# University of Alberta

# Soil carbon stabilization in the jack pine boreal forest

by

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## Abstract

Two existing disturbances in the Canadian boreal forest include fire and harvest, although climate change is expected to soon have a major effect. Hence, the overall objectives of this study were to quantify and compare soil carbon stocks and composition in (1) two jack pine chronosequences of either fire or harvest origin, and (2) along a latitudinal transect. The distribution of carbon was quantified among soil pools, and composition of the forest floors and light fractions was further characterized by CPMAS $^{13}C$ nuclear magnetic resonance (NMR). While total soil carbon stocks (0-1 m) did not differ between the fire and harvest chronosequences, these were less at the warmer southern site compared to the northern site. Soil carbon within all profiles was dominated by labile pools. The relative importance of this labile carbon increased with time since disturbance in both chronosequences, and reached a maximum at the northern-most site.

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## List of Abbreviations

| Abbreviation | Definition |
|---|---|
| ANOVA | analysis of variance |
| BFTCS | Boreal Forest Transect Case Study |
| BOREAS | Boreal Ecosystem-Atmosphere Study |
| C | carbon |
| $C_e$ | carbon enrichment factor |
| C/N | carbon to nitrogen ratio |
| $CO_2$ | carbon dioxide |
| CPMAS | cross polarization magic angle spinning |
| DOC | dissoved organic carbon |
| FID | free induction decay |
| GCTE | Global Change and Terrestrial Ecosystems |
| KCl | potassium chloride |
| LSD | least significant difference |
| MAT | mean annual temperature |
| MAP | mean annual precipitation |
| NMR | nuclear magnetic resonance |
| TMS | tetramethylsilane |

# Chapter 1 Introduction

## The boreal forest

The boreal forest (taiga) encircles the globe south of the artic, between the subarctic and the grasslands and steppes, and is the second largest forest biome on Earth with an area of 1.37 x $10^9$ ha (Bhatti et al. 2006). About 30% of the boreal forest is in Canada, extending through seven of Canada's provinces and three territories (Canadian Forest Service 2006). At 290 Gt of carbon (C), the boreal forest contains more than one third of the amount of carbon in the atmosphere (Bhatti et al. 2006).

Stand dynamics in the boreal forest are driven by large scale disturbances, including wind and snow in the maritime boreal and fire and insects in the continental boreal forest. The boreal forest landscape is dominated by spruce, fir, larch, birch/aspen or pine stands. Pine stands colonize the upland coarse texture fluvial outwash sites of the boreal with Scots pine (*Pinus sylvestris*) in Fennoscandia and Siberia and jack pine (*Pinus banksiana* Lamb.) in Canada. Jack pine is both an eastern and western Canadian boreal species, widely distributed from the Maritimes through to northern BC and the Territories (Rudolph and Laidly 1990). It is an important commercial species for pulpwood, construction and for Christmas trees where the value derives from its ability to grow on the driest and poorest sites within its range and yet produce merchantable timber (Cayford et al. 1983).

## Disturbances to the boreal forest

The global surface temperature is expected to increase by 1.8°C to 4.0°C by 2100 (Meehl et al. 2007). Warming will be greater over land than the global average (Meehl et al. 2007) and, in North America, the northern regions could experience up to 5°C warming, with most warming occurring in the winter (Christensen et al. 2007). These northern, high latitude, ecosystems are expected to be highly vulnerable to global warming (Fischlin et al. 2007). Hence carbon dynamics of these regions may experience greater changes from different temperatures and precipitation than southern areas (Apps et al. 2006).

In 1990, wildfires burned over 2 x $10^6$ ha in the continental Canadian boreal forest and subarctic ecoprovinces while harvesting, with 0.4 x $10^6$ ha, accounted for a smaller fraction of disturbance. However the area disturbed by harvesting has been steadily increasing since then (Kurz and Apps 1996). A number of studies have characterized C fluxes in boreal forests following either fire or harvest (e.g.; Howard et al. 2004; Rothstein et al. 2004), but very few have directly compared the two disturbance mechanisms (Amiro et al. 2006). Furthermore, although >80% of boreal forest C stocks are in soil, very little is known on how total soil C, and in particular its composition and distribution, responds to disturbance (Watson et al. 2000).

Boreal forest C stocks, as in other ecosystems, can be divided among above ground vegetation, forest floor and mineral soil pools (Bhatti and Apps 2000). Retention of soil organic C that originates from root turnover as well as above ground leachates and litter additions depends on the site conditions (soil texture, moisture and temperature) as well as on the quality of the litter itself (Morris and Paul 2003). A quick review of research on soil C stocks across climosequences of latitude gradients or elevation transects did not reveal any consensus on whether an increase in temperature would increase or decrease these C stocks. A Scots pine latitudinal gradient in Eastern Europe

(Vucetich et al. 2000), a study of soils in Sweden (Akselsson et al. 2005), a survey of coarse textured Nordic soils (Callesen et al. 2003) and a north south transect in Canada (Bird et al. 2002) all found C contents to be greater in the south with warmer and moister conditions. However, when using elevation transects, the greatest soil C contents were found at the higher elevation, cooler and moister soils in Brazil (Dalmolin et al. 2006), and at the mid-slope position in the Sierra Nevada range of California (Trumbore et al. 1996). Finally, research along two latitudinal transects also found an increase in C content from south to north, corresponding to decreasing temperature, one in an Alaskan black spruce transect (Kane et al. 2005) and the other on BOREAS sites in central Canada (Halliwell and Apps 1997). However, and as opposed to what is reported for C stocks, there seems to be an agreement amongst studies when examining how soil C stabilization processes are affected by climate. Namely, along climosequences, the organic C in the cooler sites was always less decomposed and more labile when compared to C at the warmer sites (Dalmolin et al. 2006; Hilli et al. 2008; Kane et al. 2005; Sjögersten et al. 2003).

### Soil Fractionation & Analysis

Soil organic C stocks are often conceptually divided among three pools: active or labile C with a turnover occurring within days to years, passive C with a turnover of years to decades, and finally recalcitrant C with a turnover ≥ 100 years (Collins et al. 2000; Khanna et al. 2001; Trumbore 2000). Practically, soil is a complex heterogeneous mixture that is difficult to separate into defined categories. Guggenberger et al. (1995) divided soil into three fractions based upon particle size, and reported that sand-sized organic matter was dominated by fresh plant residues, while the silt fraction was high in aromatic carbon and clay-sized organic matter was dominated by microbially derived compounds. Gregorich et al. (1996) further determined that while the sand-sized fraction was a transient carbon pool with little decomposition, the light fraction showed even less decomposition and was more similar to the original plant inputs. Three categories were also examined by Poirier et al. (2005), including two "free" light organic matter fractions and one heavy organic matter category. The least degraded soil organic matter, with carbohydrates mainly derived from plants, made up the light fraction, while the heavy fraction was composed of a high proportion of microbial metabolites. Taken together, these studies indicate that soil fractionation based on particle size separation yields organic carbon pools that are easier to categorize, more homogeneous and chemically identical, and have more similar turnover rates than bulk soil carbon.

Reviews of density and particle size fractionation studies by Christensen (1992; 2001), Khanna et al. (2001), and von Lützow et al. (2007) all stated that the C/N ratio represents a good decomposition index among fractions, with a typically observed decrease in C/N from the light fraction to the sand, silt and then clay fraction. In addition to changes in C/N, the isotopic ratios of $^{13}C$ to $^{12}C$ ($\delta\ ^{13}C$) and $^{15}N$ to $^{14}N$ ($\delta\ ^{15}N$) also have been proposed as indicators of the extent of decomposition in soil organic matter (Quideau et al. 2003). Simplistically, microbes discriminate in their acquisition of the heavier isotopes of carbon and nitrogen as do plants, causing litter material to be initially depleted in $^{13}C$ and $^{15}N$ compared to bulk soil organic matter, but then to become progressively enriched with increasing decomposition. For instance, $\delta\ ^{13}C$ in a mineral soil (0-10 cm) of a southern jack pine site was -26.22‰, while at 10-20 cm the soil was enriched in $^{13}$C at δ -25.48‰ (Flanagan et al. 1996).

An additional experimental approach to characterize the state of decomposition of soil organic C, particularly with regards to its labile fractions, is high-resolution solid-state cross-polarization magic-angle spinning (CPMAS) $^{13}$C nuclear magnetic resonance (NMR) spectroscopy (Dalmolin et al. 2006; Preston et al. 2006; Sjögersten et al. 2003). CPMAS $^{13}$C NMR has become the standard technique for the macromolecular characterization of soil organic matter composition (Kögel-Knabner 1997; Preston 2001; Quideau et al. 2000). Compositional differences are typically detected among soil fractions, with a relative decrease in O-alkyl (carbohydrates), and an associated increase in aromatic (lignins, tannins) and more often alkyl (lipids) C in the stabilized pools as compared to the labile pools.

## Boreal Forest Transect Case Study

The BFTCS is one of the transects identified in the Global Change and Terrestrial Ecosystems (GCTE) Core Project of the International Geosphere-Biosphere Programme (Koch et al. 1995). The BFTCS was initiated to study the effect of climate and disturbance on C stocks in representative stand types of the Canadian boreal forest, i.e., trembling aspen (*Populus tremuloides* Michx.), black spruce (*Picea mariana* (Mill.) BSP) and jack pine (Bhatti et al. 2002).

The transect is oriented southwest to northeast and covers approximately 1000 by 100 km with a generally flat topography (Price and Apps 1995). Soil types vary from predominantly chernozemic in the southwest through a mixture of luvisols, humic-ferric podzols and fibrosols (peat) overlying Canadian Shield bedrock in the north-eastern end (Bhatti et al. 2002). The BFTCS is aligned across an ecoclimatic gradient from the aspen parkland transition to the boreal forest biome and into the sparsely treed subarctic tundra (Bhatti et al. 2002). Mean annual temperature on the transect ranges from 0.5°C in the south to -5.0°C in the north, with mean annual precipitation ranging between 400 and 550 mm, again from south to north (Price and Apps 1995). Clustered about the southern end of the BFTCS are several jack pine sites of harvest origin while sites of fire origin are found along the entire length of the transect. The BFTCS also includes within its boundaries the sites previously studied under the BOREAS and Fluxnet research programs.

### Research Questions and Objectives

1. How is soil C composition in forest floors and mineral horizons affected by disturbance, and specifically, does a difference exist between soil C response to fire and harvest? Hence, the first objective of this study was to quantify and compare changes in soil C stocks and chemistry in two jack pine chronosequences of either fire or harvest origin.
2. How are soil C stocks and chemistry affected by climate (temperature and precipitation)? In an effort to elucidate this question, a climate transect of mature jack pine stands was studied in terms of soil organic C stocks and stabilization processes.

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# Chapter 2 Fire and harvest influences on jack pine soil organic carbon

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## Introduction

With an area of 1.37 x $10^9$ ha and a carbon (C) stock of 290 Pg ($10^{15}$ g), the boreal forest is the fifth largest in area and in C reservoir of the terrestrial biomes (Bhatti et al. 2006). Canada, with 410 x $10^6$ ha of forested land, accounts for about 30% of the Earth's total boreal forests (Canadian Forest Service 2006). Fire is a key stand renewal agent in these boreal forests, and is for instance required for the regeneration of coniferous trees with serotinous cones such as jack pine (*Pinus banksiana* Lamb.). Jack pine is an important commercial species for the production of timber and pulpwood within the Canadian boreal forest, even though it is a small tree growing on nutrient poor soils typically developed from coarse-textured glacial outwash and eolian deposits (Rudolph and Laidly 1990). On average, 2 x $10^6$ ha of forests in Canada burn every year, while less than 1 x $10^6$ ha are being harvested, although this figure has steadily increased for the past 70 years (Kurz and Apps 1996). A number of studies have characterized C fluxes in boreal forests following either fire or harvest (e.g.; Howard et al. 2004; Rothstein et al. 2004), but very few have directly compared the two disturbance mechanisms (Amiro et al. 2006). Furthermore, although >80% of boreal forest C stocks are in soil, very little is known on how total soil C, and in particular its composition, responds to disturbance (Watson et al. 2000).

Soil organic matter is a heterogeneous mixture of C compounds. It includes labile pools dominated by undecomposed plant residues, and a series of stabilized pools at varying stages of humification. Three key mechanisms are recognized for organic matter stabilization within soils: 1. physical inaccessibility to the decomposer communities by occlusion inside aggregates; 2. chemical stabilization by adsorption to silt and clay-sized particles; and 3. biochemical recalcitrance linked to the inherent structural composition of soil biomolecules (Christensen 2001; Six et al. 2002). From an experimental point of view, physical fractionation of soil is an attempt to isolate soil separates that correspond to these conceptual C pools (Baldock et al. 2004; Christensen 2001; Crow et al. 2006). In particular, density separation yields an unprotected C pool (i.e.; the light fraction) that closely resembles litter inputs in physical appearance and chemical composition (Christensen 2001; Poirier et al. 2005). As this light fraction is sensitive to environmental conditions, it has often been used as an indicator of management induced changes in soil organic matter (Christensen 2001; Ellert and Gregorich 1995; Khanna et al. 2001; Six et al. 2002).

High-resolution solid-state cross-polarization magic-angle spinning (CPMAS) $^{13}C$ nuclear magnetic resonance (NMR) spectroscopy has become the standard technique for the macromolecular characterization of soil organic matter composition (Kögel-Knabner 1997; Preston 2001; Quideau et al. 2000). Compositional differences are typically detected among soil fractions, with a relative decrease in O-alkyl (carbohydrates), and an associated increase in aromatic (lignins, tannins) and more often alkyl (lipids) C in the stabilized pools as compared to the labile pools. In addition, variations in the natural abundances of soil C isotopes ($^{12}C$, $^{13}C$) may provide a useful tool for the characterization of humification processes (Flanagan et al. 1996). Microbial discrimination against the heavier C isotope during catabolic processes results in $^{13}C$ enrichment in the residual organic matter. This increase in $\delta^{13}C$ with increasing humification has been reported in a number of studies, including changes monitored with depth in the soil profile (Bol et al. 1999), as well as among various soil density and particle size fractions (Preston et al. 2000; Quideau et al. 2003).

As determined using CPMAS $^{13}C$ NMR spectroscopy, changes in forest floor composition following harvesting disturbance within Canadian boreal forests may involve an increase in aromatic C concentrations indicating an increased degree of humification (Hannam et al. 2005). Forest floor following fire is also typically enriched in aromatic forms of C (e.g, Thiffault et al. 2008), although this may be best attributed to the presence of charcoal or black (pyrogenic) C (Preston and Schmidt 2006). What remains unclear, however, is how soil C composition in mineral horizons is affected by disturbance, and specifically, if a difference exists between soil C response to fire and harvest. Hence, the overall objective of this study was to quantify and compare changes in soil C stocks and chemistry in two jack pine chronosequences of either fire or harvesting origin. Specifically, six jack pine sites developed on similar soils but with variable time since fire or harvest were compared to a mature 91-year old stand of fire origin.

## Materials and methods

### Study sites and sampling design

The Boreal Forest Transect Case Study (BFTCS) encompasses a 100 km x 1000 km region located along an ecoclimatic gradient from the grasslands of southern Saskatchewan (SK) to the tundra of northern Manitoba (Price and Apps 1995). Mean annual temperature on the transect ranges from 0.5°C in the south to -5.0°C in the north, with mean annual precipitation ranging between 400 and 550 mm, again from south to north (Price and Apps 1995). The BFTCS was originally initiated to study the effect of climate and disturbance on C stocks in representative stand types of the boreal forest, i.e., trembling aspen (*Populus tremuloides* Michx.), black spruce (*Picea mariana* (Mill.) BSP) and jack pine (Bhatti et al. 2002). For this study, seven sites supporting pure jack pine stands were chosen and sampled in 2006 from the southern region of the BFTCS. These sites were further identified by disturbance mechanism and stand age at sampling (Table 2-1). Five sites (Fire 91, Fire 29, Harvest 31, Harvest 12, and Harvest 4) were clustered within a ten kilometer radius near Candle Lake, SK. Fire 11 was located about 30 km northeast of the cluster, while Fire 4 was located 110 km to the southwest near Prince Albert, SK. There were no recorded data of fire intensity or severity at the fire sites but visual evidence suggested that they were all stand replacing disturbance events. All harvesting was whole tree removal, followed by mechanical site preparation (scarification) and manual tree planting.

Reindeer lichen (*Cladina* spp.), with patches of bearberry (*Arctostaphylos uva-ursi*) and moss (*Pleurozium* spp.), dominated the ground cover at the older jack pine site (Fire 91), while green alder (*Alnus crispa*) was spread sporadically throughout the stand. Understory at the other sites varied from complete groundcover of spreading dogbane (*Apocynum androsaemifolium*) and grass at Fire 4 to clumps of bearberry over exposed mineral soil at Harvest 4. Harvest 12 and Fire 11 had sparse lichen and grass vegetation while Fire 29 had a mat of bearberry with lichen and bushes of alder. Harvest 31 was lush in groundcover with bearberry, feathermoss and grasses mixed in between prickly rose (*Rosa acicularis*), blueberry and bog cranberry (*Vaccinium myrtilloides* and *V. vitis-idaea*). All sites were located on level terrain, with the exception of Fire 11, which had a slight (< 5%) slope. At each site, four random soil profiles were excavated within a 200 m radius. One profile was fully characterized, while the three others were examined for horizon sequence and depth. All soils had formed on glacial fluvial outwash and were classified as Eluviated Dystric Brunisols according to the Canadian System of Soil Classification (Soil Classification Working Group 1998).

Approximately 1.5 kg of sample was collected from each mineral horizon (A, $Bm_1$, $Bm_2$ and C) at each soil profile for a total of 4 samples per horizon from each site. Forest floor samples were also collected from each profile except at Fire 4 and Harvest 4, where only three forest floor samples were collected due to a lack of material at one profile. Forest floor was collected in one of two ways, either from directly above the A horizon at each pit, or randomly in a 5 m radius around each pit. Samples were transported to the laboratory within 4 days of collection, where they were immediately air dried, sieved to 2 mm and stored in air tight containers until further analysis.

### Physical fractionation scheme

Samples from the A and $Bm_1$ horizons collected at each pit were fractionated using a combination of density and wet sieving techniques (Figure 2-1). Methodology was amended from a variety of sources (Christensen 1992; Christensen 2001; Preston et al. 2000; Quideau et al. 2000; Six et al. 2002) to yield the following five fractions: light fraction ($< 1$ g cm$^{-3}$) 250–2000 μm ; coarse sand (250–2000 μm); fine sand (53-250 μm); silt (2–53 μm), and clay (<2 μm). Specifically, fractionation of each sample began by adding 150 ml of distilled water to each of eight 100 g subsamples and placing these on a reciprocal shaker for one hour. Each sample was then wet sieved through a 250 μm and 53 μm mesh. The > 250 μm sample was immersed in distilled water for vacuum filtration of the light fraction and separation from the coarse sand fraction. The <53 μm solution was further separated by sedimentation (8 hours for every 10 cm of suspension) into the silt and clay fractions. All > 2 μm fractions were dried in a forced air oven overnight with a temperature ≤ 40 °C. The remaining (< 2 μm) suspension was flocculated with potassium chloride (KCl), with subsequent removal of KCl by dialysis tubing (Fisherbrand Nominal MWCO 12 000 – 14 000), and freeze-dried using a FreeZone 6 Liter Dryer (Labconco Corporation, Kansas City MO). All fractions were then weighed to calculate their relative distribution, as well as particle size distribution among sand (>53 μm), silt (2-53 μm), and clay (< 2 μm) fractions (Table 2-1). Average sample recovery was over 99%.

### Laboratory analyses

Each horizon of the fully characterized pit at each site was analyzed for pH with an Ag/AgCl pH electrode, using a soil to 0.01 M calcium chloride solution ratio of 1:2, and a settling time of 30 minutes (Kalra and Maynard 1991b). Particle size analysis for the two horizons, $Bm_2$ and C, that had not been physically fractionated were determined by a modified Bouyoucos Hydrometer method (Kalra and Maynard 1991a). Dispersal was accomplished with a 5% Calgon solution and hydrometer readings were taken at 40 s for determining % sand and at two hours for determining % clay. Whole (unfractionated) soil samples from each pit as well as all five fractions were homogenized, finely ground using a ball mill grinder (Retsch MM200, Retsch Inc. Newtown PA), and encapsulated prior to total C determination by dry combustion using a Costech ECS 4010 Elemental Combustion System with a thermocouple detector (Costech Analytical Technologies Inc. Valencia CA). This yielded a total of 420 C analyses, i.e., (5 horizons * 4 pits * 7 sites) + (5 fractions * 2 horizons* 4 pits * 7 sites).

