wardle *et al.* 2008, Brodowski *et al.* 2006). As a result, charcoal needs to be included as a separate soil carbon stock in soil carbon models, as well as interactions with surrounding soil organic matter (Krull *et al.* 2006). In the absence of a discrete black carbon model category, incorporation of black carbon into soil carbon models could be accomplished by manual adjustment of decomposition rates in the models.

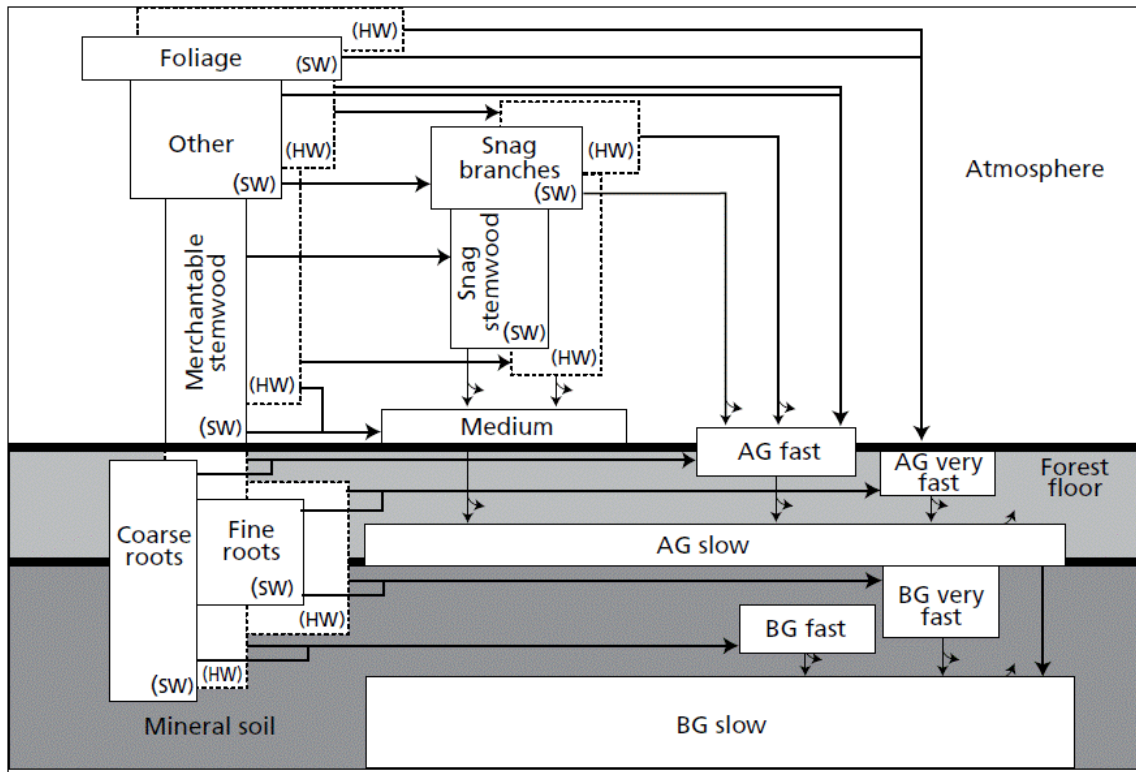


Figure 5.1 Carbon pool structure of CBM-CFS3 showing cycling rates of organic (AG) and mineral soil (BG) carbon pools ('very fast', 'fast', 'slow', 'very slow') (Kurz et al. 2009).

