

Topographic controls on black carbon accumulation in Alaskan black spruce forest soils: implications for organic matter dynamics

E. S. Kane · W. C. Hockaday · M. R. Turetsky ·
C. A. Masiello · D. W. Valentine · B. P. Finney ·
J. A. Baldock

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Abstract There is still much uncertainty as to how wildfire affects the accumulation of burn residues (such as black carbon (BC)) in the soil, and the corresponding changes in soil organic carbon (SOC) composition in boreal forests. We investigated SOC and BC composition in black spruce forests on different landscape positions in Alaska, USA. Mean BC stocks in surface mineral soils ($0.34 \pm 0.09 \text{ kg C m}^{-2}$) were higher than in organic soils ($0.17 \pm 0.07 \text{ kg C m}^{-2}$), as determined at four sites by three different ^{13}C Nuclear Magnetic Resonance Spectroscopy-based techniques. Aromatic carbon, protein, BC, and the alkyl:O-alkyl carbon ratio were

higher in mineral soil than in organic soil horizons. There was no trend between mineral soil BC stocks and fire frequencies estimated from lake sediment records at four sites, and soil BC was relatively modern ($<54\text{--}400$ years, based on mean $\Delta^{14}\text{C}$ ranging from 95.1 to -54.7‰). A more extensive analysis (90 soil profiles) of mineral soil BC revealed that interactions among landscape position, organic layer depth, and bulk density explained most of the variance in soil BC across sites, with less soil BC occurring in relatively cold forests with deeper organic layers. We suggest that shallower organic layer depths and higher bulk densities found in warmer boreal forests are more favorable for BC production in wildfire, and more BC is integrated with mineral soil than organic horizons. Soil BC

E.S. Kane, W.C. Hockaday contributed equally to this manuscript.

E. S. Kane (✉)
School of Forest Resources and Environmental Science,
Michigan Technological University, Houghton,
MI 49931, USA
e-mail: eskane@mtu.edu

W. C. Hockaday · C. A. Masiello
Department of Earth Science, Rice University,
Houston, TX 77251, USA
e-mail: bill.hockaday@rice.edu

C. A. Masiello
e-mail: masiello@rice.edu

M. R. Turetsky
Department of Integrative Biology, University of Guelph,
Guelph, ON N1G 2W1, Canada
e-mail: mrt@uguelph.ca

D. W. Valentine
Department of Forest Science, University of Alaska
Fairbanks, Fairbanks, AK 99775, USA
e-mail: ffdwv@uaf.edu

B. P. Finney
Department of Biological Sciences, Idaho State
University, Pocatello, ID 83209, USA
e-mail: finney@isu.edu

J. A. Baldock
CSIRO Land and Water, PMB 2, Glen Osmond,
SA 5064, Australia
e-mail: jeff.baldock@adl.clw.csiro.au

content likely reflected more recent burning conditions influenced by topography, and implications of this for SOC composition (e.g., aromaticity and protein content) are discussed.

Keywords Alkyl carbon · Aromatic carbon · Black carbon · Black spruce · Boreal forest · Carbon balance · Charcoal · Fire · Organic soil · Protein · Soil

Introduction

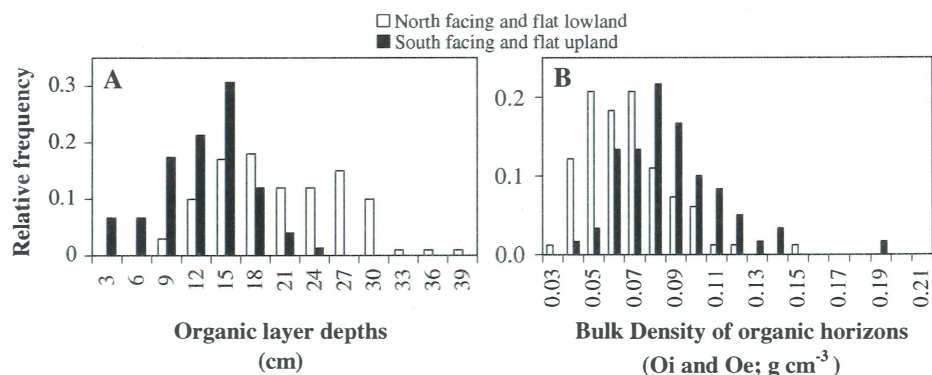
Fire is arguably the dominant disturbance in boreal forests, and the frequency of wildfire has more than doubled over the last four decades in the North American boreal region (Kasischke and Turetsky 2006). High latitude forests harbor an estimated 500 Pg carbon within the top meter of soil (Post et al. 1982; Tarnocai et al. 2009), representing approximately 30% of the world's soil organic carbon (SOC). This extensive stock of carbon can also be an effective fuel source in boreal forest wildfires, which release approximately 0.11–0.21 Pg of total organic carbon per year to the atmosphere, depending on fire severity (Kasischke et al. 2005). On the other hand, the formation of pyrogenic C (charcoal) during wildfires may act as a long-term SOC sink (e.g., Ohlson et al. 2009) because its soil residence time can be hundreds of years longer than non-pyrogenic SOC (Kuhlbusch and Crutzen 1995; Czimczik and Masiello 2007). Therefore, the concept of managing fire in the boreal forest has received growing interest (DeLuca and Aplet 2008), not only to abate carbon emissions but to sequester pyrogenic C in the soil. While fire is necessary for the sustainability of boreal forest ecosystem