The five fractions obtained from the A and Bm$_1$ horizons at each pit were composited by horizon and site prior to C isotopic composition determination. The isotopic composition of these composite samples was measured on a Costech ECS 4010 Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, CA USA) coupled to a Finnigan Deltaplus Advantage Isotopic Ratio Mass Spectrometer (ThermoFinnigan, Bremen Germany). Results were expressed in the δ-notation, the ‰ variation from the standard Pee Dee Belemnite (PDB) reference material:

$$\delta^{13}C = \left( \frac{R_{Sample}}{R_{Standard}} - 1 \right) \times 1000$$

by using BMO (-23.91‰), CS (-12.5‰), NBS 1575N (-26.3‰,), and Red Clover (-27.42‰) as working standards.

Samples of the forest floor and A horizon light fractions composited by site were used for CPMAS $^{13}$C NMR analysis. Spectra were acquired on a Varian Chemagnetics CMX 200 [$B_0 = 4.70$ T, $\nu_L(13C) = 50.3$ MHz] spectrometer with a 7.5 mm double – resonance MAS probe with high-power $^1$H decoupling. Samples were loaded into a 7.5 mm OD zirconium oxide rotor with drive tips of Kel-F, and end caps and spacers made of Teflon (DuPont, Circleville, OH). Spectra were referenced to TMS (0 ppm) by setting the high frequency adamantane peak to 38.56 ppm. A total of 6000 transients were acquired for each spectrum with a 5.0 kHz spinning rate, a 1 ms contact time, and a 2 s recycle time. Processing of the FID was performed with the MNova's MestReC 5.0 software (Mestrelab Research SL, Spain. 2007). Processing the spectra included zero filling, line broadening of 50 Hz with phase and baseline correction followed by integration within specific regions of the area under the peaks.

It is recognized that CPMAS $^{13}C$ NMR is a semi-quantitative analytical technique. Since polarization is transferred from protons to carbons, for the contact time (1ms) used to acquire the spectra presented here, carbons lacking directly bonded hydrogen may be underrepresented (Smernik et al. 2002). However, given that spectra were acquired under similar laboratory conditions, this is a systematic error and results between different spectra comparable. In this study, we chose a conservative approach and divided the acquired spectra into regions based on broad C bonding types to allow for poor signal to noise ratios and resolution of peaks (Baldock and Preston 1995). Thorough descriptions of peak identification and assignments previously published were used to classify the following four regions (Baldock and Preston 1995; Kögel-Knabner 1997; Kögel-Knabner 2002; Preston et al. 1998; Simpson and Preston 2007): alkyl (0-47 ppm), O-alkyl (47-112 ppm), aromatic and phenolic (112-165 ppm), and carbonyl (165 – 215 ppm).

**Statistical analysis**

Soil organic C contents determined for all horizons were statistically compared for differences among sites. When these data were normally distributed (e.g., forest floor C contents), they were analyzed using a one-way analysis of variance (ANOVA) and a post-hoc test of Fisher's least significant difference (LSD) with an $\alpha$ of 0.05. When these data were non-normally distributed, as with total soil C contents of the sites (i.e.; sum of horizons), they were tested for significant differences by the non-parametric Kruskal-Wallis one-way analysis of variance with an α of 0.05. All analyses were run using Systat 11 (Systat Software Inc., USA. 2004).

## Results

### Soil C content, concentration, and isotopic composition

Soil C content was determined from the forest floor and mineral soil horizons with results summed to 1 m to compare across time and disturbance type with no accounting for stone volume (> 2 mm). While there were no statistically significant differences in total carbon content among sites, Harvest 31 had the greatest content at 4.54 kg m$^{-2}$ with Harvest 12 containing the least C at 2.57 kg m$^{-2}$ (Table 2-2). Carbon content decreased with depth from the A through to the C horizon, with the exception of Fire 11 which was unusual in that the Bm$_1$ horizon contained greater C than the other horizons. Notably, the texture of all soil horizons was composed of ≤ 7% silt, except for the Fire 11 profile where silt content exceeded 8%, and reached a maximum of 26% in the Bm$_1$ horizon (Table 2-1). This increase in B horizon C caused an increase in the total C content at Fire 11 (Table 2-2). Overall, both chronosequences accumulated C with time: from Harvest 4 (2.80 kg m$^{-2}$) and Fire 4 (2.60 kg m$^{-2}$), to Harvest 12 (2.57 kg m$^{-2}$) and Fire 11 (3.93 kg m$^{-2}$), Harvest 31 (4.54 kg m$^{-2}$) and Fire 29 (3.33 kg m$^{-2}$), and finally a slight decrease for Fire 91 (3.09 kg m$^{-2}$). In addition, forest floor C content was significantly less at the younger Fire 4 and Harvest 4 sites. Forest floor C content further reached a statistically significant maximum at Fire 91, such that the percentage of total soil C held in the forest floor increased along the fire chronosequence from 2 % at Fire 4 to 33% at Fire 91. Within Fire 91, the forest floor held as much organic C (1.02 kg $m^{-2}$) as did the A horizon (1.04 kg $m^{-2}$).

Carbon concentrations in the light fractions, at over 310 g $kg^{-1}$ (data not shown), were greater than in other fractions. Carbon concentrations at all sites showed a clear trend within the mineral fractions, i.e., increasing with decreasing particle size from 10 g $kg^{-1}$ in coarse sand to 88 g $kg^{-1}$ in clay (Figure 2-2). For all of these mineral fractions (with the exception of Fire 11), the C concentration was greater in the A horizon than in the $Bm_1$. Total C content (kg $m^{-2}$) was also greater in the A than the $Bm_1$ horizon for all fractions except the clay, where the opposite relationship was observed (Table 2-3). These data further illustrated that the C within these horizons was associated mostly with the coarse sand fraction. In both the A and $Bm_1$ horizons, the proportion of C contained in the coarse sand fraction steadily increased with time since disturbance in both the harvest and fire chronosequences (Figure 2-3). This proportion reached a maximum value of 60% for the A horizon, and 50% for the $Bm_1$ horizon, at the Fire 91 site. On the other hand, relative C content slightly decreased with time in both the clay and silt sized fractions, while the proportion of light fraction C, at about 10 %, did not show any changes with time in either chronosequence.

Carbon isotopic composition ($\delta^{13}C$) in the light fractions was -26.7‰ or less at all sites (Figure 2-4). All other fractions had a greater $^{13}C$ content than the light fraction, with the greatest $^{13}C$ enrichment found in the clay sized fractions. All mineral fractions also showed an enrichment in the $Bm_1$ as compared to the A horizons, but there was no visible trend in the $\delta^{13}C$ values of either horizon with time since disturbance.

### Soil C composition as determined by CPMAS $^{13}$C NMR

All forest floor spectra, with the exception of the one acquired from Fire 11, were dominated by a peak in the O-alkyl region centered on 73 ppm (Figure 2-5). This signal may be attributed to carbohydrate biomolecules such as cellulose and hemicelluloses. Analysis of char pieces physically removed from the forest floor of Fire 4 yielded a spectrum with a characteristic broad peak around 130 ppm (Figure 2-6). The presence of char, as indicated by a similar peak at 130 ppm, was evident on spectra from both the Fire 4 and Fire 11 forest floor samples (Figure 2-5). For Fire 11, this 130 ppm signal exceeded in intensity that of the O-alkyl 73 ppm peak. Unexpectedly, there also was a large aromatic C signal centered at 130 ppm for the forest floor spectrum from the Harvest 4 site that indicated the presence of char. While there was no record of recent fire at that site, there was physical evidence of char in the three forest floor samples collected. In addition to signals in the O-alkyl and aromatic regions, all forest floor spectra exhibited a significant peak in the alkyl C region around 30 ppm corresponding to polymethylene type Cs (Keeler and Maciel 2000). This alkyl C signal increased in intensity within the harvest chronosequence with time since disturbance (Figure 2-5 and Table 2-4). Within the fire sites, the older (Fire 91) also showed the highest alkyl C signal, although there was no consistent trend with time since disturbance at the younger sites. Finally, although apparent on all spectra, signals in the carbonyl area were typically the lowest of all spectral areas (Table 2-4).

Along with the four integral areas as reported in Table 4, the alkyl to O-alkyl C and aromatic to O-alkyl C ratios were estimated as they both have been proposed as an index of organic matter decomposition (Baldock et al. 1992; Baldock and Preston 1995;

Quideau et al. 2000). Within the harvest chronosequence, the forest floor from the older Harvest 31 site exhibited the largest alkyl/O-alkyl ratio, which may be best explained from the increase in alkyl C with time since disturbance (Table 2-4). The fire forest floors did not show any consistent change with time in their alkyl/O-alkyl ratios. Yet, in the aromatic/O-alkyl ratios, there was a definite decrease with time for these fire sites, from values > 1 at Fire 4 and Fire 11, to 0.74 at Fire 29, and a low of 0.21 at Fire 91. Furthermore, the aromatic/O-alkyl ratios at Fire 4 and Fire 11 were greater than at any of the harvested sites. Decreases in the aromatic/O-alkyl ratios along the fire chronosequence may be in part attributed to the strong aromatic signal at 130 ppm indicative of charcoal that was present in both Fire 4 and Fire 11 forest floors. There was also a relative increase in the O-alkyl region from 22-28 % at Fire 4 and Fire 11, to 34 % at Fire 29, and 50 % at Fire 91.

In contrast to the forest floor samples, the light fractions isolated from the A horizons at the harvested sites did not change in alkyl/O-alkyl ratios with time (Table 2-4), as the three spectra were similar in peak shape and intensity (Figure 2-7). However, the light fractions of the fire sites showed a consistent trend with time since disturbance, where the O-alkyl C decreased while the alkyl and aromatic signals tended to increase (Table 2-4). This resulted in smaller alkyl to O-alkyl ratios (0.34-0.38) at Fire 4 and Fire 11 when compared to the Fire 29 and Fire 91 sites (0.54-0.55). For these fire sites, the aromatic to O-alkyl ratios of the light fractions showed an even stronger change with time than did the alkyl/O-alkyl ratios, and increased from 0.51-0.65 at Fire 4 and Fire 11, to 0.92 at Fire 29, and finally to >1 at Fire 91. This trend was reverse to what was observed in the forest floors, where the two youngest sites (Fire 4 and Fire 11) had greater (>1) aromatic to O-alkyl ratios than Fire 29 (0.74) and Fire 91 (0.21).

## Discussion

### Soil C concentration and isotopic composition

The increase in C concentration with decreasing particle size as determined in this study for the A horizons (Figure 2-2) is consistent with what has been reported in previous studies (Christensen 1992; Preston et al. 2000; Quideau et al. 1998; von Lützow et al. 2007). Increasing C concentration with decreasing particle size also held true for the $Bm_l$ horizon at about half the concentration of that for the A horizon (Figure 2-2). As with other studies using fractionation (Christensen 2001; Quideau et al. 2000), a reverse trend to the C concentrations occurred in the C to nitrogen ratios (data not shown), where ratios were greatest in the light (23.8-36.8) and coarse fractions (25.6-28.5) and then decreased with decreasing particle size to the clay (9.1-11.9).

The light fractions exhibited the lowest $\delta^{13}C$ values of all fractions obtained from either the A or $Bm_l$ horizons at all sites (Figure 2-3). At Fire 91, the light fraction $\delta^{13}C$ was -26.7 ‰ for both horizons, which was either similar, or slightly enriched when compared to previously measured isotopic contents in vegetation from the same site, including jack pine twigs (-27.1‰; Preston et al. 2006), cones (-27.4 ‰; Preston et al. 2006), and needles, which varied between -26.6 ‰ and -27.2 ‰ when sampled in 1993-1994 (Brooks et al. 1997; Flanagan et al. 1996), and were slightly lower at -27.9 ‰ when measured in 2000 (Preston et al. 2006). On the other hand, the light fractions were depleted in $^{13}C$ when compared to a lichen sample (-25.7 ‰) obtained from the Fire 91 site (Brooks et al. 1997). With the notable exception of Fire 91, a $^{13}C$ enrichment occurred from the A to the $Bm_1$ horizon for soils at both the fire and harvest chronosequences (Figure 2-4). This is consistent with the idea of increased humification in the $Bm_1$ as compared to the A (Bol et al. 1999). Unlike other sites, the groundcover at Fire 91 was dominated by lichen. Hence, it is probable that for Fire 91, the importance of lichen as a $^{13}C$ enriched input to its Ahe horizon may have masked the expected $\delta^{13}C$ increase linked to humification processes between the Ahe and $Bm_1$ horizons.

For both the A and $Bm_1$ horizons, further $^{13}C$ enrichment occurred within the physically separated fractions from the light fraction to the silt and clay size separates (Figure 2-4). Within the Ahe horizon at Fire 91, the $\delta^{13}C$ values increased from the light (- 26.7‰) and coarse sand (- 25.8‰) fractions to the silt (- 25.4‰) and clay (- 24.1‰). Enrichment within the Bm horizon at the same site was even greater, and corresponded to 2.2‰ for the silt and 4.8‰ for the clay as compared to the light fraction. A similar, albeit smaller, increase was observed between soil fractions isolated from a southern Saskatchewan jack pine site, where a $\delta^{13}C$ enrichment of 0.7‰ in the Ah and 1.0‰ in the Bm occurred from the light fraction to the <63 μm fraction (Preston et al. 2000). Taken together, these results are consistent for our study with an increase in humification along the fractionation scheme, from the more labile light and coarse sand fractions to the stabilized silt and clay separates.

### Soil C composition

The CPMAS $^{13}C$ NMR spectrum acquired for the Fire 91 forest floor in our study (Figure 2-5) closely resembled spectra from a previously published forest floor spectrum from the same site (Preston et al. 2006), a jack pine forest floor from the Prince Albert region (Preston et al. 2000), as well as a pre burn Scots pine forest floor from Siberia (Czimczik et al. 2003). Prevalent signals in the O-alkyl and alkyl regions are characteristic of all of these spectra. These have been attributed to the dominant contribution to the forest floor composition at these pine ecosystems from lichen that contains no lignin and little aromatic C (Czimczik et al. 2003; Preston et al. 2006). Our measured $\delta^{13}$C value for the Fire 91 light fraction isolated from the Ahe horizon (Figure 2-4) supports such a hypothesis, where organic matter sources seem to be a composite of lichen and jack pine vegetative inputs.

The spectrum from the forest floor at Fire 4 (Figure 2-5) resembled that of a Siberian Scots pine forest floor sampled two days after fire (Czimczik et al. 2003). Both exhibited a decrease in the O-alkyl region and a three-fold increase in the aromatic region when compared to their respective mature forest floors. The aromatic region in both was further dominated by a broad peak centered about 125 – 130 ppm, which is characteristic of charred biomass or soil organic matter (Czimczik et al. 2002; Preston and Schmidt 2006). The importance of charcoal and its predominant role in the aromatic NMR region was further confirmed by examining spectra from all other potential C inputs. A $^{13}$C NMR spectrum of jack pine roots that were physically isolated from the Ahe horizon of Fire 91 did not display a large aromatic region or peak at 130 ppm (Figure 2-6), and neither did spectra previously published from lichen, jack pine needles, twigs or cones (Preston et al. 2006).

The ratio of the recalcitrant alkyl saturated C moieties to the more readily decomposed O-alkyl carbohydrates has been proposed (Baldock and Preston 1995), and extensively used (Alarcón-Gutiérrez et al. 2008; Lorenz et al. 2000), as an index of decomposition. Within the forest floors from the harvest chronosequence, the higher alkyl/O-alkyl ratio observed at the older Harvest 31 site (Table 2-4) is consistent with such an increase in decomposition with time since disturbance. However, such a trend was not seen in the light fractions isolated from the A horizons at these harvest sites. Furthermore, within the fire sites, while the alkyl/O-alkyl ratios of the light fractions also showed an increase along the chronosequence, this trend was overshadowed by changes in the aromatic/O-alkyl ratios. Although changing aromatic intensity has been proposed as an index of decomposition (Baldock et al. 1992), in our study, it may be better linked to the presence of charcoal (Preston and Schmidt, 2006). For the forest floors, the aromatic/O-alkyl ratios were highest (> 1) at the youngest Fire 4 and Fire 11 sites while the mature (Fire 91) forest floor showed the lowest ratio (Table 2-4). Interestingly, the opposite relationship with time since fire disturbance held true in the light fractions, with the older sites (Fire 29 and Fire 91) showing the highest aromatic/O-alkyl ratios. The movement of char through the soil profile with increasing time since fire has been hypothesized for the boreal forests (Preston and Schmidt 2006). However, to our knowledge, our results are the first direct indication that with time char indeed transfers from the forest floor to the mineral soil.

### Soil C content and stabilization processes

Statistical analysis failed to identify significant differences in total soil C content between the fire and harvest chronosequences (Table 2-2). Estimated values were similar to results from other studies in similar ecosystems (Table 2-5). The Fire 91 soil contained

3.1 kg C $m^{-2}$ (Table 2-2) while results from two other studies determined C content to be 2.9 kg C $m^{-2}$ (Table 2-5; Gower et al. 1997; Howard et al. 2004). A third study reported C content of jack pine forest floor at 1.1 kg C $m^{-2}$ in Saskatchewan (Nalder and Wein 1999), similar to the 1.0 kg C $m^{-2}$ estimated for the Fire 91 forest floor (Table 2-2). Results from a model exercise indicated that in Scots pine forest soils C content may differ after two 100-year fire cycles and harvest rotations due to divergent C processes (Liski et al. 1998). Furthermore, statistically different soil nitrogen dynamics have been reported in jack pine fire and harvest disturbed stands from Michigan (LeDuc and Rothstein 2007), therefore differences in soil C content after fire and harvest were expected in our results. The lack of statistical differences as observed in our study likely reflects the difficulties associated with selecting appropriate sites for a chronosequence, as well as the inherently high spatial variability in soil carbon within each site (Ryan et al. 1992), which made it impossible to detect differences using reasonable sampling schemes.

The theory, or pattern of changing soil C content following disturbance, was first proposed by Covington (1981), who suggested that most of the forest floor in a stand is lost within 15 years of disturbance, following which forest floor C content steadily increases to return to pre-disturbance levels by stand maturation. A review by Johnson (1992) further concluded that the assumption that forest disturbance leads to decreases in soil C was not supported by the literature. Johnson determined that fire effects on soil C were dependent on fire severity and intensity, while C losses were negligible with harvesting and reforestation. With additional review of various forest ecosystems and a meta-analysis, Johnson and Curtis (2001) reinforced their original conclusions in support of Covington's theory, i.e., that forest disturbance does not alter soil C content on a permanent basis. While forest soil C contents decrease after fire or harvest disturbance, their results further confirmed that, with time, these return to pre-disturbance levels.

In contrast to the conclusions from Johnson and Curtis (2001), studies that quantified the temporal response of total soil C to either fire or harvest disturbance in pine ecosystems fail to present a uniform story (Table 2-5). For instance, C content of the forest floor and mineral soil along a harvest chronosequence in Saskatchewan decreased with time and showed a minimum at the oldest site (Howard et al. 2004). Along a jack pine fire chronosequence in northern lower Michigan, C content in the mineral soil did not statistically change with time since disturbance, while forest floor increased to reach a maximum at the older (72 year old) site (Rothstein et al. 2004). In a Scots pine fire chronosequence from Siberia, Wirth et al. (2002) found that C content in the mineral soil originally peaked at 14 years. However, when taken together, these results indicate that total soil C tends to be higher at the older (mature) stands (Table 2-5). Results from our study also indicated an accumulation of soil C with time along both the fire and harvest chronosequences (Table 2-2). Furthermore, our results showed that for these jack pine ecosystems, soil C levels returned to pre-disturbance levels after about 30 years.