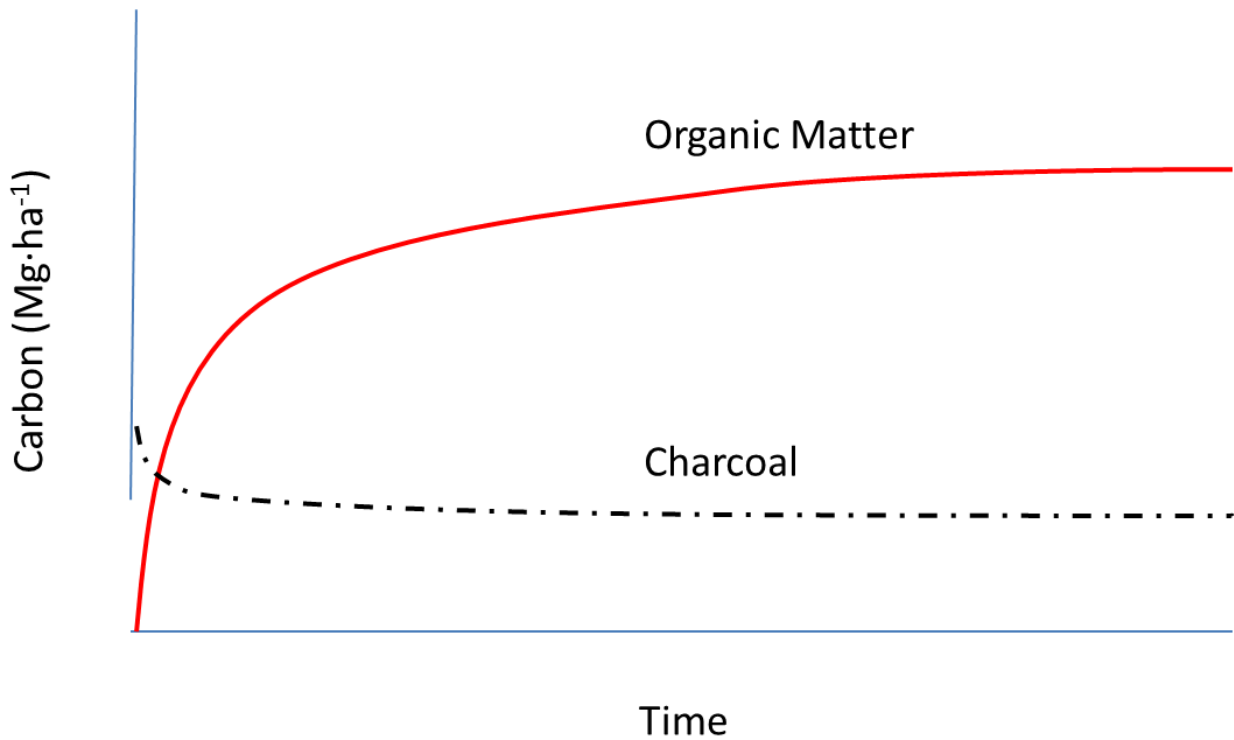


Figure 5.2 Change in charcoal and non-black carbon soil organic matter with increasing time since fire (soil organic matter line adapted from (Seedre *et al.* 2011)).

Boreal soil carbon stocks are very large, playing a critical role in global carbon balance (IPCC 2007). Even small discrepancies in carbon changes over time can result in very large differences. In this study, charcoal stocks were found to be equivalent to 2.7-3.1% of soil carbon and 2.5-5.6% of living biomass. Even more than 200 years after fire, charcoal still represented 1.1 Mg ha^{-1} of carbon, or 1.4-1.6% of soil carbon, with a carbon content of 50-60%, much higher than that of the surrounding soil organic matter. Failure to include the amount and longevity of black carbon in soil organic matter stocks will result in an overestimation of the mineralization of soil organic matter in response to soil warming (Lehmann *et al.* 2008), thus likely overestimating predicted soil carbon loss due to climate change (Figure 5.3). The recalcitrance of black carbon may act as a buffer to soil organic matter loss due to soil warming.

Inclusion of charcoal in soil carbon models is therefore imperative in order to accurately model soil carbon responses to changes in climate, fire regimes, and forest composition. By quantifying boreal soil charcoal stocks and changes in carbon content over time, this thesis can provide a starting point for inclusion of charcoal into soil carbon models.