functions (e.g., stand regeneration (Zackrisson 1977; Johnstone et al. 2009) and forest productivity (Thiffault et al. 2008)), relatively little is known of the long-term consequences of wildfire for changes in SOC chemical composition or SOC stocks (Wardle et al. 2003, 2008; Harden et al. 2004; Lehmann and Sohi 2008).

Pyrogenic C exists as a continuum from partially-charred plant material to more condensed aromatic black carbon (BC) particles (Hedges et al. 2000; Masiello 2004), owing to microclimatic variation in burn temperature, burn duration, fuel type, and oxygen availability during a fire (Sekiguchi et al. 1983; Shindo 1991; Gleixner et al. 2001). These factors make it difficult to consistently identify and quantify BC in soils, complicating estimates of BC turnover times (e.g., Schmidt et al. 2001). For example, the diverse spectrum of BC physical properties makes it exceedingly challenging to measure BC using physical or chemical isolation techniques. On the other hand, spectroscopic techniques such as ^{13}C nuclear magnetic resonance (NMR) allow for the detection and quantification of the aromatic carbon in BC generated via charring (Skjemstad et al. 1999; Simpson and Hatcher 2004; Hammes et al. 2007).

Some physiographic constraints to soil organic matter combustion, and pyrogenic C formation, have been identified for boreal black spruce (*Picea mariana* [Mill.] BSP) forests. The total amount of soil organic matter combusted in black spruce forest fires is largely constrained by the interplay among pre-fire soil organic layer depths (Oi, Oe, and Oa horizons), soil moisture, and bulk density (Miyanishi and Johnson 2002; Kasischke and Johnstone 2005; Harden et al. 2006; Kane et al. 2007; Shetler et al. 2008), and these three factors are highly influenced by differences in landscape position (e.g., Fig. 1).

Fig. 1 Frequency distributions of total organic layer depths (a) and integrated bulk densities (b) of organic horizons for the 176 soil pits described in this study



North-facing and toe-slope forests receive less insolation than forests on southerly slopes and therefore are cooler, wetter, and have deeper (and less dense) fibric (Oi) organic layers with a longer persistence of seasonally frozen ground (Rieger 1983; Hinzman et al. 2006; Ping et al. 2006). In turn, frozen soil layers (and permafrost) impede soil drainage and therefore largely dictate the amount of dry fuel available for combustion. Thus, changes in organic layer and litter depths, soil moisture, and soil bulk density occurring with changes in slope and aspect likely constrain the combustion process itself by influencing both the temperature and mode of combustion (e.g., flaming or smoldering) via changes in soil O₂ concentrations (e.g., Sekiguchi et al. 1983; Gleixner et al. 2001). These factors likely influence the quality, quantity, and vertical stratification of burn residues. For example, a previous study showed more complete consumption of total organic layer depths and higher concentrations of surface mineral soil BC in south-facing black spruce forests compared to north-facing and toe-slope forests (Kane et al. 2007). However, it remains unclear exactly how organic layer characteristics influence BC formation rates, and how this affects patterns of soil BC in different landscape positions.

Here, we discuss three main factors that influence the abundance of pyrogenic C in boreal forest soils:

- (i) physiographic controls on BC formation (charring),
- (ii) preservation or protection of BC from decomposition or re-burning during subsequent fires, owing to integration with mineral soil,
- (iii) and fire frequency.