Of the mineral horizons, the A horizon was found to contain the greatest amount of C at all the sites (Table 2-2). Although the coarse sand fraction had the lowest C concentration (Figure 2-2), determination of C content (kg m$^{-2}$) for each of these fractions (Table 2-3) revealed that the majority of C in both the A and Bm$_1$ horizons was contained within this fraction (Figure 2-3). Organic C associated with the coarse sand size fraction has been classified as an unprotected labile C pool (Christensen 2001; Gregorich et al. 1996). This labile C pool was not only the largest, but it also increased in proportion with time in both the fire and the harvest chronosequences (Figure 2-3). On the other hand, analysis of the macromolecular composition of the forest floors and A horizon light fractions showed that there was a distinct difference in the chemical nature of the C between the two disturbance types. In contrast to the harvest sites, the Fire 29 and Fire 91 A horizon light fractions, and the Fire 4 and Fire 11 forest floors were dominated by a large aromatic region, likely black C. Assuming that the light fraction of Harvest 31 is representative of a mature stand without charcoal, the difference between the aromatic areas of the Fire 91 and Harvest 31 spectra (i.e., 6%) was taken to represent the proportion of charcoal C in the light fraction for Fire 91. This difference represented 0.005 kg $m^{-2}$ or 0.6% of the total Ahe horizon C content at Fire 91 and 0.2% of the total soil content. Since under the conditions used here, NMR analysis is known to under-represent condensed aromatic molecules such as charcoal (Smernik et al. 2002), this should be seen as a conservative estimate of charcoal content at Fire 91. In addition, this only represented the contribution of charcoal from the A horizon light fraction, and this estimate would obviously increase if the other four fractions and all horizons were to be included. Therefore, while mineral soil organic C at both the harvest and fire chronosequences was dominated by the labile pool associated with the coarse sand fraction, the light fractions at the older fire sites also contained a proportion of char, which may provide a means of C stabilization within these soils.

## Conclusions

Soil organic C content determined for seven sites across two jack pine chronosequences of either fire or harvest origin were comparable to C contents reported for similar ecosystems in Siberia and North America. In accordance to Covington's theory, while total soil C content decreased after disturbance, it returned to pre-disturbance levels by stand maturation in both the harvest and fire chronosequences. Labile C contained within the coarse sand fraction was the dominant C pool in all soils. Furthermore, the two chronosequences were similar in that the proportion of this labile C pool increased with time following both fire and harvest. However, when examining the macromolecular chemistry of the forest floors and A horizon light fractions, a difference between disturbance type was evident. Chemical composition did not greatly vary with time or horizon within the harvested stands. On the other hand, fire disturbed forest floors showed an initial large aromatic peak, likely due to the presence of char, and our results further indicated that with time, there was a transfer of this black (pyrogenic) C from the forest floors to the A horizons.

# Tables and Figures

Table 2-1. Site characteristics and general soil properties of fire and harvest jack pine forest soils chronosequences in Saskatchewan

| Site Name | Latitude (Decimal degrees) | Longitude (Decimal Degrees) | Disturbance | Stand Origin Date | Stand Age at Sampling | Horizon | pH | % Sand | % Clay | % Silt |
|---|---|---|---|---|---|---|---|---|---|---|
| Harvest 4 | 53.9487 | -104.6451 | Harvest | (2002.000) | (4.000) | Ahe | 4.5 | 94 | 1 | 5 |
| | | | | | | Bm$_1$ | 4.5 | 93 | 1 | 6 |
| | | | | | | Bm$_2$ | 4.4 | 90 | 6 | 4 |
| | | | | | | C | 4.4 | 94 | 4 | 2 |
| Harvest 12 | 53.9080 | -104.6560 | Harvest | (1994.000) | (12.000) | Ahe | 4.5 | 95 | 1 | 4 |
| | | | | | | Bm$_1$ | 4.6 | 96 | 1 | 3 |
| | | | | | | Bm$_2$ | 4.5 | 90 | 4 | 6 |
| | | | | | | C | 4.8 | 95 | 4 | 1 |
| Harvest 31 | 53.8757 | -104.6453 | Harvest | (1975.000) | (31.000) | Ah | 4.4 | 93 | 1 | 5 |
| | | | | | | Bm$_1$ | 4.5 | 91 | 1 | 7 |
| | | | | | | Bm$_2$ | 4.2 | 90 | 4 | 6 |
| | | | | | | C | 5.6 | 96 | 2 | 2 |
| Fire 4 | 53.2257 | -105.9780 | Fire | (2002.000) | (4.000) | Ahe | 4.9 | 92 | 2 | 6 |
| | | | | | | Bm$_1$ | 4.9 | 93 | 1 | 6 |
| | | | | | | Bm$_2$ | 4.7 | 87 | 6 | 7 |
| | | | | | | C | 4.7 | 94 | 4 | 2 |
| Fire 11 | (54.189) | -(104.620) | Fire | (1995.000) | (11.000) | Ae | 5.2 | 87 | 1 | 12 |
| | | | | | | Bm$_1$ | 4.7 | 71 | 2 | 26 |
| | | | | | | Bm$_2$ | 4.6 | 89 | 4 | 8 |
| | | | | | | C | 5.2 | 87 | 4 | 9 |
| Fire 29 | 53.9672 | -104.6387 | Fire | (1977.000) | (29.000) | Ahe | 4.5 | 93 | 1 | 6 |
| | | | | | | Bm$_1$ | 4.4 | 93 | 1 | 6 |
| | | | | | | Bm$_2$ | 4.3 | 90 | 4 | 6 |
| | | | | | | C | 4.5 | 96 | 2 | 2 |
| Fire 91 | 53.9147 | -104.6902 | Fire | (1915.000) | (91.000) | Ahe | 4.9 | 97 | 0 | 2 |
| | | | | | | Bm$_1$ | 5.2 | 98 | 0 | 2 |
| | | | | | | Bm$_2$ | 5.0 | 96 | 1 | 3 |
| | | | | | | C | 5.1 | 96 | 1 | 3 |

Table 2-2. *Total soil organic carbon content (kg m$^{-2}$) for the fire and harvest* jack pine chronosequences. Numbers in parentheses represent one standard deviation from the mean (n=4). Statistical differences between the total content of the sites and between the horizon content of sites with alpha = 0.05.

| Site | Horizon | Depth (cm) | Carbon Content (kgm$^{-2}$) | | |
|---|---|---|---|---|---|
| Harvest 4 | LFH | 1-0 | 0.030 | **c** | (0.007) |
| | Ahe | 0-6 | 1.316 | | (0.480) |
| | Bm$_1$ | 6-18 | 0.571 | | (0.067) |
| | Bm$_2$ | 18-36 | 0.374 | | (0.083) |
| | C | 36-100 | 0.508 | | (0.156) |
| | Total | | 2.799 | | (0.537) |
| Harvest 12 | LFH | 2-0 | 0.575 | **b** | (0.275) |
| | Ae | 0-9 | 0.892 | | (0.378) |
| | Bm$_1$ | 9-18 | 0.511 | | (0.129) |
| | Bm$_2$ | 18-50 | 0.304 | | (0.124) |
| | C | 50-100 | 0.288 | | (0.021) |
| | Total | | 2.570 | | (0.628) |
| Harvest 31 | LFH | 1-0 | 0.356 | **b** | (0.145) |
| | Ahe | 0-6 | 2.123 | | (1.026) |
| | Bm$_1$ | 6-16 | 0.777 | | (0.266) |
| | Bm$_2$ | 16-39 | 0.591 | | (0.261) |
| | C | 39-100 | 0.695 | | (0.263) |
| | Total | | 4.542 | | (1.294) |
| Fire 4 | LFH | 1-0 | 0.056 | **c** | (0.010) |
| | Ahe | 0-10 | 0.852 | | (0.223) |
| | Bm$_1$ | 10-23 | 0.510 | | (0.054) |
| | Bm$_2$ | 23-40 | 0.535 | | (0.258) |
| | C | 40-100 | 0.646 | | (0.087) |
| | Total | | 2.598 | | (0.256) |
| Fire 11 | Ae | 0-10 | 0.977 | | (0.380) |
| | Bm$_1$ | 10-18 | 1.466 | | (1.318) |
| | Bm$_2$ | 18-56 | 0.320 | | (0.066) |
| | C | 56-100 | 1.165 | | (0.792) |
| | Total | | 3.929 | | (1.650) |
| Fire 29 | LFH | 4-0 | 0.691 | **b** | (0.204) |
| | Ahe | 0-7 | 1.159 | | (0.447) |
| | Bm$_1$ | 7-24 | 0.693 | | (0.126) |
| | Bm$_2$ | 24-34 | 0.308 | | (0.070) |
| | C | 34-100 | 0.475 | | (0.065) |
| | Total | | 3.326 | | (0.474) |
| Fire 91 | LFH | 4-0 | 1.020 | **a** | (0.187) |
| | Ahe | 0-10 | 1.039 | | (0.809) |
| | Bm$_1$ | 10-24 | 0.471 | | (0.219) |
| | Bm$_2$ | 24-41 | 0.201 | | (0.050) |
| | C | 41-100 | 0.359 | | (0.124) |
| | Total | | 3.089 | | (0.992) |

Table 2-3. Total organic carbon content (kg $m^{-2}$) for the soil fractions obtained from the Ahe and Bm$_1$ horizons at the fire and harvest jack pine chronosequences. Numbers in parentheses represent one standard deviation from the mean (n =4).

| Site | Horizon | Coarse Sand* | Fine Sand† | Silt‡ | Clay§ | Light Fraction‖ | Sum |
|---|---|---|---|---|---|---|---|
| Harvest 4 | Ahe | 0.628 (0.281) | 0.297 (0.106) | 0.273 (0.110) | 0.073 (0.027) | 0.123 (0.133) | 1.394 (0.133) |
| | Bm$_1$ | 0.150 (0.015) | 0.059 (0.006) | 0.149 (0.032) | 0.100 (0.023) | 0.029 (0.016) | 0.487 (0.016) |
| Harvest 12 | Ae | 0.385 (0.100) | 0.159 (0.041) | 0.161 (0.047) | 0.042 (0.005) | 0.112 (0.081) | 0.860 (0.081) |
| | Bm$_1$ | 0.152 (0.041) | 0.042 (0.005) | 0.097 (0.018) | 0.065 (0.004) | 0.022 (0.006) | 0.379 (0.006) |
| Harvest 31 | Ahe | 0.729 (0.435) | 0.292 (0.150) | 0.242 (0.054) | 0.063 (0.006) | 0.139 (0.089) | 1.464 (0.089) |
| | Bm$_1$ | 0.352 (0.219) | 0.118 (0.056) | 0.117 (0.031) | 0.086 (0.026) | 0.046 (0.014) | 0.720 (0.014) |
| Fire 4 | Ahe | 0.336 (0.076) | 0.139 (0.016) | 0.172 (0.026) | 0.055 (0.010) | 0.085 (0.034) | 0.788 (0.034) |
| | Bm$_1$ | 0.092 (0.011) | 0.064 (0.014) | 0.116 (0.032) | 0.091 (0.008) | 0.039 (0.008) | 0.403 (0.008) |
| Fire 11 | Ae | 0.374 (0.195) | 0.216 (0.128) | 0.113 (0.019) | 0.061 (0.019) | 0.082 (0.014) | 0.846 (0.014) |
| | Bm$_1$ | 0.352 (0.274) | 0.206 (0.148) | 0.572 (0.573) | 0.247 (0.199) | 0.079 (0.062) | 1.457 (0.062) |
| Fire 29 | Ahe | 0.681 (0.316) | 0.262 (0.147) | 0.235 (0.032) | 0.045 (0.010) | 0.132 (0.073) | 1.355 (0.073) |
| | Bm$_1$ | 0.260 (0.077) | 0.072 (0.017) | 0.118 (0.031) | 0.076 (0.016) | 0.058 (0.015) | 0.584 (0.015) |
| Fire 91 | Ahe | 0.530 (0.195) | 0.125 (0.047) | 0.135 (0.041) | 0.023 (0.016) | 0.087 (0.057) | 0.901 (0.057) |
| | Bm$_1$ | 0.223 (0.154) | 0.049 (0.026) | 0.083 (0.045) | 0.025 (0.010) | 0.062 (0.042) | 0.443 (0.042) |

*Coarse sand 250-2000 µm

†Fine sand 53-250 µm

‡Silt 2-53 µm

§Clay <2 µm

‖Light fraction <1 $gcm^{-3}$

Table 2-4. Forest floor and A horizon light fraction CPMAS $^{13}C$ NMR spectra percent integral areas for fire and harvest disturbed jack pine forest soil chronosequences

| Site | Horizon | carbonyl | aromatic | O-alkyl | alkyl | alkyl/O-alkyl | aromatic/O-alkyl |
|---|---|---|---|---|---|---|---|
| Harvest 4 | FF | 11 | 34 | 36 | 19 | 0.54 | 0.94 |
| | Ahe | 18 | 25 | 37 | 20 | 0.53 | 0.67 |
| Harvest 12 | FF | 11 | 12 | 54 | 23 | 0.43 | 0.22 |
| | Ae | 18 | 28 | 33 | 22 | 0.65 | 0.85 |
| Harvest 31 | FF | 10 | 17 | 43 | 30 | 0.68 | 0.38 |
| | Ahe | 15 | 28 | 38 | 19 | 0.51 | 0.74 |
| Fire 4 | FF | 14 | 36 | 28 | 22 | 0.80 | 1.29 |
| | Ahe | 19 | 26 | 40 | 15 | 0.38 | 0.65 |
| Fire 11 | FF | 10 | 54 | 22 | 15 | 0.67 | 2.48 |
| | Ae | 14 | 24 | 46 | 16 | 0.34 | 0.51 |
| Fire 29 | FF | 11 | 26 | 34 | 29 | 0.84 | 0.74 |
| | Ahe | 15 | 32 | 35 | 19 | 0.54 | 0.92 |
| Fire 91 | FF | 9 | 10 | 50 | 31 | 0.61 | 0.21 |
| | Ahe | 18 | 34 | 31 | 17 | 0.55 | 1.10 |

Table 2-5. Total organic carbon content (kg m-2) in forest floor and mineral soils for pine ecosystems across different stand ages. Values are means with standard deviations in parentheses.

| | | Stand age (years) | | | |
|---|---|---|---|---|---|
| Location | Disturbance | 0-5 | 10-19 | 20-35 | > 60 |
| Forest floor | | | | | |
| Saskatchewan[*] | Harvest | 1.24 (0.28) | 1.09 (0.23) | 1.1 (0.36) | 0.86 (0.12) |
| Saskatchewan[†] | Fire | | 0.9 (0.1) | | 1.1 (0.2) |
| Saskatchewan[‡] | Fire | | | (1.810) | 1.46 |
| Michigan[§] | Fire | 0.15 (0.07) | 0.12 (0.05) | 0.38 (0.05) | 1.24 (0.2) |
| Siberia[‖] | Fire | 1.89 (0.58) | 0.70 (0.63) | 1.21 (0.42) | 1.25 (0.32) |
| Mineral soil | | | | | |
| Saskatchewan[*] | Harvest | 2.2 (0.58) | 2.79 (1.34) | 2.78 (1.07) | 2.09 (0.3) |
| Saskatchewan[‡] | Fire | | | 2.02 | (1.420) |
| Michigan[§] | Fire | 2.11 (0.24) | 2.6 (0.26) | 2.21 (0.05) | 2.08 (0.31) |
| Siberia[‖] | Fire | 1.37 (0.31) | 1.72 (0.94) | 0.93 (0.21) | 0.88 (0.11) |

[*] Howard et al. 2004

[†] Nalder and Wein 1999

[‡] Gower et al. 1997

[§] Rothstein et al. 2004

[‖] Wirth et al. 2002

Figure 2-1. Fractionation scheme for separating mineral soil horizons into five fractions: light fraction (< 1 g cm$^{-3}$ of 250–2000 µm); coarse sand (250–2000 µm); fine sand (53-250 µm); silt (2–53 µm), and clay (<2 µm)

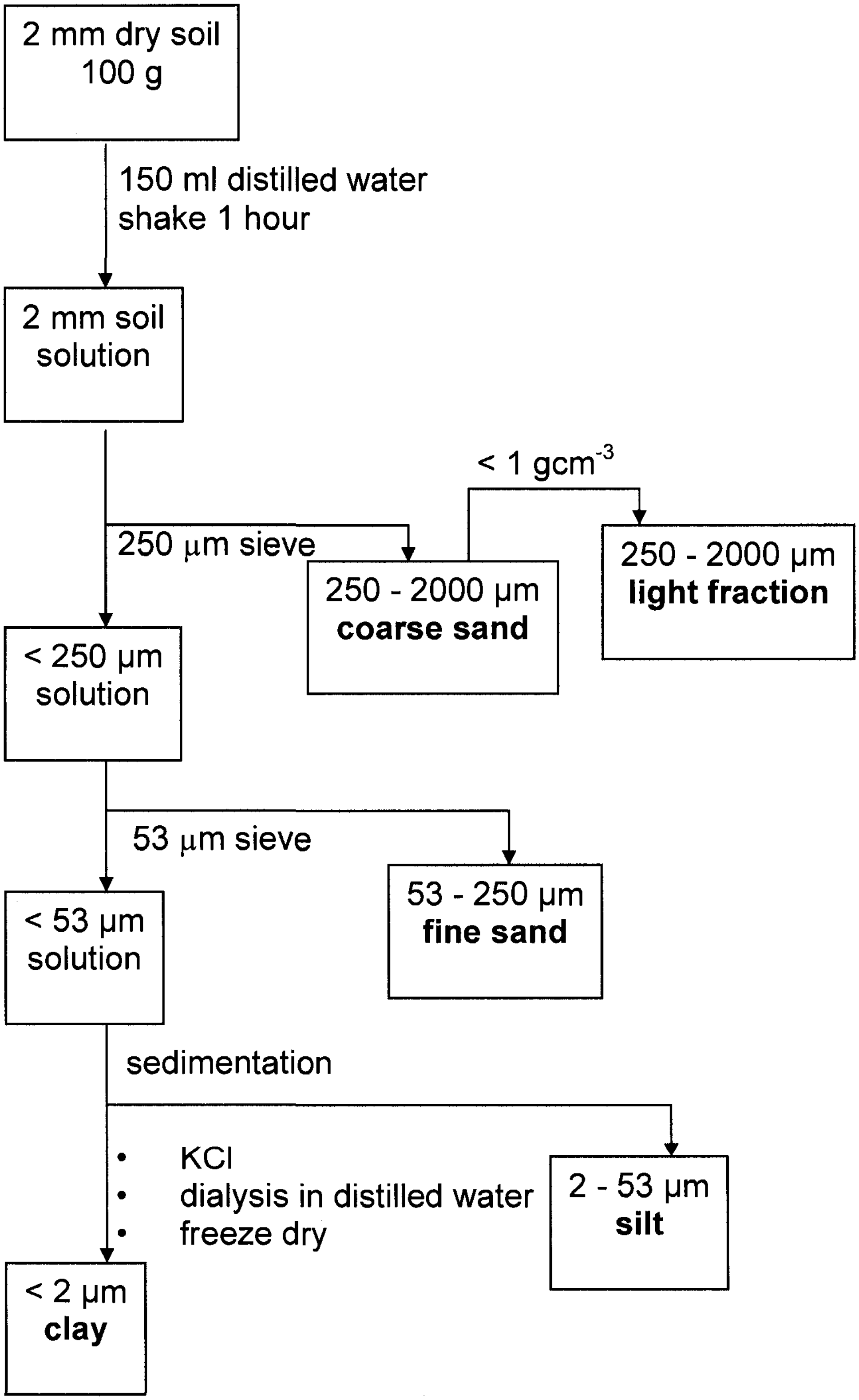


Figure 2-2. Organic carbon concentration (g kg$^{-1}$) in mineral fractions obtained from the A and Bm$_1$ horizons at the fire and harvest jack pine chronosequences. Results are plotted as a function of time since disturbance (years), and error bars represent one standard deviation from the mean (n =4).