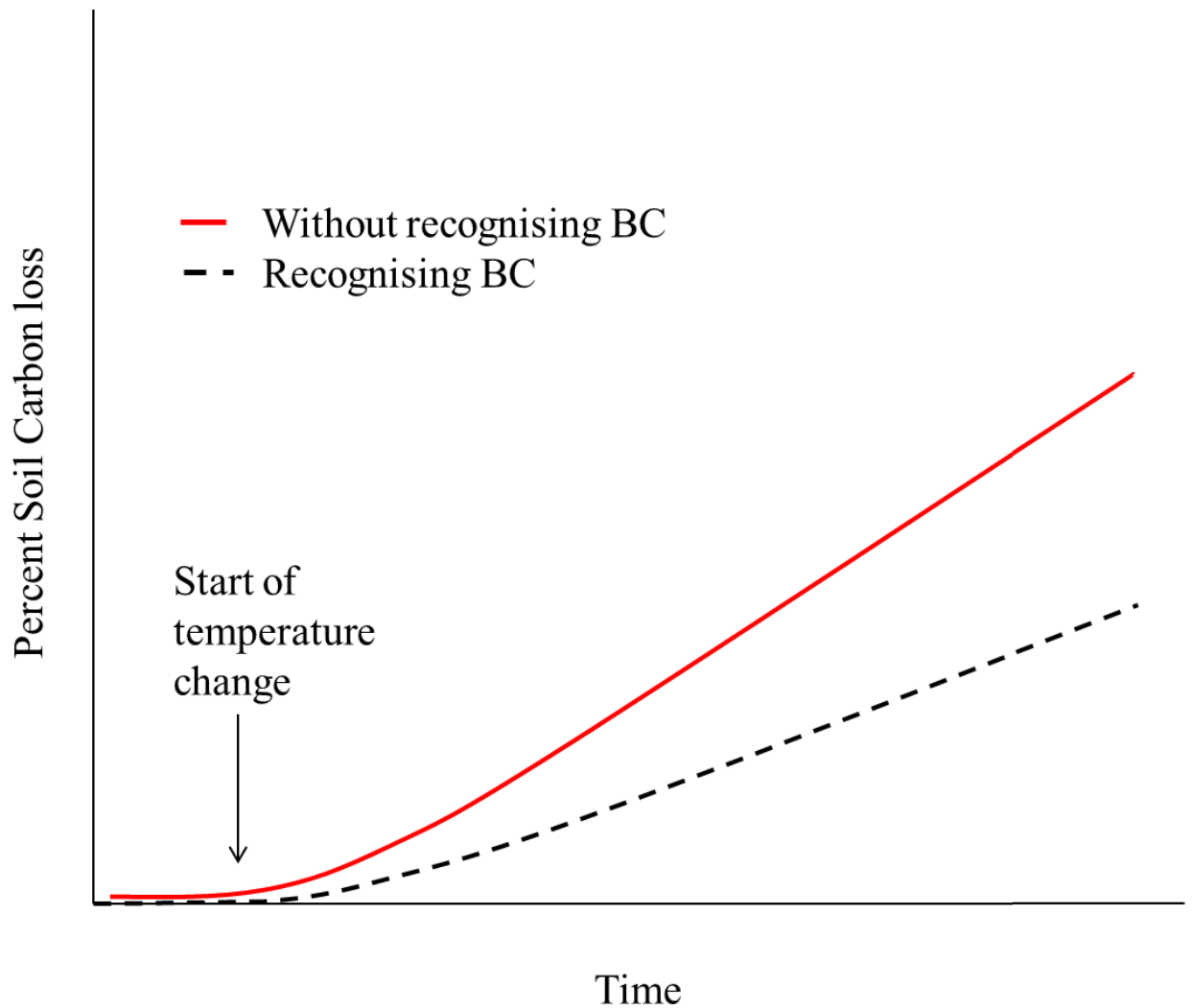


Figure 5.3 Conceptual model of the influence of charcoal (BC) on model of total soil organic matter (SOM) response to climate warming (adapted from Lehmann *et al.* 2008).

6 General conclusions

Charcoal is an important component of boreal soil carbon stocks. From this limited study or a relatively restricted area of North American boreal forest, charcoal quantities in North American boreal forest soils appear high enough to have beneficial effects on soil function and carbon storage. Charcoal stocks found in this study suggest that North American boreal charcoal stocks may be much greater than those reported in other boreal regions. As a result, estimates of global boreal charcoal carbon stocks may need to be revised upwards to account for larger charcoal quantities in boreal regions prone to stand replacing wildfires. Although highly recalcitrant, boreal charcoal stocks undergo reductions in complexity and carbon content over time.

Although soluble components of charcoal can contribute to increased soil respiration, this effect does not occur in the presence of charcoal in the soil, suggesting that charcoal may increase the stability of other SOM stocks through protection from microbial attack or by moderating nutrient availability. Although ephemeral, carbon accounting may require that estimates of charcoal carbon amendments be downgraded somewhat to account for initially high mineralization of charcoal following application.

Management of boreal forest charcoal stocks may be necessary in the absence of fire and decreased organic matter inputs due to forest harvesting. Maintaining active boreal forest soil carbon stocks is imperative in the face of intense forest harvesting, fire suppression and climate change. Although much more research is needed, managing boreal charcoal stocks is technically feasible. Laboratory produced charcoal can replicate many of the properties of wildfire charcoal, while logging residues can produce charcoal quantities comparable to those resulting from low to moderate intensity fires. Incorporating charcoal into boreal forest management through the use of

prescribed burns and wildfire can help to maintain future soil carbon stocks and the long term productivity of boreal ecosystems.

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