South-facing forests are prone to more complete consumption of O horizons during a wildfire. We hypothesized that these sites would have less BC in O horizons, since the entire O horizon (including pre-existing BC) was more likely to be consumed in any fire event. We also hypothesized that since south-facing sites burned to the mineral soil more completely, they were more likely to have BC deposited in their mineral horizons. Moreover, we hypothesized that sites with a higher frequency of burning would harbor more BC in mineral soil horizons, due to the accumulation of more products from burning over time. Finally, since soil charcoal can indirectly stimulate microbial activity (Wardle et al. 2008;

Steiner et al. 2008; Thies and Rillig 2009), we hypothesized that BC content would correlate to molecular indices of organic matter decomposition (e.g., alkyl:O-alkyl ratio) derived from NMR data.

Methods and materials

To address these hypotheses, we examined changes in BC and other chemical properties in surface mineral and organic soil horizons in 16 sites (spanning 63–65°N latitude and 142–150°W longitude) occurring on different landscape positions in interior Alaska, USA. We determined the BC content of surface mineral soil by a chemical and thermal oxidation procedure (Kuhlbusch 1995) at all 16 sites. We measured the BC in both organic and mineral soil horizons with three ¹³C NMR spectroscopy techniques (Simpson and Hatcher 2004; Baldock et al. 2004) at two north-facing and two south-facing sites. This allowed for intensive study at four sites (NMR) and extensive study at all 16 sites (chemical/thermal oxidation) of the landscape biophysical controls on soil BC stocks in interior Alaska. In addition to quantifying BC, ¹³C NMR spectroscopy allowed us to estimate the major classes of organic compounds (carbohydrate, lignin, lipid, and protein) in the different soil horizons occurring on different landscape positions, providing a more comprehensive view of the legacy of wildfire on soil organic matter dynamics. Finally, four of these sites were positioned around lakes from which the frequency of fires over the last 1000 years was determined by charcoal particle counts in stratified lake sediment cores (e.g., Lynch et al. 2002). This allowed us to investigate how mineral soil BC accumulation related to fire frequency over the last 1000 years.

Extensive study of mineral soils

Sixteen sites were selected along north- and south-facing toposequences (including flat uplands, backslopes, toe-slopes, and lowlands). Biophysical properties of all 16 sites are presented in Table 1. Soil descriptions, sampling, stand measurements, and elemental analyses were conducted as previously described (Kane et al. 2005). Briefly, at each site three 20 m² plots were established (spaced 20 m apart), and four soil pits (approximately 0.6 × 0.6 m)

Table 1 Biophysical properties of the 16 interior Alaskan black spruce forests

Site ^a	Analysis method ^b	Latitude (°N)	Longitude (°W)	Aspect (°)	Elevation (m)	Stand age (y)	Landform
TH	Therm. Ox.	63.397	142.489	147	730	80	Back slope
TL	Therm. Ox.	63.660	142.290	283	993	81	Back slope
PH	Therm. Ox.; NMR	64.765	148.300	165	455	160	Back slope
PM	Therm. Ox.	64.766	148.295	340	520	110	Back slope
PL	Therm. Ox.; NMR	64.770	148.280	360	427	153	Back slope
MH	Therm. Ox.; NMR	64.954	147.992	200	227	76	Back slope
MM	Therm. Ox.	64.955	148.241	180	549	74	Back slope
ML	Therm. Ox.; NMR	64.958	148.241	330	549	75	Back slope
EH	Therm. Ox.	65.102	147.882	360	427	120	Back slope
EM	Therm. Ox.	65.106	147.882	330	366	173	Back slope
TM	Therm. Ox.	63.460	142.468	Flat	877	70	Flat upland
Dune	Therm. Ox.; Paleo	64.450	149.900	Flat	134	66	Flat upland
Deuce	Therm. Ox.; Paleo	64.870	147.930	Flat	170	75	Lowland
Oops	Therm. Ox.; Paleo	65.440	147.630	Flat	1600	169	Lowland
Jan	Therm. Ox.; Paleo	63.600	143.950	Flat	503	101	Toe slope
EL	Therm. Ox.	65.108	147.882	330	335	144	Toe slope

^a References for site information: TH, TL, PH, PM, PL, MH, MM, ML, EH, EM, TM, EL (Kane et al. 2005); Jan (Carlson and Finney 2004); Oops (Finney and Krumhardt 2004); Deuce and Dune (Gregory-Ives et al. 2000)