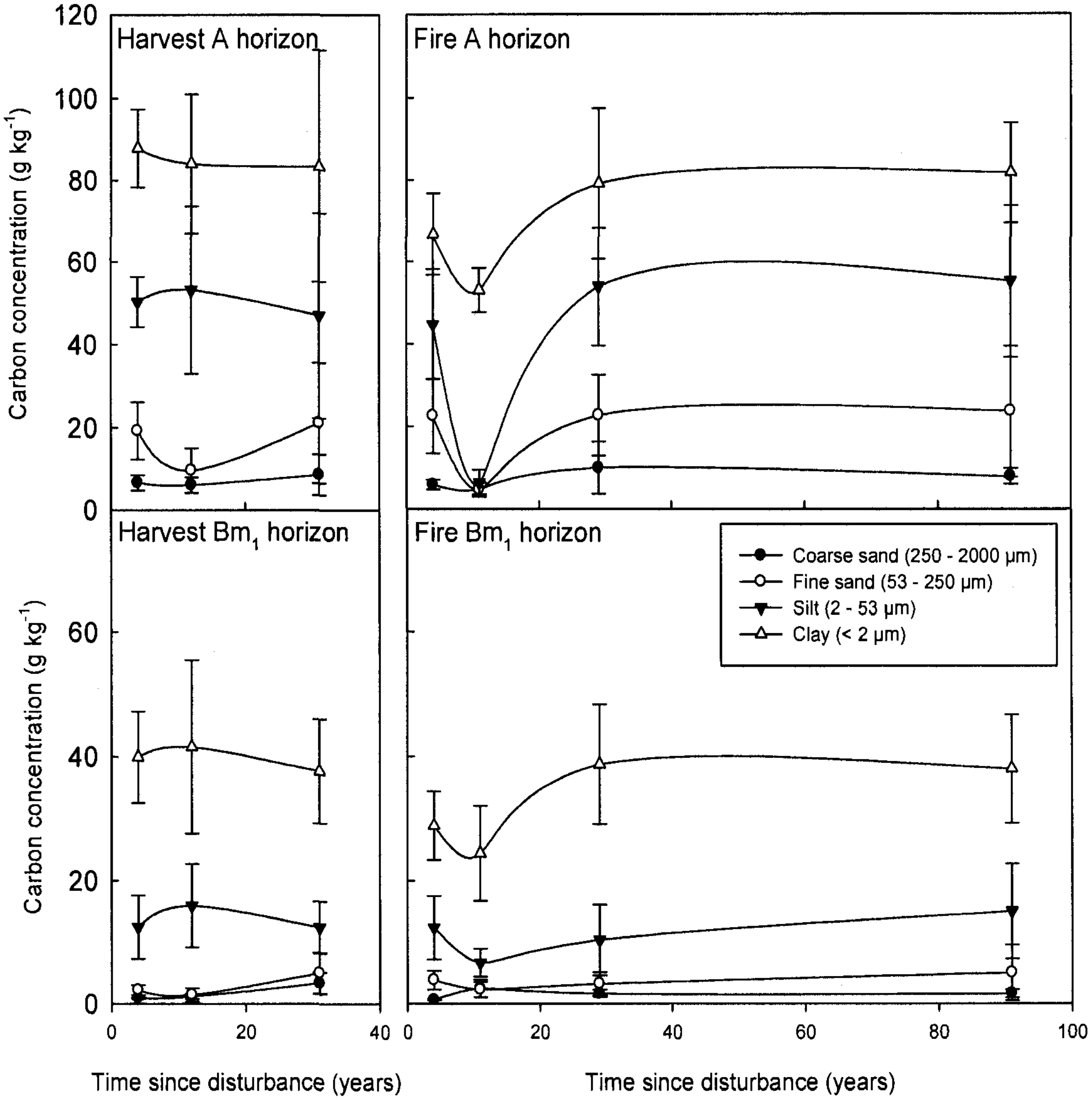


Figure 2-3. Organic carbon distribution (% of total soil carbon) in fractions obtained from the A and Bm$_1$ horizons at the fire and harvest jack pine chronosequences.

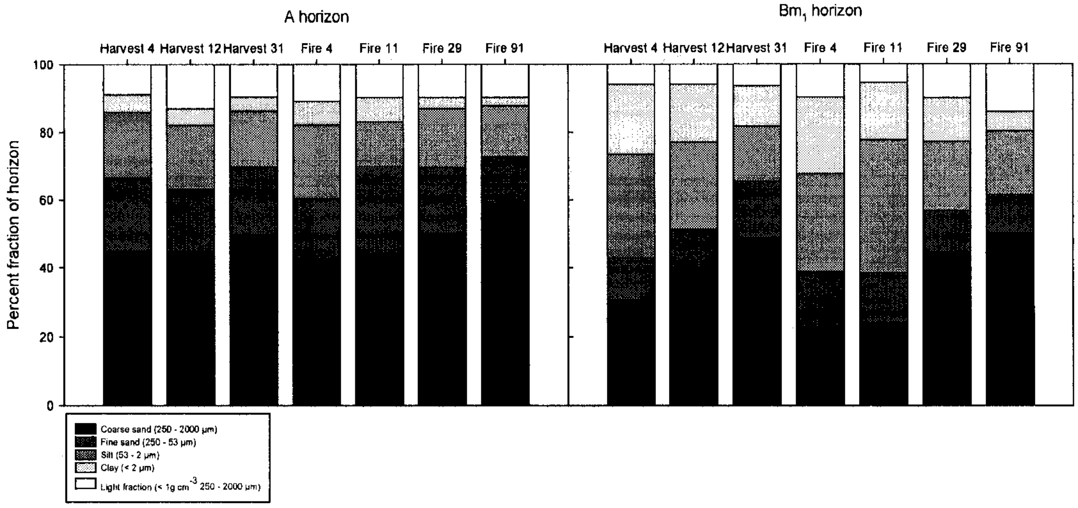


Figure 2-4. Isotopic composition ($\delta^{13}C$) in fractions obtained from the A and Bm$_1$ horizons at the fire and harvest jack pine chronosequences.

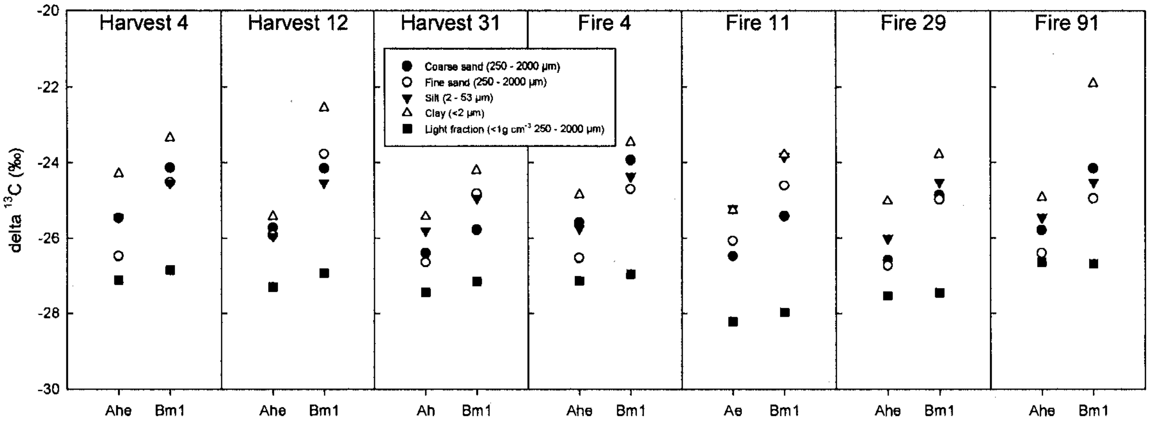


Figure 2-5. Representative CPMAS $^{13}$C NMR spectra of forest floor samples from the fire and harvest jack pine chronosequences.

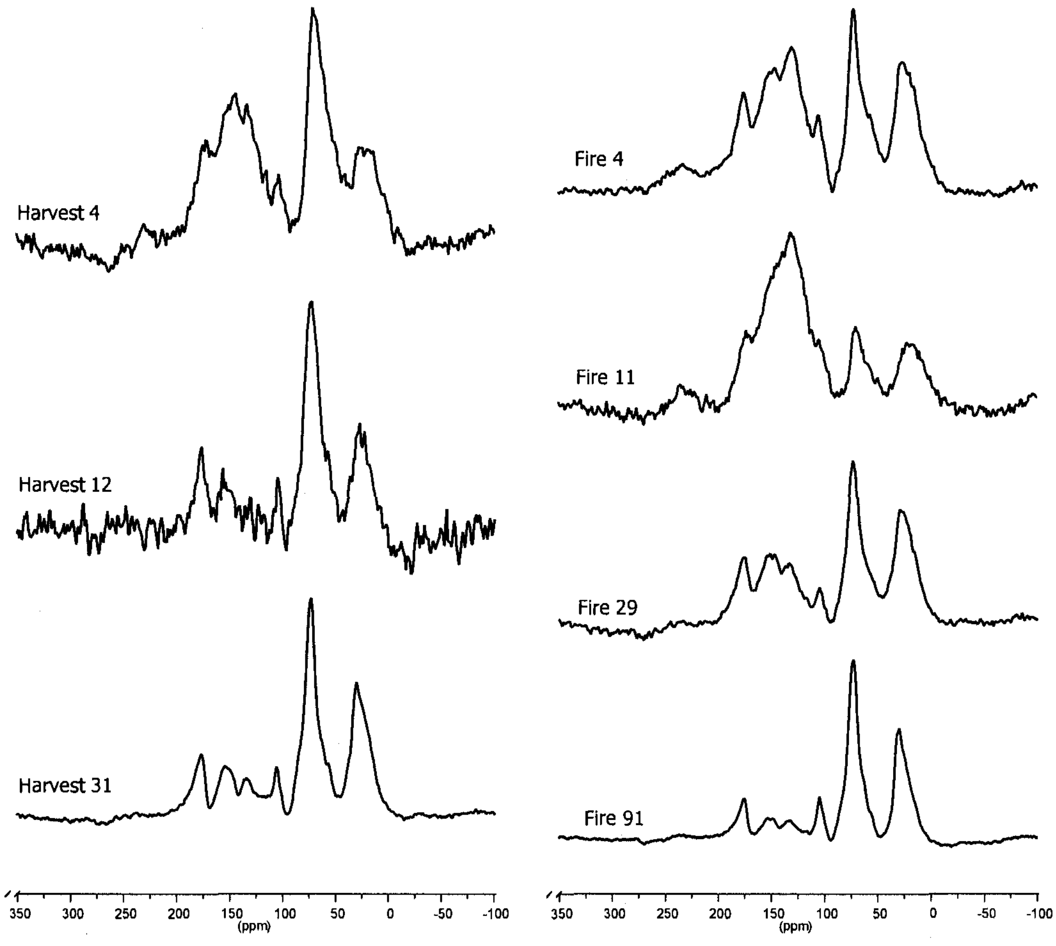


Figure 2-6. Representative CPMAS $^{13}C$ NMR spectra of char physically separated from the Fire 4 forest floor and jack pine roots physically separated from the A horizon of Fire 91.

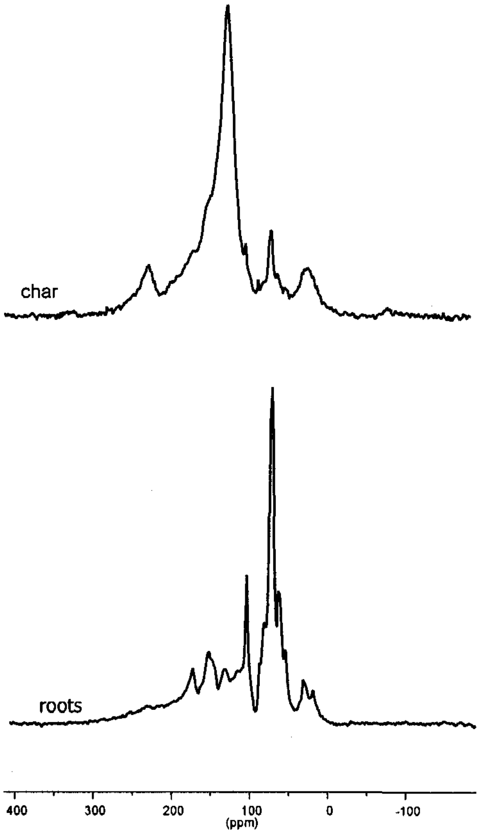
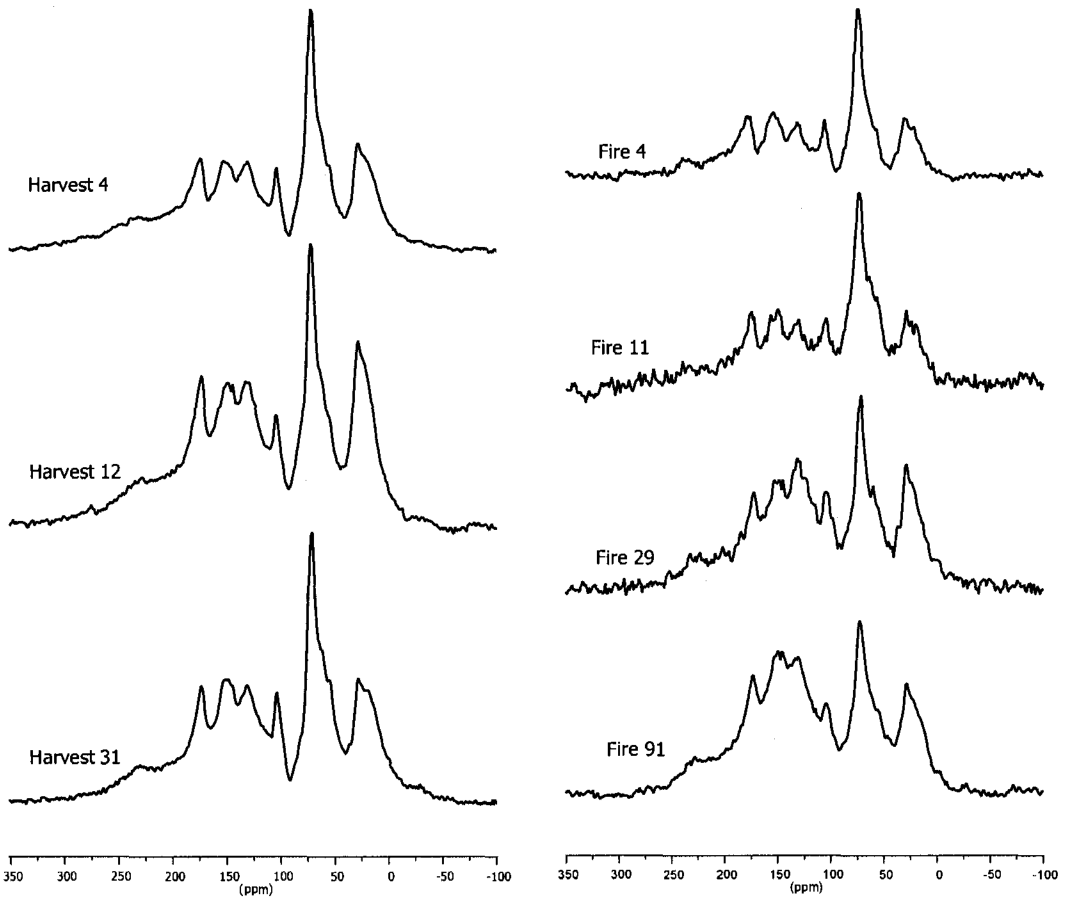


Figure 2-7. Representative CPMAS $^{13}$C NMR spectra of A horizon light fractions obtained from the fire and harvest jack pine chronosequences.



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# Chapter 3 Jack pine soil carbon stabilization along the Boreal Forest Transect Case Study

## Introduction

Global surface temperature is expected to increase 1.8°C to 4.0°C by 2100 with warming to be greater over land than the global average (Meehl et al. 2007). The northern, high latitude, ecosystems are expected to be highly vulnerable to global warming (Fischlin et al. 2007). In North America, the northern regions will experience up to 5°C warming, with most warming in the winter (Christensen et al. 2007). Encircling the northern polar region, the boreal forest lies within the high latitude region and is the second largest forest biome on Earth with an area of $1.37 \times 10^9$ ha (Bhatti et al. 2006). At 290 Gt, the boreal forest contains more than one third of the amount of carbon (C) in the atmosphere and over 10% of the global soil C stocks (Bhatti et al. 2006). Hence C dynamics of these regions may experience greater changes in temperatures and precipitation than southern areas (Apps et al. 2006).

Modeling soil carbon dynamics in order to predict changes in carbon stocks is typically accomplished using three pools with distinct turnover times, namely active or labile, passive and recalcitrant C pools (Collins et al. 2000; Khanna et al. 2001; Trumbore 2000). Soil however is not composed of such finite categories, although the separation into particle size categories imposes some order on this highly heterogeneous matter. For instance, Guggenberger et al. (1995) divided soil into three fractions based upon particle size and reported that sand-sized organic matter was dominated by fresh plant residues, whereas the silt fraction was high in aromatic C and the clay was dominated by microbially derived compounds. Further comparing C between the sand-sized and a light, lower density fraction, Gregorich et al. (1996) found that while the sand sized fraction was a transient C pool with little decomposition, the light fraction showed even less decomposition and was more similar to the original plant inputs. Further study reinforced that the light fraction was less degraded, with carbohydrates mainly derived from plants, and that the heavier fraction was composed of a higher proportion of microbial metabolites (Gregorich et al. 2006; Poirier et al. 2005).

As reported in several reviews of particle size and density fractionation studies, a decreasing C/N ratio represents increased decomposition in soil organic matter (Christensen 1992; Christensen 2001; Khanna et al. 2001; von Lützow et al. 2007). Within fractions, a decrease in C/N ratio is typically observed from the light fraction to the sand, silt and finally clay fraction. In addition to changes in C/N, the isotopic ratio of $^{13}C$ to $^{12}C$ ($\delta\ ^{13}C$) has been proposed as an index of the extent of soil organic matter decomposition (Bird et al. 2002b). Microbes discriminate in their acquisition of the heavier isotope of C as do plants causing litter matter to be initially depleted in $^{13}C$ compared to bulk soil organic matter, but then to become progressively enriched with increasing decomposition. For instance, C isotope distribution determined in a Brown Podzolic soil from the British uplands showed an increase in $\delta\ ^{13}C$ with depth that corresponded to an increase in age, from a $\delta\ ^{13}C$ of -26.7‰ and 6 years in apparent age within the forest floor (LF) layer to -25.4‰ and 4098 years in the first B horizon (Bol et al. 1999). Increased depth and decomposition in soils not only increases $\delta\ ^{13}C$ but also enriches $\delta\ ^{15}N$, which may provide another indicator of decomposition in organic C (Tiunov 2007). For example, soil particle size separates under two different types of vegetation displayed $^{15}$N isotopic enrichment compared to the original litter, increasing from the light (2‰) to the clay (3.5‰) fraction (Quideau et al. 2003).

Not only do the C/N ratio and isotopic values vary among size fractions, but so does C turnover time. As reviewed by von Lützow et al. (2007), turnover times derived from $\delta$ $^{13}$C values range from 0.5 to 374 years for sand, 115 to 676 years for silt, and 76 to 190 years for clay fractions, while reported mean residence times based on $^{14}$C are 800-1660 for silt and 75-4409 years for clay separates. Therefore, physical fractionation of soil based on particle size may lead to C pools with distinct turnover times. Clay with its well decomposed microbially derived organic matter and long residence time is a passive to recalcitrant pool. Similarly, organic C associated with silt has long turnover times and is included in the passive pool as the C, enriched in plant derived aromatics, is chemically stabilized to the silt-size particles. Finally, the labile pool encompasses the sand-sized organic matter as well as the light fraction as neither has a means of protecting or stabilizing the C. This labile C pool greatly resembles plant inputs and provides a means of monitoring relatively rapid changes in soil organic matter following variations in land use or management practices (Gregorich et al. 2006).

The alkyl/O-alkyl ratio determined from cross polarization magic angle spinning $^{13}$C nuclear magnetic resonance (CPMAS NMR) provides a means of monitoring changes in the chemical composition of the labile C pool (Baldock and Preston 1995). CPMAS NMR provides a semi-quantitative examination of the macromolecular chemistry of the C where the resulting spectra are divided into different C types and the peaks along with their integral areas describe the form, or the relative decomposition, of C. An increasing alkyl/O-alkyl ratio demonstrates increased decomposition where O-alkyl C from labile carbohydrates is preferentially decomposed when compared to alkyl C from more recalcitrant moieties such as waxes.

The boreal forest landscape is typically dominated by spruce, fir, larch, birch/aspen or pine stands. Pine stands colonize the upland coarse texture fluvial outwash sites of the boreal with Scots pine (*Pinus sylvestris*) in the Russian taiga (Wirth et al. 2002) and the Fennoscandia landscape while in Canada jack pine (*Pinus banksiana* Lamb.) dominates. These jack pine stands may be particularly sensitive to temperature and moisture variations due to the xeric conditions under which they grow (Rudolph and Laidly 1990). In the comparison of a jack pine stand, two black spruce forest types, and a fen in the boreal forest of northern Manitoba , soil C was found to have the shortest turnover time within the jack pine site (Trumbore and Harden 1997). Halliwell and Apps (1997) noted that mineral soil C and detrital C stocks for aspen and jack pine stands were greater in northern than in southern sites along an ecoclimatic gradient in central Canada. The authors attributed the difference to decreased decomposition due to cooler temperatures in the northern region. Specific processes of soil C stabilization in these stands however were not analyzed.

With the high latitude boreal forest expected to experience greater than average global surface temperature warming by 2100, knowledge on the influence of warming on the soil C dynamics in this forest is critical. This is particularly important since the boreal forest by itself stores ≥ 10% of the global C stocks. In an effort to elucidate how climate may affect boreal forest C stocks, the objective of this study was to characterize soil organic C stocks and stabilization processes along a climate transect of jack pine stands.

## Materials and methods

### Study sites and sampling design

The jack pine transect is part of the Boreal Forest Transect Case Study (BFTCS) project (Price and Apps 1995). The BFTCS is one of the transects identified in the Global Change and Terrestrial Ecosystems (GCTE) Core Project of the International Geosphere-Biosphere Programme (Koch et al. 1995). The BFTCS was originally initiated to study the effect of climate and disturbance on C stocks in representative stand types of the Canadian boreal forest, i.e., trembling aspen (*Populus tremuloides* Michx.), black spruce (*Picea mariana* (Mill.) BSP) and jack pine (Bhatti et al. 2002). The transect is aligned with an ecoclimatic gradient (Ecoregions Working Group 1989) and spans several major vegetation biomes – proceeding in a northeast direction from the aspen parkland transition to the boreal forest biome and into the sparsely treed subarctic tundra (Figure 3-1).

Along the BFTCS, climatic conditions change from warm and dry in the southwest to cold and wet in the northeast. The general thermal and moisture patterns from four climate stations (Thompson, Flin Flon, Prince Albert, and Saskatoon) are similar, but show large moisture deficiency at the southern stations, especially during the spring and fall seasons, with generally increasing precipitation and decreasing temperatures northeastward. Mean annual temperature (MAT) on the transect ranges from 0.5°C in the south to -5.0°C in the north, with mean annual precipitation (MAP) ranging between 400 and 550 mm, again from south to north (Price and Apps 1995).

For this study, four sites supporting pure mature jack pine stands were sampled in 2006 along the BFTCS. These sites represented the different ecoclimatic regions with

PJM2 in the parkland to low boreal transition near Prince Albert, STOJP in the mid boreal region, FJM3 in the high boreal near Flin Flon and NTOJP further north in the high boreal near Thompson MB (Table 3-1).

Reindeer lichen (*Cladina* spp.), with patches of bearberry (*Arctostaphylos uva-ursi*) and moss (*Pleurozium* spp.), dominated the ground cover at all the jack pine sites, with the occasional green alder (*Alnus crispa*) spread throughout the stand. All sites were located on level terrain. At each site, four random soil profiles were excavated within a 200 m radius. One profile was fully characterized, while the three others were examined for horizon sequence and depth. The soil of the northern site, NTOJP, is derived from glaciolacustrine parent material deposited by Glacial Lake Agassiz while that of FJM3, STOJP and PJM2 are of glaciofluvial origin. All soils were classified as Eluviated Dystric Brunisols according to the Canadian System of Soil Classification (Soil Classification Working Group 1998).

Approximately 1.5 kg of sample was collected from each mineral horizon (A, $Bm_1$, $Bm_2$ and C) at each soil profile for a total of 4 samples per horizon from each site. Forest floor samples were also collected randomly in a 5 m radius around each pit. Samples were transported to the laboratory within 4 days of collection, where they were immediately air dried, sieved to 2 mm and stored in air tight containers until further analysis.

### Physical fractionation scheme

Each mineral soil sample collected was fractionated using a combination of density and wet sieving techniques. Methodology was amended from a variety of sources

(Christensen 1992; Christensen 2001; Preston et al. 2000a; Quideau et al. 2000; Six et al. 2002) to yield the following five fractions: light (< 1 g $cm^{-3}$) 250–2000 μm fraction; coarse sand (250–2000 μm); fine sand (53-250 μm); silt (2–53 μm), and clay (<2 μm). Specifically, fractionation of each sample began by adding 150 ml of distilled water to each of eight 100 g subsamples and placing these on a reciprocal shaker for one hour. Each sample was then wet sieved through a 250 μm and 53 μm mesh. The > 250 μm sample was immersed in distilled water for vacuum filtration of the light fraction and separation from the coarse sand fraction. The <53 μm solution was further separated by sedimentation (8 hours for every 10 cm of suspension) into the silt and clay fractions. All > 2 μm fractions were dried in a forced air oven overnight with a temperature ≤ 40 °C. The remaining (< 2 μm) suspension was flocculated with potassium chloride (KCl), with subsequent removal of KCl by dialysis tubing (Fisherbrand Nominal MWCO 12 000 – 14 000), and freeze-dried using a FreeZone 6 Liter Dryer (Labconco Corporation, Kansas City MO). All fractions were then weighed to calculate their relative distribution, as well as particle size distribution among sand (>53 μm), silt (2-53 μm), and clay (< 2 μm) fractions (Table 3-1). Average sample recovery was over 99%.

**Laboratory analyses**

Each horizon of the fully characterized pit at each site was analyzed for pH with an Ag/AgCl pH electrode, using a soil to 0.01 M calcium chloride solution ratio of 1:2, and a settling time of 30 minutes (Kalra and Maynard 1991). Whole (unfractionated) soil samples from each pit as well as all five fractions were homogenized, finely ground using a ball mill grinder (Retsch MM200, Retsch Inc. Newtown PA), and encapsulated prior to total C determination by dry combustion using a Costech ECS 4010 Elemental Combustion System with a thermocouple detector (Costech Analytical Technologies Inc. Valencia CA). This yielded a total of 400 C analyses, i.e., (5 horizons * 4 pits * 4 sites) + (5 fractions * 4 horizons* 4 pits * 4 sites).

Dissolved organic carbon (DOC) content (kg $m^{-2}$) for a horizon was determined as the difference between whole soil C content ($C_W$) for the horizon and the sum of the C content of the individual fractions ($C_{F,}$), from the same horizon:

$$[1] \qquad DOC = C_W - C_F$$

where $C_W$ and $C_F$ were further calculated using:

$$[2] \qquad C_W = \frac{\left[ \sum_i W_i d_i \rho * 0.01 \right]}{n_i}$$

and:

$$[3] \qquad C_F = \frac{\left[ \sum_i F_i d_i \rho * 0.01 * x \right]}{n_i}$$

where W is the carbon concentration (mg $g^{-1}$) for the undivided soil horizon, F is the carbon concentration (mg $g^{-1}$) for a given soil fraction, d represents the depth (cm) of the soil horizon, and $\rho$ is the soil density (g $cm^{-3}$). The proportion of the fraction to the whole horizon is given as x. As there were four pits per site, and therefore replicate samples of each horizon, the average value was determined where n is the number of replicate horizons per site and i represents each of the horizons.

C enrichment ($C_e$) is an index of comparison for C concentrations between isolated fractions from different soils which removes the effects of varying soil organic C levels (Christensen 1992). The factor for the soil fractions ($C_e$) was determined using the formula:

$$[4] \qquad C_e = \frac{F}{W}$$

The five fractions obtained from each horizon at each pit were composited by horizon and site prior to C isotopic composition determination. The isotopic composition of these composite samples was measured on a Costech ECS 4010 Elemental Analyzer (Costech Analytical Technologies Inc., Valencia, CA USA) coupled to a Finnigan Deltaplus Advantage Isotopic Ratio Mass Spectrometer (ThermoFinnigan, Bremen Germany). Results were expressed in the δ-notation, the ‰ variation from the standard Pee Dee Belemnite (PDB) reference material:

$$\delta^{13}C = \left(\frac{R_{Sample}}{R_{S\tan dard}} - 1\right) \times 1000$$

by using BMO (-23.91‰), CS (-12.5‰), NBS 1575N (-26.3‰,), and Red Clover (-27.42‰) as working standards.

Samples of the forest floor and light fractions composited by site were used for CPMAS $^{13}$C NMR analysis; however there was insufficient sample for the C horizon of PJM2 and STOJP. Individual samples of jack pine needles, jack pine roots and lichen collected from STOJP were also analyzed by NMR. Spectra were acquired on a Varian Chemagnetics CMX 200 [$B_0 = 4.70$ T, $\nu_L(13C) = 50.3$ MHz] spectrometer with a 7.5 mm double – resonance MAS probe with high-power $^1$H decoupling. Samples were loaded into a 7.5 mm OD zirconium oxide rotor with drive tips of Kel-F, and end caps and spacers made of Teflon (DuPont, Circleville, OH). Spectra were referenced to TMS (0 ppm) by setting the high frequency adamantane peak to 38.56 ppm. A total of 6000 transients were acquired for each spectrum with a 5.0 kHz spinning rate, a 1 ms contact time, and a 2 s recycle time. Processing of the FID was performed with the MNova's MestReC 5.0 software (Mestrelab Research SL, Spain. 2007). Processing the spectra included zero filling, line broadening of 50 Hz with phase and baseline correction followed by integration within specific regions of the area under the peaks.

It is recognized that CPMAS $^{13}C$ NMR is a semi-quantitative analytical technique. Since polarization is transferred from protons to carbons, for the contact time (1ms) used to acquire the spectra presented here, carbons lacking directly bonded hydrogen may be underrepresented (Smernik et al. 2002). However, given that spectra were acquired under similar laboratory conditions, this is a systematic error and the results between different spectra are comparable. In this study, we chose a conservative approach and divided the acquired spectra into regions based on broad C bonding types to allow for poor signal to noise ratios and resolution of peaks (Baldock and Preston 1995). Thorough descriptions of peak identification and assignments previously published were used to classify the following four regions (Baldock and Preston 1995; Kögel-Knabner 1997; Kögel-Knabner 2002; Preston et al. 1998; Simpson and Preston 2007): alkyl (0-47 ppm), O-alkyl (47-112 ppm), aromatic and phenolic (112-165 ppm), and carbonyl (165 – 215 ppm).

### Statistical analysis

Soil organic C contents for the forest floor and the total content of the sites were statistically compared for differences among sites. These data were normally distributed and were analyzed using a one-way analysis of variance (ANOVA) and a post-hoc test of

Fisher's least significant difference (LSD) with an α of 0.1. All analyses were run using Systat 11 (Systat Software Inc., USA. 2004).

## Results

### Soil organic carbon content

Forest floor (LFH) C content at PJM2 (0.2 kg $m^{-2}$) was significantly less ($p<0.084$) than at the other three sites (Table 3-2). Forest floor C content then increased from south to north with the largest quantity present at NTOJP with 1.4 kg $m^{-2}$, although there was no significant difference among STOJP, FJM3 and NTOJP. Content within the entire soil profile (0 – 1 m) was also significantly less for PJM2 at 1.72 kg $m^{-2}$ ($p<0.088$). The STOJP, FJM3 and NTOJP soil profiles were not statistically different in overall C content but similarly to the forest floor layers, increased along the jack pine transect with increasing latitude, from PJM2 to 59% more C at NTOJP (4.18 kg $m^{-2}$). The C horizon at NTOJP was striking in that it held the most content of the mineral soil horizons and held a content more than double that of the other C horizons (Figure 3-2).

No statistical difference was found in C contents among the sites when determined by the sum of the content of fractions for each horizon, but as with whole horizon analysis, C content tended to increase along the transect (Table 3-2). Excluding the forest floor, C content was 1.37 kg $m^{-2}$ at PJM2, 1.78 kg $m^{-2}$ at STOJP, and, 2.32 kg $m^{-2}$ at FJM3, although the northern most site, NTOJP, showed a slight decrease from FJM3 with 1.89 kg $m^{-2}$.

C content values for the whole soil (0-1 m) and the sum of the fractions were plotted against each other in Figure 3-3 where the difference in C contents between the two, with the content by sum of fractions always less, was believed to be due to the loss of DOC during the fractionation procedure. This difference was incorporated with the C contents of the fractions to represent the proportional contribution of each fraction to the overall soil C content in Figure 3-4. There was little difference between whole soil content and the sum of the fractions for PJM2 (0.1 kg $m^{-2}$) while the other sites exhibited greater differences in content, namely 0.29 kg $m^{-2}$ for STOJP and 0.24 kg $m^{-2}$ for FJM3. The largest difference in C content between the two methods was for NTOJP with 0.87 kg $m^{-2}$ accounted for as DOC (Figure 3-3). These differences in content for NTOJP were apparent in all horizons however the greatest discrepancy was 0.52 kg $m^{-2}$ in the C horizon. As for NTOJP, half of the DOC at FJM3 was from the C horizon with the remainder from the other subsoil mineral horizons.

Soil C stocks at the southern sites (PJM2 and STOJP) mostly derived from the coarse sand sized fraction (Figure 3-4). However at the northern sites (FJM3 and NTOJP), in addition to the coarse sand, silt was an important contributor. The A horizon contained the greatest quantity of C in the southern sites. Results from the fractionation exercise revealed that almost half of the C content in the A horizon was contained within the coarse sand fraction, and this reached 64% if the fine sand was included. Yet, at the northern sites, less than 34% of the total C content was accounted for in the coarse sand. For the northern sites, C content was greatest in the $Bm_1$ horizon, where, at NTOJP, the main contribution was split between the silt and coarse sand fraction. The silt sized fraction provided the greatest proportion of C at FJM3.

### Ratios and enrichments of soil carbon fractions

Carbon enrichment was greatest in the light fractions when compared to the silt and clay fractions, and values increased with increasing depth in the soil profiles (Figure 3-5). Both the silt and the clay fractions also increased in enrichment with increasing depth through the soil profile, where clay was always greater in ratio than silt. Not only did enrichment of the fine fractions increase with depth but the spread in ratio between the silt and clay fractions also increased.

Forest floor C/N ratios ranged between 18 at PJM2 and STOJP, to 37 at FJM3 and 41 at NTOJP (Figure 3-6). The soil fractions ranged in C/N values from 2 to 65, with the largest ratios observed in the light fractions. These ratios then decreased with decreasing particle size from sand to silt and finally clay. Although ratios in the A horizons were relatively small (i.e.; <30) in both the silt and clay fractions when compared to the light fractions, they still both decreased with increased depth within the soil profiles to below 14 in the C horizons. While the rate of decrease in ratio for the fine fractions was similar across PJM2, STOJP and NTOJP, the spread of the values differed for NTOJP. Specifically, both the silt (13 – 16) and clay (12 – 14) fractions showed the smallest variations in ratio among all horizons. Alternatively, and contrary to all other fractions, ratios for the light fractions increased with depth in the soil profiles and this pattern was most pronounced at NTOJP. Furthermore, and again in opposition to the fine fractions, the light fractions at NTOJP exhibited the greatest variation in C/N between the A and the C horizons. Finally, the sand fractions did not display any consistent trend as they showed no difference among horizons of different sites or in the ratios themselves other than a general decrease with depth (data not shown).

The isotopic ratios of $^{13}C$ to $^{12}C$ (‰) ranged from -28.3 ‰ in the light fraction of the PJM2 C horizon to -21.6 ‰ for the fine sand fraction of the $Bm_2$ horizon at NTOJP (Figure 3-7). Within a given horizon, ratios were always smallest for the light fractions, followed by the silt, and then the clay fractions. Enrichment also occurred for the mineral fractions from the A to the C horizon except for the coarse sand where the $\delta\ ^{13}C$ of the C horizon was less than that of the $Bm_2$. This also held true for the fine sand fractions at the NTOJP and FJM3 sites (data not shown). In general, values for the sand fractions did not show any consistent trend with depth, but fell somewhere within the same range as the other fractions (fine sand -27.4 to -21.6 ‰ and coarse sand -25.6 to -22.2 ‰). A noticeable feature was the steady linear progression of enrichment from the A to the C horizon for the fine (< 53 μm) fractions, one that was more rapid for PJM2 than for NTOJP (Figure 3-7). Light fractions were an exception to this observed enrichment with increasing depth as their $\delta\ ^{13}C$ values did not vary at NTOJP, FJM3 or STOJP, and only minimally at PJM2.

The range in $^{15}N$ isotopic values for this data set span - 4.4‰ to 9.2‰ (Figure 3-8). The greatest enrichment from the A to the C horizon in the fine (< 53 μm) fractions occurred in the silt fraction at PJM2 (6.7‰), while at NTOJP enrichment was <1‰ for the same fraction. Coarse sand-sized fractions were the most depleted in $^{15}N$ ($\leq$1.0‰), with the fine sand and light fractions having similar values while silt and clay were the most enriched in the heavier isotope ($\geq$ 2.2‰). Both the silt and clay sized fractions increased in $\delta^{15}N$ values with increasing depth in the soil profile, yet the sand fractions followed the opposite trend and decreased with depth. At NTOJP, the light fraction (2.69

– 1.14‰) and fine sand (2.52 – -0.21‰) both showed a similar decreasing trend in $^{15}N$ with depth.

**NMR analysis of forest floor and light fraction carbon**

All of the CPMAS $^{13}C$ NMR spectra (Figure 3-9) showed six main peaks and were typically dominated by the O-alkyl C region with a sharp peak at 73 ppm from the C2, C3 and C5 carbons of cellulose (Baldock and Preston 1995). The O-alkyl region which generally exhibited the largest of the spectra integral areas, was greatest for the forest floor and least for the A horizon samples (Table 3-3). Within the O-alkyl C region, a strong peak from the C1 carbon of crystalline cellulose was apparent on all spectra at 105 ppm (Kögel-Knabner 1997; Vane et al. 2006), although the peak did merge with the aromatic area on the A and $Bm_2$ spectra of STOJP and in the FJM3 A horizon.

Alkyl C, at 30 ppm (Baldock and Preston 1995), presented the second highest peak across all spectra, except for FJM3 where in the A horizon it was the tallest (Figure 3-9). Other than for the A horizon at FJM3, the greatest integral area for the alkyl region was in the forest floor (Table 3-3). The alkyl area then decreased with increasing depth through the mineral soil horizons. There was little evidence of peak splitting for methyl and ethyl carbons from the long chain alkyl C compounds (Vane et al. 2006) but for the northern sites in the B and C horizons.

Aromatic C was the region that varied the most among intensity in the different spectra. Light fractions of the A and $Bm_2$ horizons at STOJP and of the A horizon at FJM3 were unique among samples as the aromatic region was the largest of the four integral areas (Figure 3-9, Table 3-3). Two defined peaks on the spectra were around

130 and 150 ppm. Lignin, from the C1 and C2 of guaiacyl monomeric units in gymnosperms, can give rise to a peak at 131 ppm (Kögel-Knabner 2002) while C3 and C4 from guaiacyl may cause peaks at 148 and 151 ppm (Kögel-Knabner 2002; Vane et al. 2006). The peak at 130 ppm may also be attributed to black C (Preston and Schmidt 2006). The intensity of the aromatic region was least in the forest floor and varied through the mineral soil horizons. Some peak splitting was evident in the 150 ppm region of the A horizon at NTOJP, otherwise, the aromatic region was generally represented by the two broad peak shapes.

The integral area representing carbonyl C was a sharp peak throughout all spectra and may have derived from hemicellulose (Vane et al. 2006) or cutin (Preston et al. 2000b) carboxyl, amide or ester C. The proportion of carbonyl C in a spectrum was least in the forest floor for all sites, except for FJM3 where it reached a minimum in the C horizon, and increased to between 11 and 19% for the light fractions of the mineral soil. Finally, the alkyl/O-alkyl ratio was calculated as an index of decomposition of the labile C pool for the forest floor and light fractions (Table 3-3). For STOJP and FJM3 the greatest alkyl/O-alkyl ratio was found in the forest floor while for PJM2 and NTOJP it was for the A horizon. In the deeper mineral soil horizons (i.e.; $Bm_1$, $Bm_2$ and C), the light fraction ratios varied from 0.27 to 0.43 with no apparent increase with increasing soil depth or any major change along the transect.

## Discussion

### Soil organic C content along climate transects

The soil C content, including the forest floor, at NTOJP (4.2 kg $m^{-2}$) and STOJP (3.1 kg $m^{-2}$) were both greater than values reported by Trumbore and Harden (1997) for NTOJP (2.9 kg $m^{-2}$), Gower et al. (1997) for NTOJP (3.73 kg $m^{-2}$) and STOJP (2.87 kg $m^{-2}$), and Howard et al. (2004)for STOJP (2.95 kg $m^{-2}$). While all values included forest floor C, the integrated depth varied from 70 cm in Gower et al. (1997) to 80 cm in Trumbore and Harden (1997) and 1 m in Howard et al. (2004). With such variation in depth and inherent variability in forest floor C, the larger values here were not unexpected. STOJP, with a forest floor content of 1.0 kg $m^{-2}$, was similar to the content for forest floor reported for central Saskatchewan (1.1 kg $m^{-2}$) while NTOJP was greater (1.4 kg $m^{-2}$) than that for a central Manitoba jack pine stand (0.9 kg $m^{-2}$) (Nalder and Wein 1999).

Soil C content was statistically less (1.7 kg $m^{-2}$) at PJM2, the southern site, than at the northern sites of FJM3 (3.9 kg $m^{-2}$) and NTOJP (4.2 kg $m^{-2}$). The soil organic carbon (C) content, although not statistically different, increased as mean annual temperature (MAT) decreased and the mean annual precipitation (MAP) increased along the transect from PJM2 to NTOJP (Table 3-2). Results were in agreement with what was reported for the BOREAS sites in Halliwell and Apps (1997). Similarly a black spruce climate gradient in Alaska increased in mineral soil organic C content with decreasing number of growing degree days (Kane et al. 2005). Instead of changing latitude, variation in elevation also has been used to study the effects of MAT and MAP on soil C dynamics. For a climosequence in Brazil, the soil organic C content increased as the elevation increased which corresponded to decreased temperature and increased humidity (Dalmolin et al. 2006). In the Sierra Nevada range of California, the lowest soil C content was found at the base of the hillside with content increasing upslope as the temperature fell; the maximum content was observed at mid-elevation (Trumbore et al. 1996). In contrast to the results above and to what is reported in Table 3-2, soil organic C along a Scots pine latitudinal gradient in Eastern Europe was found to be greatest in the southern sites, where temperature and precipitation were the greatest (Vucetich et al. 2000). In Sweden, C sequestration decreased from the warm and moist southwest to the north (Akselsson et al. 2005), and in a survey of coarse textured Nordic soils the soil organic C again decreased from the south to the decreased MAT and MAP in the north (Callesen et al. 2003). Finally, a north-south transect in Canada, with the greatest temperature and precipitation again in the south, also showed C content decreasing northward (Bird et al. 2002a). Results from these studies on C content and MAT were mixed. However, when the MAP or moisture and humidity were included with the MAT data the greatest C content always corresponded to the area with the greatest moisture.

### Stabilization of soil organic carbon along the jack pine transect

With increasing latitude along the transect, not only did the forest floor content increase but the C content in the B and C soil horizons increased as well (Table 3-2). This increase in deep mineral soil C content was likely due to the transport of DOC as results of the fractionation scheme indicated that the contribution of DOC to soil C was greatest for the C horizon at NTOJP (Figures 3-3 and 3-4). The contribution of leached organic C to jack pine deep mineral soil C has previously been noted (Trumbore and Harden 1997).

The proportion of C content in the coarse sand varied by soil horizon but was always highest in the C horizon, except at NTOJP (Figure 3-4). From 22% to 64% of the C content was associated with the sand sized fractions while light fraction C ranged from 1% to 23%. The estimated proportion of dissolved organic C (DOC) for each horizon was up to 51%. In reviews by Christensen (1992) and von Lutzow (2007) of soil fractionation studies in cultivated temperate soils, C content from the sand size fractions never exceeded 25% of the whole soil content. Our results then represent an unusually high proportion of organic C associated with the sand fraction. The difference could be due to the coarser texture of the studied soils and the cool boreal climate.

The C enrichment factors ($C_e$) increased with depth for the four sites in the clay, silt and light fractions (Figure 3-5). The enrichment factor, when used to compare the C distribution in silt and clay fractions among different soils has never been reported to exceed 11(Christensen 1992). However for our study sites, the degree of enrichment was unusually higher, as it ranged from 8 to 85 for the clay and from 4 to 50 for the silt fractions. This indicated the increased importance of the clay and silt sized particles in holding C at depth in these sandy soils. A further interesting feature of these data was how the spread between the silt and clay enrichment factors increased through the soil profiles. Increased decomposition with depth would increase the C concentration of both the silt and clay fractions thus increasing their $C_e$ while the decrease in C concentration for the whole horizon through the profile would accentuate the enrichment. Therefore the C associated with silt and clay fractions at depth may be more stabilized and plentiful than that near the surface.

The C/N ratios indicated a gradient of increasing decomposition from the light (>35) to the sand (<40) fractions, which subsequently decreased with decreasing particle size (silt and clay <20) as has been previously reported (Christensen 2001). Decomposition also increased with depth in the profiles as evidenced by decreasing ratios from the forest floor in to the mineral soil fractions (Figure 3-6). Furthermore, the rate of decrease in C/N ratio for the fine (silt and clay) fractions was greater in the south. Therefore, decomposition seemed to more readily occur in the organic matter of PJM2 and STOJP.

With enrichment in $^{15}$N and $^{13}$C from the A horizon through to the $Bm_2$ in the isotopic data, the light fraction C at the southern sites may be speculated to be more decomposed than at the northern sites. While at FJM3 and NTOJP, $^{13}$C did not change from the A to C horizon and $^{15}$N decreased (Figure 3-7 and 3-8). For the sand sized fractions there was enrichment in $^{13}$C with depth, and $\delta^{15}$N values decreased, but neither showed a clear trend along the transect. A slight climate trend however was evident in the range of isotopic ratios for the clay and silt fractions. The range between the A and C horizons of the silt fraction was greater for both $^{15}$N (6.7‰) and $^{13}$C (2.8‰) at PJM2 than at NTOJP (1.0‰ and 1.0‰). Isotopic results hence provide further evidence, along with the C/N ratios, that the organic matter of the southern sites undergoes more decomposition than in the north.

The general trend in $\delta^{13}$C isotopic composition of the organic C seemed to be a greater isotopic enrichment with depth in the south when compared to the northern sites. An isotopic enrichment with depth was also measured in central Siberian Scots pine soils where $^{13}$C increased from -26.75‰ within the 0 – 5 cm layer to -22.8‰ at 45 – 60 cm where enrichment was attributed to microbial degradation (Bird et al. 2002b). Across a north – south transect in western Canada soil was separated into size fractions and analyzed for $\delta^{13}C$ and, as with results here, $^{13}C$ increased with decreasing particle size with the silt and clay sized fractions more enriched in $^{13}C$ than either the coarse (>2000 μm) or 63-2000 μm fraction (Bird et al. 2002a). In terms of the effect of climate, in a survey of surface soils from different latitudes, Bird et al. (1996) determined that the $\delta^{13}C$ increased with increasing latitude, a trend which was attributed to either temperature effects, forest type or different rates of incorporation of atmospheric $CO_2$ into the soils. Similar results were also found for a north – south transect in western Canada (Bird et al. 2002a) and in Alaska (Kane et al. 2005). In contrast, our results did not demonstrate enrichment with latitude. However, our results were from soil fractions and not, as in the other studies, of the whole soil.

To determine how the light fraction and other fractions relate to possible litter inputs, jack pine needles, jack pine roots and lichen from the forest floor of STOJP were analyzed for their C/N ratio and $\delta^{13}C$ and $\delta^{15}N$ (Table 3-4). Previously needle litter from the same location was reported at 144 and the forest floor itself was 41 (Preston et al. 2006) both higher than results here. However our needles (45) were collected from the forest floor and were not recent litter fall therefore likely more decomposed. The forest floor C/N of 18 may also have resulted from differing sampling methodologies. From the same study jack pine needle litter from STOJP was measured at $\delta^{13}C$ -27.9‰ and $\delta^{15}N$ -4.0‰, nearly identical to values reported here ($\delta^{13}C$ -27.8‰ and $\delta^{15}N$ -3.8‰), while at NTOJP the needles were slightly more depleted in $^{13}C$ with -28.1‰ and enriched in $^{15}N$ -3.5‰ (Preston et al. 2006). The forest floor meanwhile was enriched compared to the needle input at $\delta^{13}C$ -27.3‰ and $\delta^{15}N$ -2.7‰ for STOJP and -27.5‰ and -1.4‰ for NTOJP (Preston et al. 2006). The measured isotopic ratios of jack pine needles, roots and lichen from STOJP, and the forest floor from the previous study, were all possible litter inputs to the light fraction as the light fraction was comparatively enriched in $^{13}C$. An anomaly was the C horizon at PJM2 which was more depleted in $^{13}C$ than any of the measured inputs with a $^{13}C$ of -28.3‰.

## Macromolecular chemistry of labile organic carbon along the jack pine transect

Tannin, with its distinctive peak splitting at 145 and 155 ppm (Preston et al. 2000b), is known to be present in jack pine needles (Nierop et al. 2005). However our CPMAS $^{13}C$ NMR spectra showed no evidence of this double peak. Rather, lignin dominated the input to the aromatic region (Figure 3-9) with its peaks at 130 ppm and 148 ppm (Kögel-Knabner 2002). As for the A and $Bm_2$ horizons from STOJP, and the A horizon from FJM3, the aromatic region of the light fraction also appeared to have an intense aromatic area around 130 ppm derived from black C (Czimczik et al. 2002; Preston and Schmidt 2006).

Contrary to reports of increasing alkyl/O-alkyl ratio with increasing depth in the soil profile (Alarcón-Gutiérrez et al. 2008; Baldock and Preston 1995; Quideau et al. 2000), calculated ratios in our study were greater in either the forest floor (STOJP and FJM3 soils) or the A horizon (PJM2 and NTOJP soils). Two proposed theories for the accumulation of alkyl C and therefore an increased alkyl/O-alkyl ratio include: 1. the hydrophobic properties of alkyl C (Baldock et al. 2004) where the microbial breakdown of organic matter increases alkyl C by selective preservation compared to the preferential decomposition of more labile moieties such as carbohydrates, and 2. byproduct generation and microbial synthesis of alkyl compounds (Christensen 2001). Both the selective preservation (Nierop et al. 2001) and the microbial synthetic activities (Kögel-Knabner et al. 1992) were shown to accumulate alkyl C with depth in the soil profile. Yet data from our study indicated that there was neither preservation nor increase in alkyl C content with increasing depth, hence suggesting that the light fractions did not display increased decomposition with depth.

Lichen, one of the two main litter inputs to the forest floor, was composed almost solely of O-alkyl C, and the second input, jack pine needles, was high in alkyl C but low in aromatic C (Figure 3-10 and Table 3-5). The forest floor spectra were low in both aromatic and carbonyl C but high in O-alkyl intensity, in agreement with inputs, while the A horizon spectra were greater in aromatic region and almost double in carbonyl region. This may indicate that the A horizon C was of a more decomposed form than the forest floor. With decomposition an increase in alkyl intensity from the forest floor to the A horizon would be expected however FJM3 was the only site to show this. Perhaps the addition of fresh inputs of a different composition, such as roots which are low in alkyl C but high in O-alkyl and aromatic C, would account for the decrease in alkyl C.

Root input alone would account for the integral areas in the B and C horizons, except for $Bm_2$ at STOJP which showed the influence of char inputs. Jack pine roots had 8% of alkyl C, half the amount contained in needles (17%). Yet the B and C horizons contained 13-18% alkyl C, therefore the increase was likely due to microbial byproducts or to selective preservation of the alkyl C. While the alkyl/O-alkyl ratio for roots was 0.15, much lower than any of the light fractions, the area associated with aromatic C was surprisingly consistent. For needles the average aromatic intensity was 19% and about 24% for roots. The light fractions for the B and C horizon were between 17% and 36% with all but two of the samples above 23% in aromatic intensity. Aromatic C has been discussed and shown to be less palatable to the microbial community and will therefore accumulate or not decrease in proportion relative to O-alkyl C (Dalmolin et al. 2006; Quideau et al. 2000). Therefore the $Bm_1$ and $Bm_2$ and C horizons appeared to owe most of the organic C to jack pine roots while the forest floor was of aboveground biomass, jack pine needles and lichen, and the A horizon showed the addition of roots to a decomposed form of the forest floor.

Minimal change in the C chemistry of the light fraction of the $Bm_1$, $Bm_2$ and C horizons of NTOJP was in contrast to PJM2 which showed greater decomposition. STOJP had the highest above ground biomass (Preston et al. 2006), was the second warmest and was also the highest in alkyl/O-alkyl ratio for the forest floor while NTOJP, with the lowest MAT and aboveground biomass, had the lowest forest floor ratio. Therefore the forest floor and light fractions of the northern colder and moister site were composed of organic C that had undergone little decomposition as compared to the southern sites. These same trends were noted in a Brazilian climosequence where the O-alkyl C decreased from the colder and humid conditions to the warmer sites (Dalmolin et al. 2006).

### Implications under changing climate on jack pine soil organic carbon

In sandy soils with no evidence of bioturbation, root matter was found to be an important part of soil organic matter (Nierop 1998). An average taproot length of 60 cm, and a maximum length of 2.7 m, was observed in sandy soils of mature jack pine trees in Saskatchewan before the roots forked or divided into rootlets (Rowe and Acton 1985). However, within the jack pine stands of the NTOJP and STOJP sites, roots were found to concentrate in the upper 10 cm of soil (Steele et al. 1997). As low temperatures favor the production of below ground biomass (Oades 1988), significantly more fine root biomass (< 2 mm) was noted at NTOJP than at STOJP (Steele et al. 1997). At STOJP, 2%, or 0.16 kg $m^{-2}$, of the total C biomass was comprised of fine root (< 2 mm) biomass (Kalyn and Van Rees 2006). This is comparable to the sum of the light fractions (0.178 kg $m^{-2}$) that was measured for STOJP in our study (Table 2). In addition to a similar mass for the light fraction and roots at STOJP, the macromolecular chemistry, as discussed above, strongly suggested that the light fraction from the B and C horizon resulted from root inputs and that roots were also an important input to the A horizon. Therefore these results indicate that much of the organic C of the light fractions derived from roots.

During the fractionation conducted for this study, water solutions of the deeper mineral horizons at the northern sites were of a much darker color than those from the south (personal observation). Several studies have determined that sorption of DOC occurs most strongly in the deeper mineral horizons of sandy soils (Guggenberger and Kaiser 2003; Moore 2003). For instance, in a Spodosol, organic C sorption decreased in the following order BS2>C>BS1>Bh>E (Ussiri and Johnson 2004). DOC may derive from plant tissues and decomposing soil organic matter (Moore 2003) where it is an intermediate of organic matter decomposition that may degrade to humified material or alternatively be respired as $CO_2$ (Guggenberger et al. 1994). Comparing different plant tissue types in the Douglas fir forest of the Cascade Mountains in Oregon, fine roots were found to produce more water extractable DOC than comparable needles or wood litter (Yano et al. 2005). Percolation of DOC from roots, needles and litter were all potential sources for the DOC observed at depth in this study.

Since MAT at STOJP is higher than at NTOJP, and since soil temperature (5 cm) for that site does not fall below -5°C, the minimum allowable temperature for soil respiration (Clein and Schimel 1995), for more than one month of the year (Preston et al. 2006), it is easy to conclude that there is increased soil respiration and hence decomposition at STOJP when compared to NTOJP. If a soil sample from NTOJP were translocated to STOJP a loss of C would be likely, perhaps as occurred with a Scots pine soil that was translocated from Jädraås (Sweden) to Haldon (UK) (Bottner et al. 2000). There, with the 7°C increase in temperature and a doubling in precipitation, the Scots pine soil decreased in total C by about 15% as compared to the control (Bottner et al. 2000).

Although the C content was greatest in the northern sites of our transect, from the chemical data, it is also evident that the C present was of a less decomposed and more labile form than within the southern sites. In a Finland Scots pine latitude transect, the water soluble extracts from the forest floor, the most labile fraction of C, were also highest in concentration in the north; yet the overall stocks were greater in the south where the climate was moister and warmer (Hilli et al. 2008). Higher amounts of labile C in the soil organic matter were found at the northern end of a climosequence for both the tundra heath and mountain birch systems of Norway (Sjögersten et al. 2003). Finally, within a black spruce transect with the wetter and cooler temperatures to the north in

Alaska, the amount of labile C in mineral soil organic matter was found to decrease with increased temperature and stand productivity (Kane et al. 2005).

Macromolecular chemical results discussed above indicate that aboveground biomass contributed to the C contained in the forest floor and the A horizon. However the largest contributions to C content of the deeper mineral horizons came from three additional sources, namely roots, DOC and black C. The quantity of C in the soil was greatest at NTOJP, the most northerly site, and the C associated with that site was of an undecomposed, highly labile form. On the other hand, C content at PJM2, the southernmost site, was statistically the least and was of a less labile form. The total stocks and nature of C in these jack pine soils therefore appear to be dependent on climatic factors, with the C likely more decomposed, i.e. stabilized at the southern sites. Therefore if the projected 5°C warming of the northern latitudes does occur, then these data suggest that the northern soils will become a larger source of $CO_2$ than the more southerly ones.

## Conclusions

Soil organic C content was statistically less at PJM2, the most southerly site, and content increased going northeast with cooler and moister conditions. These results are in agreement with previous studies on the same transect and in agreement with many other transect studies where increasing C content was associated with increasing moisture or MAP. Labile C dominated the type of C present at the northern site, whether it was in the form of DOC or undecomposed roots, forest floor or light fraction. While C contained within the sand fractions was the dominant soil pool at PJM2, it was of a comparatively more decomposed nature than at the more northerly sites. While litter inputs did not greatly vary across sites, the macromolecular chemistry of soil C did, thus indicating differences with regards to the degree of decomposition. If the MAT were to increase in the northern boreal forest, these results suggest that while the overall jack pine soil C stocks would decrease, the remaining C would become more humified, and likely more stabilized than what is currently present within the soils.

Table 3-1: Site characteristics and general soil properties of a jack pine forest soil transect

| Site Identification | Stand Origin Date | Region | Latitude (Decimal degrees) | Longitude (Decimal Degrees) | MAT (°C) | MAP (mm) | Horizon | pH | % Sand | % Clay | % Silt |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PJM2 | 1927 | Prince Albert | 53.2256 | -105.9436 | 0.50 | 398 | Ahe | 4.8 | 97.7 | 0.6 | 1.7 |
| | | | | | | | Bm$_1$ | 5.1 | 98.0 | 0.5 | 1.5 |
| | | | | | | | Bm$_2$ | 5.5 | 98.7 | 0.4 | 0.9 |
| | | | | | | | C | 4.9 | 98.0 | 0.5 | 1.4 |
| STOJP | 1915 | Candle Lake | 53.9147 | -104.6902 | 0.25 | 440 | Ahe | 4.9 | 97.3 | 0.4 | 2.2 |
| | | | | | | | Bm$_1$ | 5.2 | 97.6 | 0.3 | 2.1 |
| | | | | | | | Bm$_2$ | 5.0 | 96.2 | 0.6 | 3.2 |
| | | | | | | | C | 5.1 | 96.0 | 0.6 | 3.1 |
| FJM3 | 1933 | Flin Flon | 54.8400 | -102.5127 | -0.50 | 474 | Ahe | 3.9 | 97.8 | 0.2 | 2.0 |
| | | | | | | | Bm$_1$ | 4.7 | 98.5 | 0.1 | 1.2 |
| | | | | | | | Bm$_2$ | 5.2 | 97.8 | 0.2 | 1.9 |
| | | | | | | | C | 5.2 | 98.0 | 0.2 | 1.6 |
| NTOJP | 1936 | Nelson House | 55.9283 | -98.6218 | -3.50 | 544 | Ae | 4.3 | 97.1 | 0.3 | 2.6 |
| | | | | | | | Bm$_1$ | 4.9 | 97.0 | 0.5 | 2.4 |
| | | | | | | | Bm$_2$ | 5.3 | 96.0 | 0.6 | 3.3 |
| | | | | | | | C | 5.3 | 97.5 | 0.3 | 2.1 |

Table 3-2: Total soil organic carbon content (kg m$^{-2}$) for a jack pine transect. Numbers in parentheses represent one standard deviation from the mean (n = 4). Different letters indicate statistical differences in total carbon content among horizons with alpha = 0.10.

| Site | Horizon | | Whole | | Coarse Sand | Fine Sand | Silt | Clay | Light Fraction | Sum of Fractions |
|---|---|---|---|---|---|---|---|---|---|---|
| PJM2 | LFH | 2-0 | 0.23 (0.09) | y | | | | | | |
| | Ahe | 0-6 | 0.54 (0.24) | | 0.26 (0.03) | 0.08 (0.04) | 0.07 (0.02) | 0.03 (0.01) | 0.05 (0.02) | 0.49 (0.09) |
| | $Bm_1$ | 6-14 | 0.31 (0.09) | | 0.07 (0.03) | 0.03 (0.02) | 0.05 (0.01) | 0.04 (0.01) | 0.04 (0.02) | 0.24 (0.06) |
| | $Bm_2$ | 14-31 | 0.24 (0.04) | | 0.13 (0.01) | 0.02 (0.01) | 0.04 (0.01) | 0.05 (0.01) | 0.03 (0.03) | 0.27 (0.03) |
| | C | 31-100 | 0.40 (0.10) | | 0.24 (0.08) | 0.01 (0.01) | 0.05 (0.03) | 0.07 (0.02) | 0.01 | 0.37 (0.15) |
| | Total | | 1.71 (0.09) | b | | | | | | 1.37 (0.13) |
| STOJP | LFH | 4-0 | 1.02 (0.19) | z | | | | | | |
| | Ahe | 0-10 | 1.04 (0.81) | | 0.53 (0.20) | 0.12 (0.05) | 0.14 (0.04) | 0.02 (0.02) | 0.10 (0.07) | 0.92 (0.33) |
| | $Bm_1$ | 10-24 | 0.47 (0.22) | | 0.21 (0.13) | 0.05 (0.03) | 0.08 (0.05) | 0.03 (0.01) | 0.07 (0.05) | 0.43 (0.25) |
| | $Bm_2$ | 24-41 | 0.20 (0.05) | | 0.06 (0.05) | 0.01 (0.01) | 0.04 (0.02) | 0.03 (0.01) | 0.01 (0.01) | 0.14 (0.04) |
| | C | 41-100 | 0.36 (0.12) | | 0.16 (0.05) | 0.02 (0.01) | 0.05 (0.02) | 0.06 (0.03) | 0.00 (0.00) | 0.29 (0.08) |
| | Total | | 3.09 (0.50) | ab | | | | | | 1.78 (0.63) |
| FJM3 | LFH | 3-0 | 1.37 (0.38) | z | | | | | | |
| | Ahe | 0-8 | 0.74 (0.22) | | 0.25 (0.07) | 0.14 (0.04) | 0.15 (0.05) | 0.04 (0.02) | 0.18 (0.15) | 0.75 (0.24) |
| | $Bm_1$ | 8-34 | 1.17 (0.49) | | 0.24 (0.07) | 0.11 (0.05) | 0.36 (0.13) | 0.00 (0.01) | 0.24 (0.18) | 0.95 (0.40) |
| | $Bm_2$ | 34-61 | 0.31 (0.09) | | 0.18 (0.12) | 0.01 (0.01) | 0.05 (0.02) | 0.02 (0.01) | 0.03 (0.01) | 0.28 (0.11) |
| | C | 61-100 | 0.46 (0.07) | | 0.24 (0.01) | 0.01 (0.00) | 0.06 (0.04) | 0.03 (0.02) | 0.01 (0.00) | 0.35 (0.02) |
| | Total | | 3.93 (0.26) | a | | | | | | 2.33 (0.25) |
| NTOJP | LFH | 6-0 | 1.41 (0.71) | z | | | | | | |
| | Ae | 0-23 | 0.62 (0.55) | | 0.21 (0.22) | 0.06 (0.04) | 0.10 (0.07) | 0.05 (0.05) | 0.09 (0.10) | 0.52 (0.47) |
| | $Bm_1$ | 23-30 | 0.75 (0.51) | | 0.21 (0.14) | 0.08 (0.07) | 0.20 (0.15) | 0.12 (0.10) | 0.05 (0.02) | 0.66 (0.47) |
| | $Bm_2$ | 30-39 | 0.42 (0.25) | | 0.07 (0.07) | 0.04 (0.02) | 0.09 (0.05) | 0.04 (0.04) | 0.02 (0.03) | 0.26 (0.17) |
| | C | 39-100 | 0.98 (0.31) | | 0.12 (0.13) | 0.09 (0.04) | 0.16 (0.07) | 0.08 (0.06) | 0.03 | 0.46 (0.18) |
| | Total | | 4.18 (0.47) | a | | | | | | 1.90 (0.54) |

Table 3-3: Forest floor and light fraction CPMAS $^{13}C$ NMR spectra percent integral areas for a jack pine forest soil transect

| Site | Horizon | carbonyl | aromatic | O-alkyl | alkyl | alkyl/o-alkyl |
|---|---|---|---|---|---|---|
| PJM2 | FF | 8 | 15 | 52 | 24 | 0.47 |
| | Ahe | 17 | 27 | 38 | 19 | 0.50 |
| | $Bm_1$ | 18 | 20 | 43 | 18 | 0.43 |
| | $Bm_2$ | 18 | 24 | 44 | 14 | 0.32 |
| STOJP | FF | 9 | 10 | 50 | 31 | 0.61 |
| | Ahe | 18 | 34 | 31 | 17 | 0.55 |
| | $Bm_1$ | 18 | 27 | 39 | 15 | 0.39 |
| | $Bm_2$ | 17 | 36 | 34 | 13 | 0.39 |
| FJM3 | FF | 10 | 15 | 53 | 22 | 0.42 |
| | Ahe | 19 | 28 | 27 | 26 | 0.96 |
| | $Bm_1$ | 14 | 25 | 44 | 17 | 0.40 |
| | $Bm_2$ | 18 | 24 | 42 | 16 | 0.39 |
| | C | 7 | 28 | 48 | 17 | 0.36 |
| NTOJP | FF | 9 | 16 | 56 | 19 | 0.35 |
| | Ahe | 16 | 27 | 39 | 18 | 0.45 |
| | $Bm_1$ | 11 | 17 | 56 | 15 | 0.27 |
| | $Bm_2$ | 15 | 23 | 48 | 14 | 0.30 |
| | C | 14 | 25 | 47 | 13 | 0.29 |

Table 3-4: Isotopic composition ($^{13}C$ and $^{15}N$ ) and C/N ratios from jack pine needles, jack pine roots and lichen (*Cladina* sp.).

| Sample | C/N | $\delta^{13}C$ (‰) | $\delta^{15}N$ (‰) |
|---|---|---|---|
| needles | 44.8 | -27.76 | -3.85 |
| roots | 92.6 | -26.8 | -1.2 |
| lichen | 100.8 | -25.49 | -5.6 |

Table 3-5: Percent integral areas of CPMAS $^{13}C$ NMR spectra for jack pine needles, jack pine roots and lichen (*Cladina* sp.)

| Sample | carbonyl | aromatic | O-alkyl | alkyl | alkyl/o-alkyl |
|---|---|---|---|---|---|
| needles | 13 | 19 | 52 | 17 | 0.33 |
| roots | 12 | 24 | 55 | 8 | 0.15 |
| lichen | 4 | 1 | 89 | 6 | 0.06 |

Figure 3-1. Location and major ecological zonations of jack pine sites on the Boreal Forest Transect Case Study.

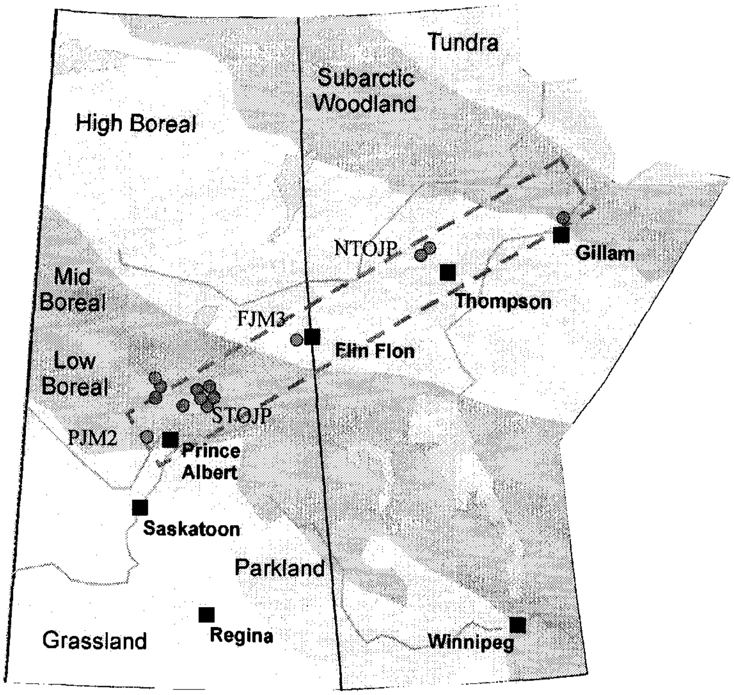


Figure 3-2. Organic C content (kg $m^{-2}$) along a jack pine transect from PJM2 in the southwest to NTOJP in the northeast.

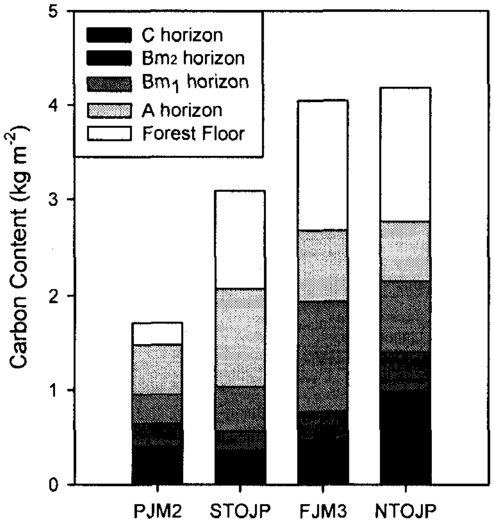


Figure 3-3. Total soil C content (kg $m^{-2}$) by site for a jack pine forest transect either by whole horizon (x axis) or by the sum of the fractions across all horizons. If the values were equal the point would fall on the regression line (1:1).

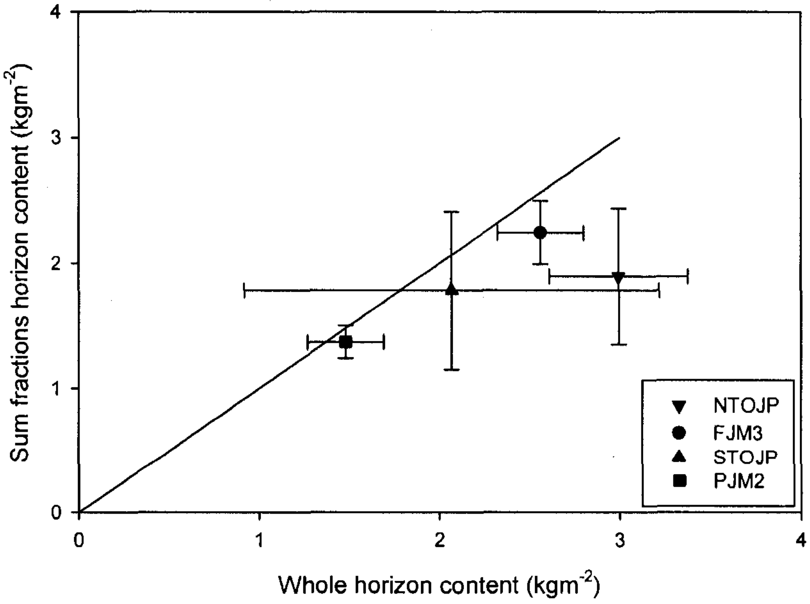


Figure 3-4. Organic C distribution (% of total soil carbon) in fractions obtained from the A, $\mathrm{Bm}_1$, $\mathrm{Bm}_2$ and C horizons of a jack pine forest transect.

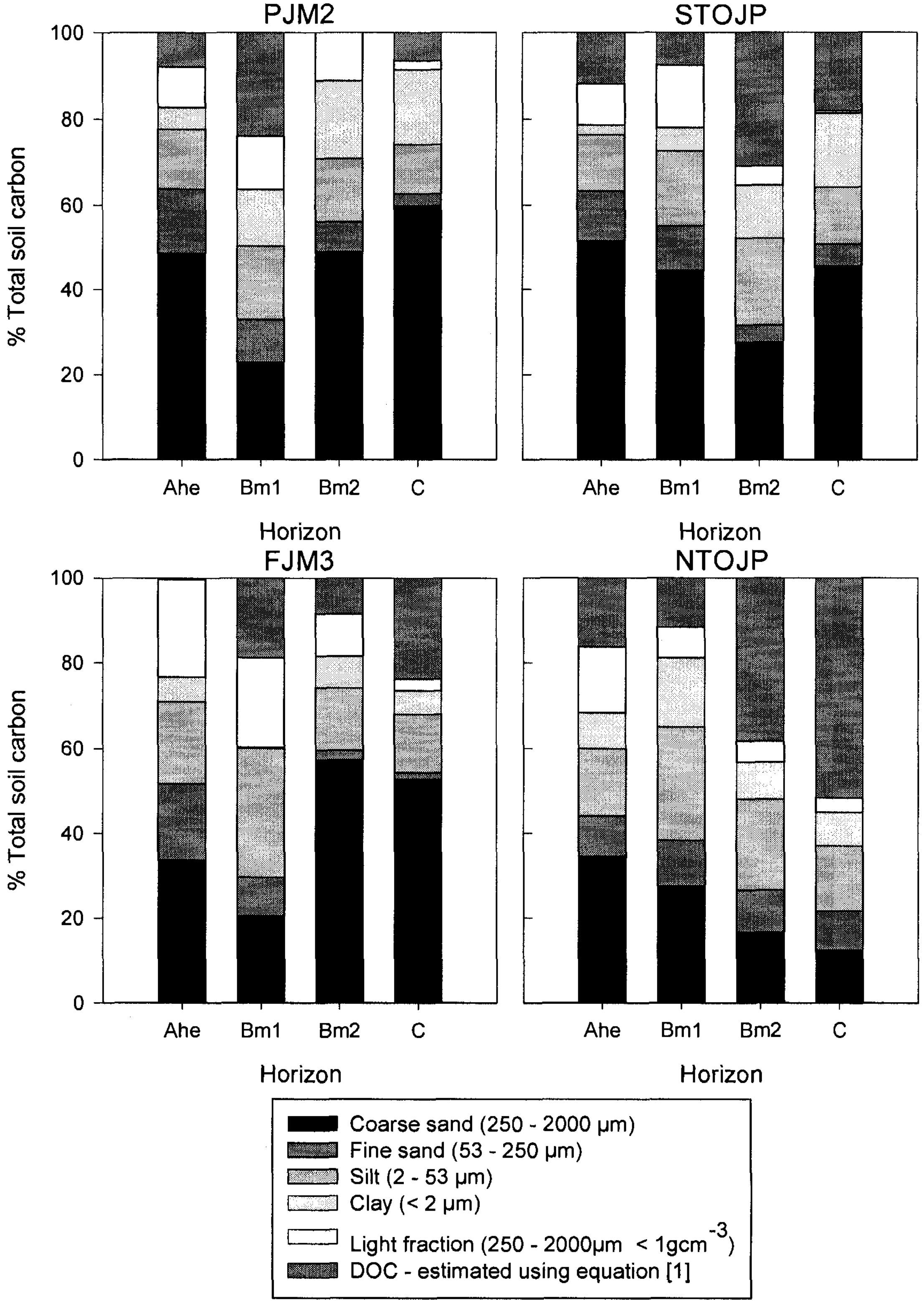


Figure 3-5. C enrichment ($C_e$) in silt, clay and light fractions obtained from the A, $Bm_1$, $Bm_2$ and C horizons of a jack pine forest transect.

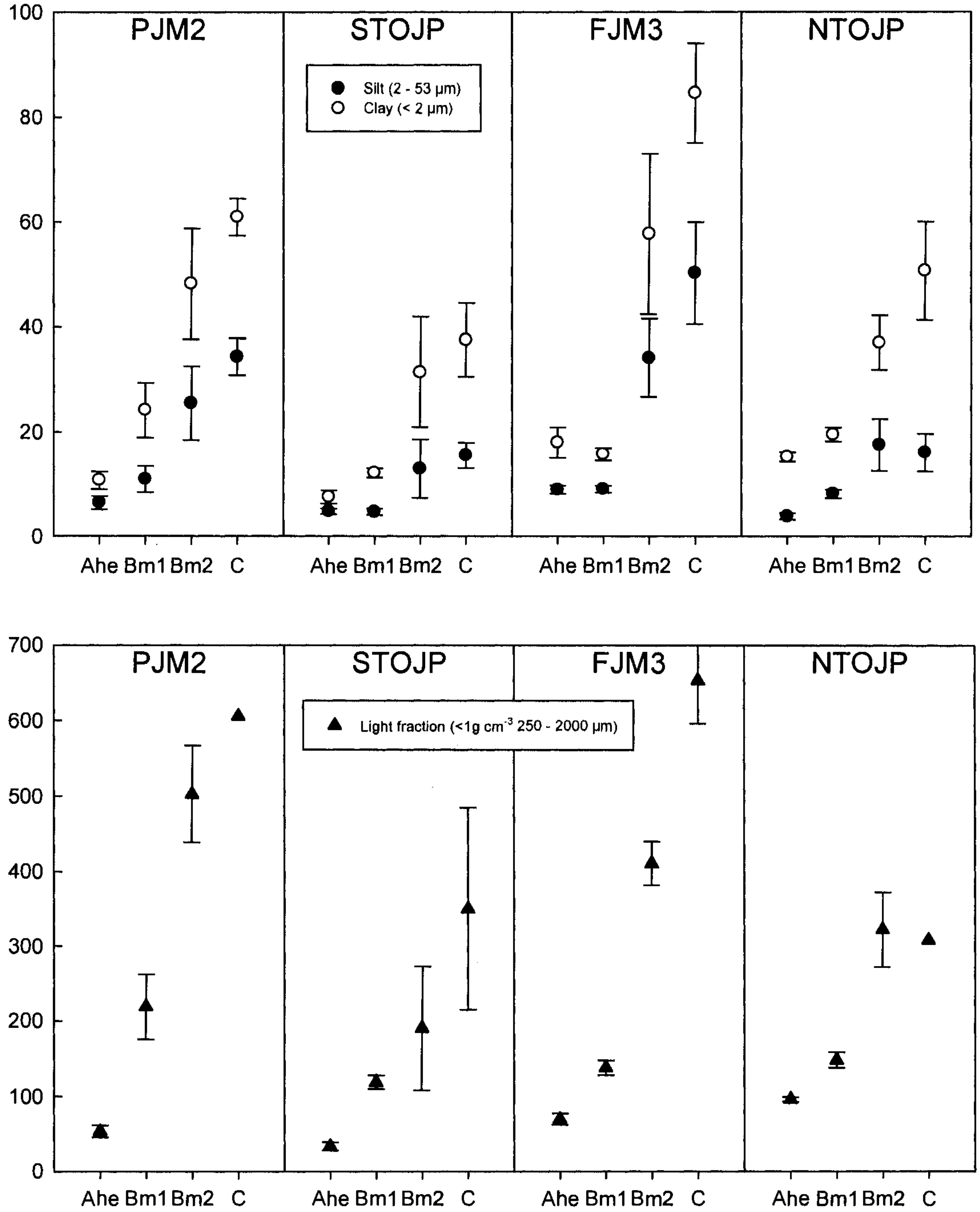


Figure 3-6. C to N ratio of the forest floor and the silt, clay and light fractions obtained from the A, $Bm_1$, $Bm_2$ and C horizons of a jack pine forest transect.

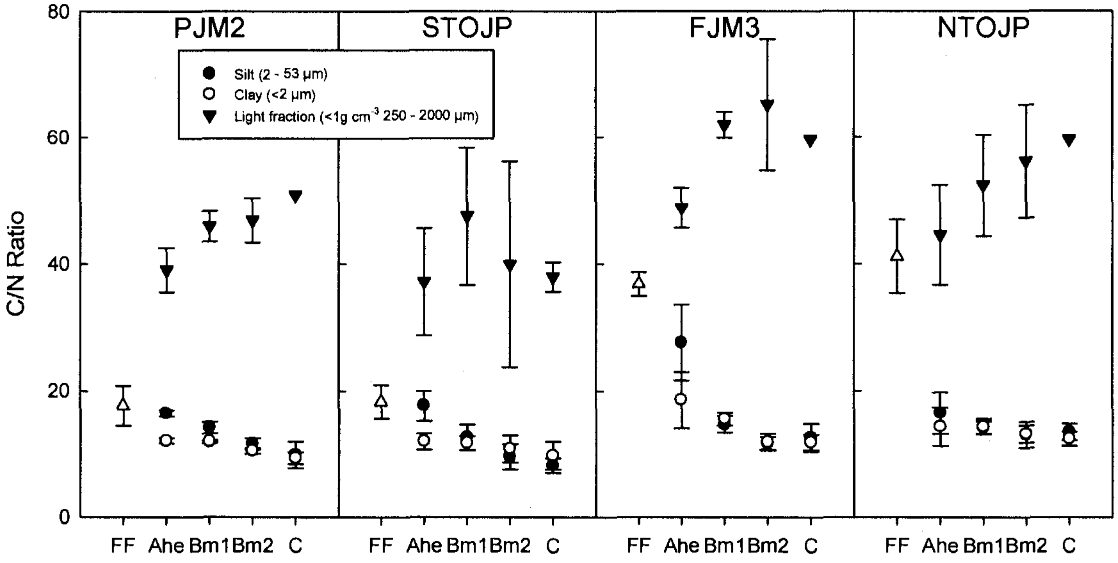


Figure 3-7. Isotopic composition ($\delta^{13}C$) in the silt, clay and light fractions obtained from the A, $Bm_1$, $Bm_2$ and C horizons of a jack pine forest transect.

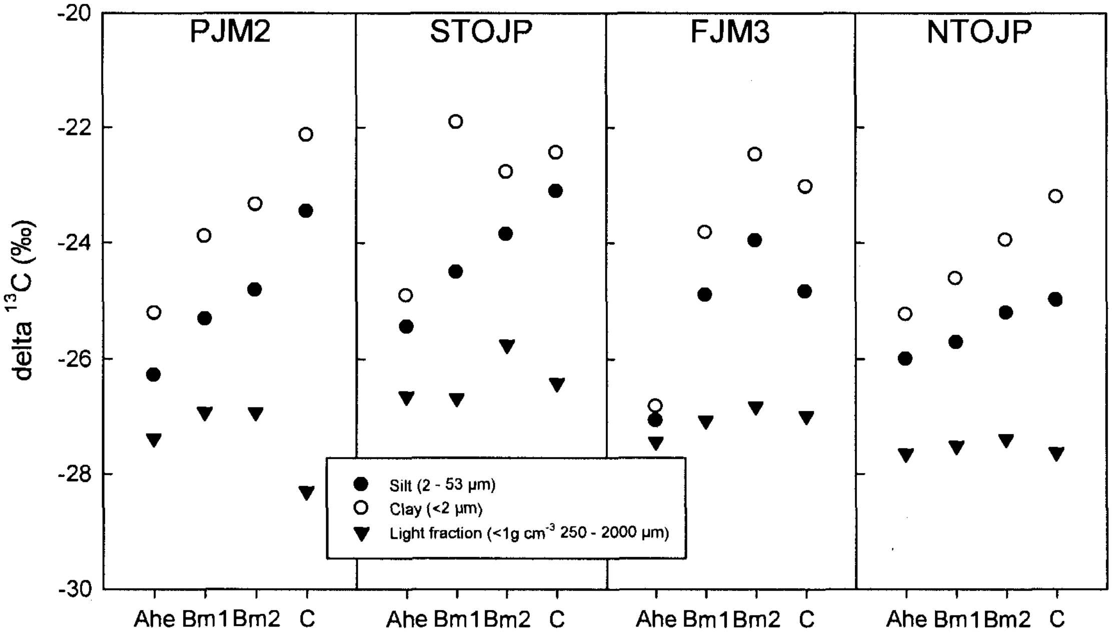
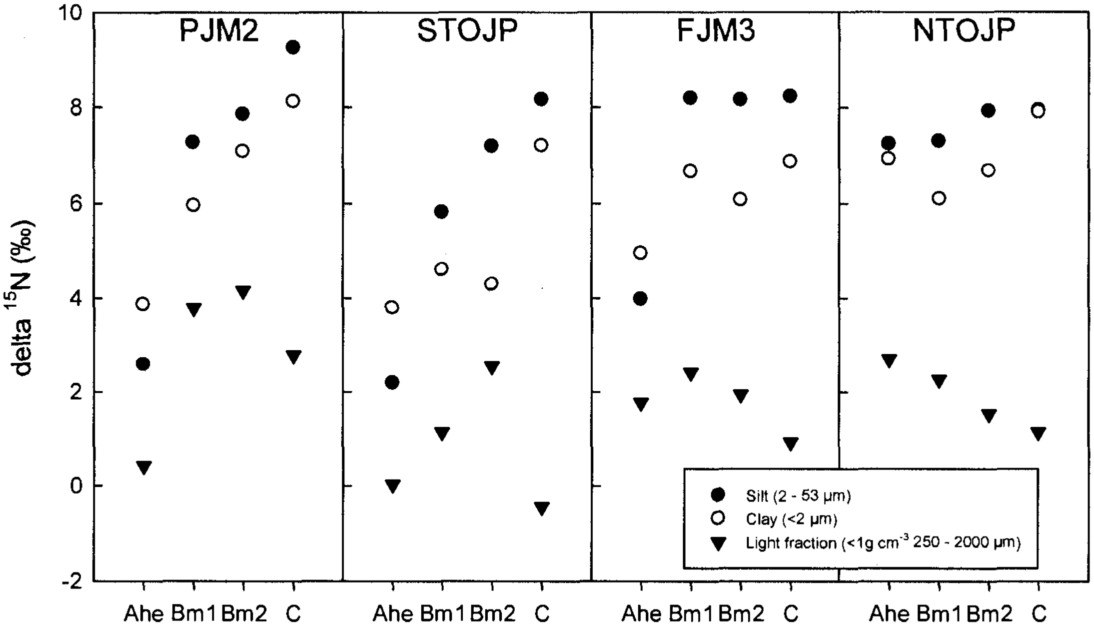


Figure 3-8. Isotopic composition ($\delta^{15}N$) of all fractions obtained from the A, $Bm_1$, $Bm_2$ and C horizons of a jack pine forest transect.



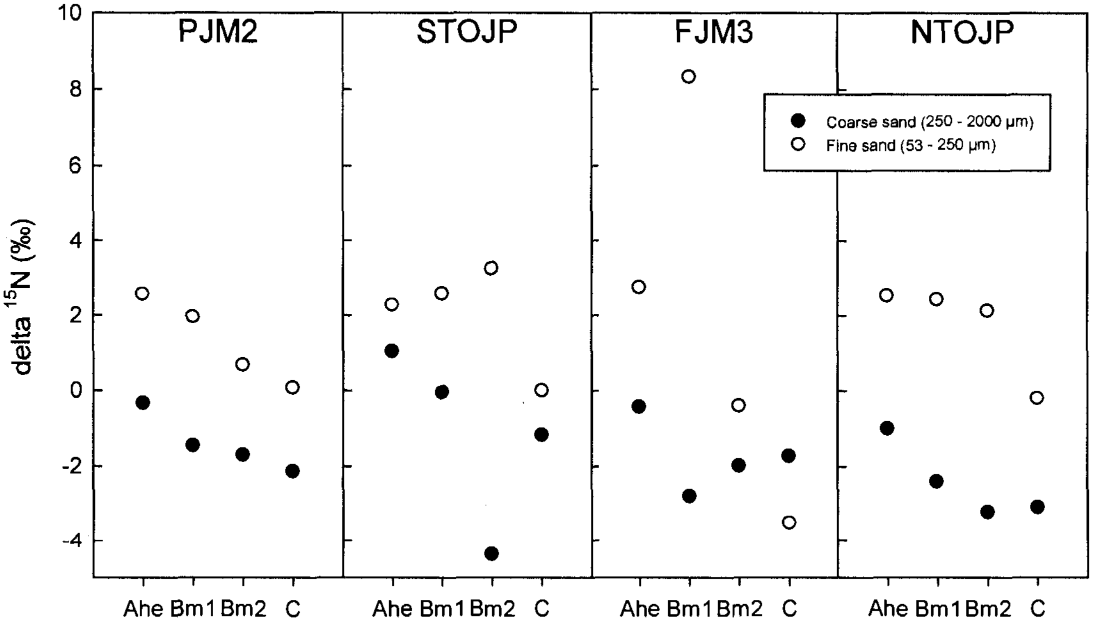
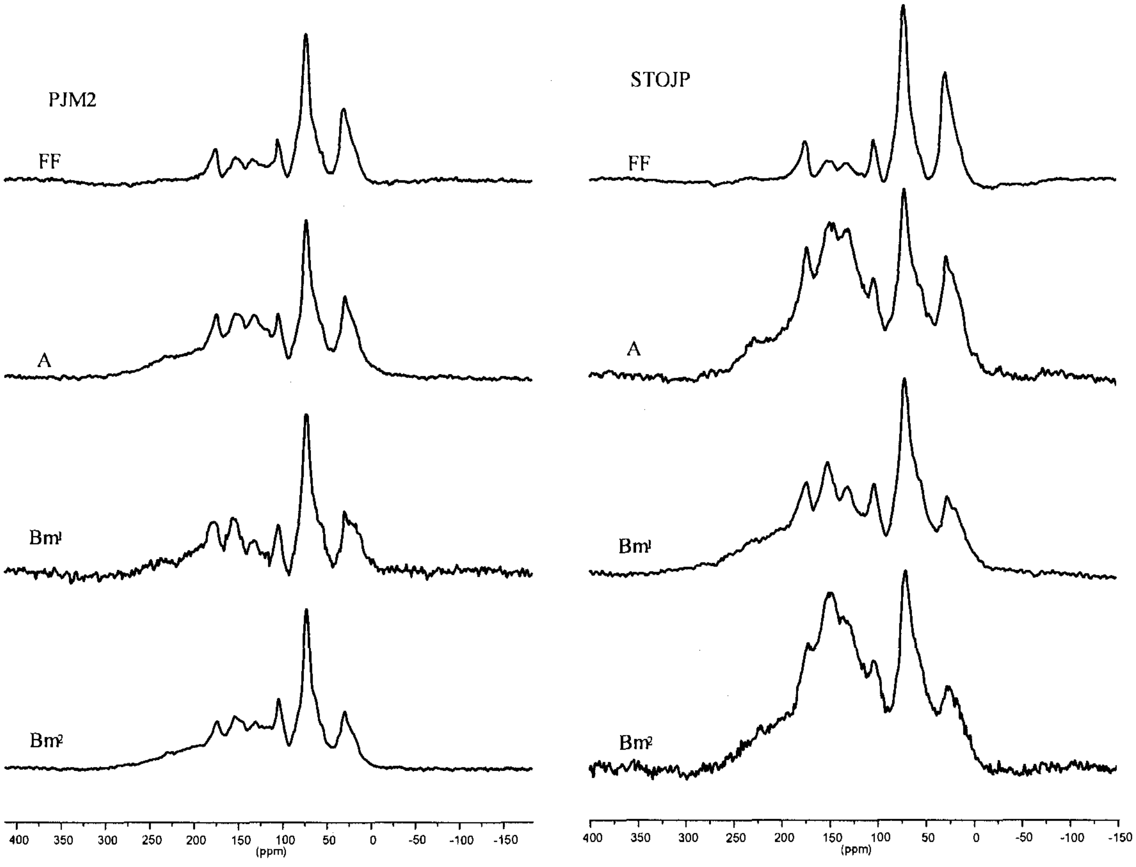


Figure 3-9. Representative CPMAS $^{13}C$ NMR spectra from a jack pine transect of forest floor samples and light fractions from A, $Bm_1$, $Bm_2$ and C horizons

a) PJM2 and STOJP sites.



b) FJM3 and NTOJP sites.

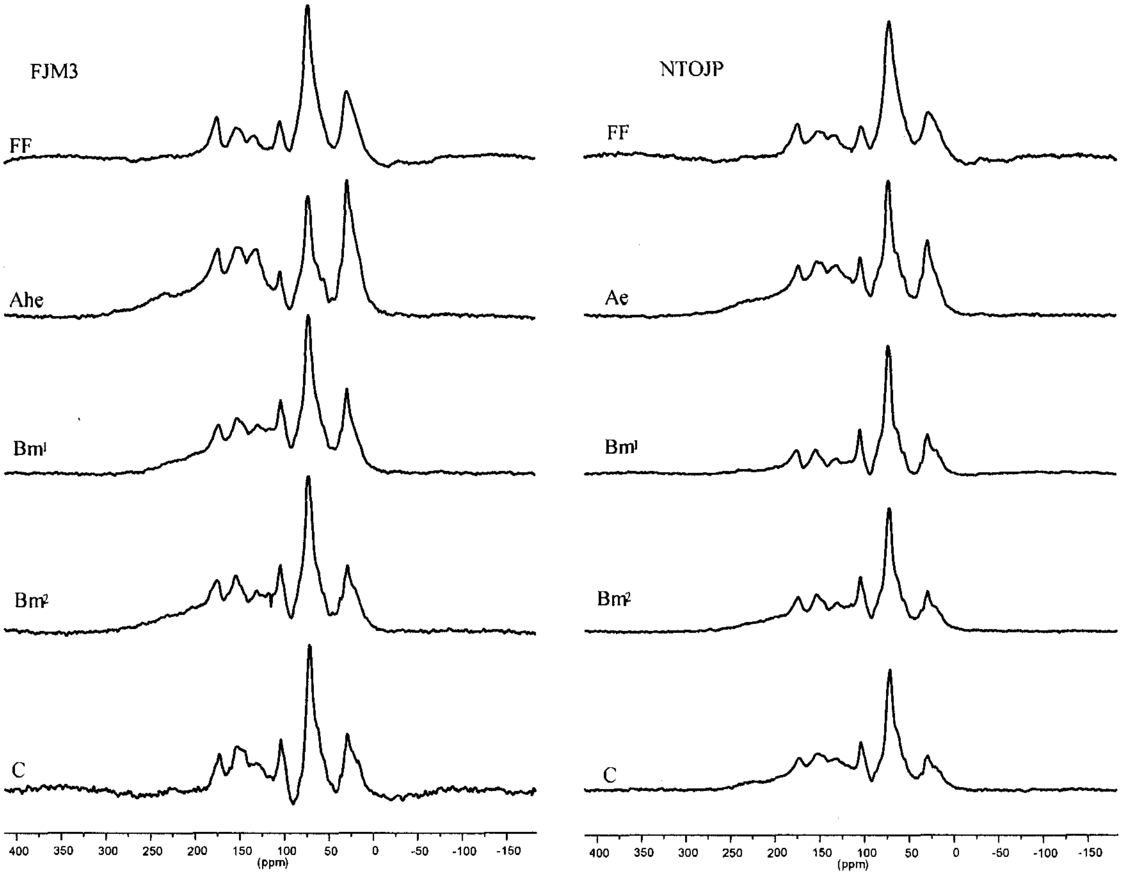
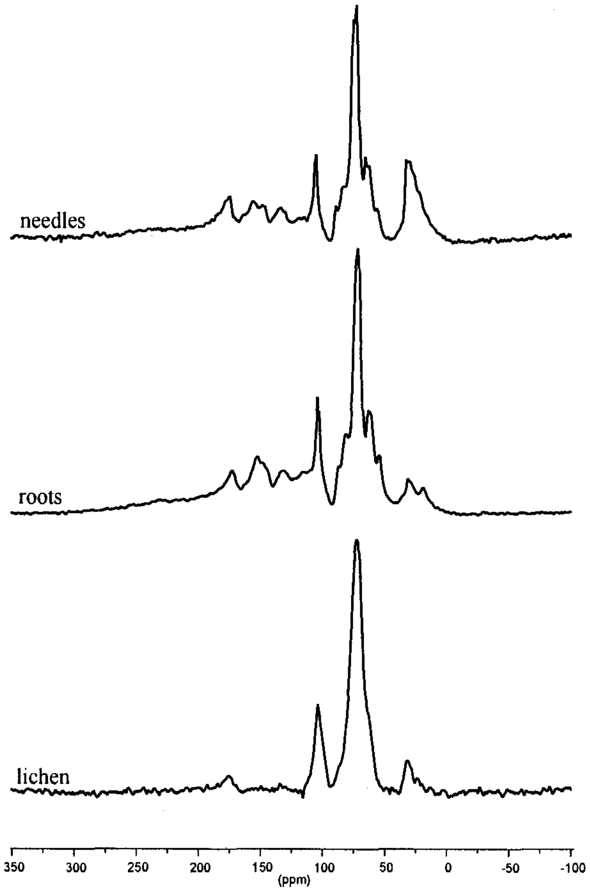


Figure 3-10. Representative CPMAS $^{13}$C NMR spectra of jack pine needles, jack pine roots and lichen from STOJP.



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# Chapter 4 Conclusions

## Objectives

The specific objectives of this study were:

1. To quantify and compare changes in soil C stocks and chemistry in two jack pine chronosequences of either fire or harvest origin

2. To elucidate how climate affects boreal forest stocks of mature jack pine stands in terms of soil organic C content and stabilization.

## Fire vs. Harvest

Soil organic C content determined for seven sites across two jack pine chronosequences of either fire or harvest origin were comparable to C contents reported for similar ecosystems in Siberia and North America. In accordance to Covington's theory, while total soil C content decreased after disturbance, it returned to pre-disturbance levels by stand maturation in both the harvest and fire chronosequences. Labile C contained within the coarse sand fraction was the dominant C pool in all soils. Furthermore, the two chronosequences were similar in that the proportion of this labile C pool increased with time following both fire and harvest. However, when examining the macromolecular chemistry of the forest floors and A horizon light fractions, a difference between disturbance type was evident. Chemical composition did not greatly vary with time or horizon within the harvested stands. On the other hand, fire disturbed forest floors showed an initial large aromatic peak, likely due to the presence of char, and results further indicated that with time, there was a transfer of this black (pyrogenic) C from the forest floors to the A horizons.

### Climate

Soil organic C content was statistically less at PJM2, the most southerly site, and content increased going northeast with cooler and moister conditions. These results are in agreement with previous studies on the same transect but in disagreement with many other climate studies which demonstrated decreasing C content with decreasing temperature. The dominant C pool at PJM2 was within the sand fractions. While labile C also dominated the type of C present at the northern site it was in a less decomposed form. While litter inputs did not greatly vary across sites, the macromolecular chemistry of soil C did, thus indicating differences with regards to the degree of decomposition. If the MAT were to increase in the northern boreal forest, these results suggest that while the overall jack pine soil C stocks would decrease, the remaining C would also become more humified, and likely more stabilized than what is currently present within the soils.

### Climate and disturbance

The total carbon content at NTOJP, the coolest and wet site, was 4.18 kg $m^{-2}$ while at the other end of the climate transect the C content was 1.71 kg $m^{-2}$ for PJM2. This almost 2.5 kg $m^{-2}$ difference in C content was greater than the 2 kg $m^{-2}$ difference between Harvest 12 and Harvest 31, the largest variation for different disturbance chronosequences, and certainly greater than the difference between Fire 91 and Harvest 31, 1.5 kg $m^{-2}$. Overall, the projected increase in MAT would therefore cause a greater change to the jack pine soil C stocks than increased harvest disturbance. However model projections of soil C stocks on Scots pine stands with two rotations indicate a 14%

decrease in on soil C (Liski et al. 1998) therefore the implications of multiple rotations on soil C stocks should also be considered. Furthermore, disturbance patterns are expected to vary with climate change, and in particular the fire return interval is predicted to increase (Field et al. 2007), which may in turn decrease soil C stocks. Lastly, in parallel to the increase in MAT, MAP may increase with climate change (Christensen et al. 2007) and therefore mitigate some of the decrease in soil C stocks.

## Project limitations and suggestions for future research

Two previously mentioned limitations included the difference in texture between Fire 11 and the other 6 sites from the two chronosequences. The results from Fire 11 should therefore be examined with caution. The second limitation concerns the climate transect, which could not be considered a true climosequence according to Jenny's (1980) soil forming model. Although some state factors may be considered to be equivalent across sites (i.e.; organisms, relief and time), the change in parent material at NTOJP compared to the other sites prevented the transect from being classified as a true climosequence.

The study on fire and harvest disturbance only included one site for each time step, with four steps for the Fire and three steps for the Harvest chronosequence. Variation among steps in the chronosequences may have been lost with so few time intervals. Furthermore, one site per interval (i.e. the lack of replicate sites) makes it difficult to determine if differences between sites are significant and truly related to disturbance. This is particularly true as within stand variation was difficult to determine due to the small number of samples, n=4. Yet increased replication would have increased the number of samples to an unfeasible volume, as the total number of samples processed for this thesis was already 820.

Further research on C stocks, stabilization and global differences in the boreal forest would be intriguing. Of particular interest is whether the results determined here would hold true for the other stands in the Canadian boreal forest, for instance black spruce and aspen. Following that it would be interesting to know if the patterns found for the Canadian boreal forest soils also represent the soils of Fennoscandia and Siberian boreal forests.

## Conclusions

C contents of jack pine forest soils in the Canadian boreal forest are small, ranging from 2.6 kg $m^{-2}$ in a four year old fire disturbed stand to 4.5 kg $m^{-2}$ in a 31 year old harvested stand and 4.2 kg $m^{-2}$ in a mature stand. Within these soils, the greatest proportion of C was found associated with the sand sized fractions, fractions which contain the most labile C. There was no statistical difference in C content between the fire and harvest stands but the nature of the C was more labile in the harvested stands while the fire stand exhibited the presence of black C, a recalcitrant C. The predominance of undecomposed labile C as well as the increased forest floor and soil C stocks at the northern range of the sites studied suggested that these soils are especially susceptible to release $CO_2$, during the increase in temperature forecasted to happen with global warming. Mitigation of global warming impacts on jack pine forest soils is therefore complex as stabilization is provided by recalcitrant C, here that is either black C or humified C. To stabilize the greater C contents in the northern jack pine soils by generation of black C or humification would generate $CO_2$ and therefore provide a positive feedback to global warming.

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