^b *Therm. Ox.* chemical and thermal oxidation (Kuhlbusch 1995); *NMR* Bloch decay and cross-polarization nuclear magnetic resonance (Nelson and Baldock 2005); *Paleo record* terrestrial soil pits obtained around lakes with sediment records quantifying long-term charcoal particle deposition rates within the lake bed

were dug into 5 cm of the B mineral horizon at each plot (12 soil pits per site). The genetic horizons were described in the field (Schoenberger et al. 2002) and parsed into organic horizons overlying the mineral soil (e.g., Fig. 1), which consisted of fibric (Oi), hemic/mesic (Oe), and sapric/humic material (Oa; which rarely occurred), and then two surface mineral soil horizons (A horizon and B horizon). Three soil cores were obtained from each descriptive pit for elemental analysis and bulk density determination by horizon. At the four lake margin sites, soil pits were dug at eight locations (separated by 45 degrees from lake center) encircling the lake. In total, 176 soil pits were described and analyzed (bulk product of 528 soil cores).

Black carbon determination

We measured the BC content of surface mineral soils (A horizons) obtained from six randomly selected soil pits at each of the 16 sites using methods previously described in detail (Kuhlbusch 1995; Kane et al. 2007). Briefly, this method entailed quantifying

organic carbon in soil samples after two pretreatments: a solvent extraction (alternating NaOH and HNO₃) followed by a thermal treatment (340°C, 2 h, O₂ atmosphere). The C that was resistant to these treatments was determined by the difference in SOC contents in each fraction using a LECO CNS analyzer (LECO Co., St. Joseph, Michigan). This method provides a conservative estimate of BC as it likely does not isolate slightly charred biomass in the soil (Schmidt et al. 2001) and therefore reflects more graphitic BC, charcoal, and soot particles (Masiello 2004). However, this method is not well suited to organic soils, as it is difficult to oxidize the large quantities of non-pyrogenic C present in organic horizons.

Intensive study of organic and mineral soil horizons

¹³C NMR was used to measure BC concentrations in the organic and mineral soil horizons at four of the sampling sites described in Table 1 (PH, PL, MH, and ML). The NMR techniques allowed for intensive study of organic and mineral soil BC at four sites,

while the chemical/thermal oxidation procedure allowed for more extensive study of surface mineral soil BC at all 16 sites. BC occurs along a continuum of structurally-related carbonaceous particles which form under changing pyrolysis conditions (such as temperature, moisture, fuel chemistry, and O₂ availability) occurring in a wildfire (Hedges et al. 2000; Hammes et al. 2007). Therefore three different ¹³C NMR techniques were applied in this study because they quantify BC formed in different regions of the pyrolysis continuum. We provide a brief explanation of each method, and a generalization of the selectivity of each method for a given region of the BC continuum, based upon the knowledge gained from the analysis of BC standards (Hammes et al. 2007; <http://www.geo.uzh.ch/oldphys/bc/>).

Hypochlorite oxidation and Bloch decay (BD) NMR

Soil samples were subjected to the hypochlorite oxidation procedure described by Simpson and Hatcher (2004). Approximately 2 g of soil were placed in a 50 mL polyethylene centrifuge tube, to which 2 g of sodium chlorite and 2 mL of glacial acetic acid were added. The tube was filled to 50 mL with deionized water and placed on a shaker until the reaction was complete (approximately 2 h), as indicated by the cessation of bubbling. The tube was centrifuged and the supernatant was decanted. This procedure was performed three times, followed by three rinses with deionized water. The hypochlorite ion, formed under the mildly acidic reaction conditions, can selectively oxidize and depolymerize benzylic and phenolic structures (e.g., lignin, tannin, and plant pigments) but does not significantly oxidize hydrolyzable structures such as carbohydrates, lipids, and proteins in soils (Simpson and Hatcher 2004). The dry mass of the sample and its carbon content were measured before and after hypochlorite oxidation. A ¹³C BD NMR spectrum was acquired (see below (*BD NMR + model*) for methods) following hypochlorite oxidation for the purpose of quantifying the hypochlorite-resistant aromatic carbon (i.e., the BC content). BC concentrations were calculated based on the carbon mass of the untreated sample.

Hammes et al. (2007) showed that hypochlorite oxidation + BD NMR is selective for BC with highly condensed aromatic structures, as found in soot and

high-temperature charcoals, but does not detect some charcoal BC formed at low temperatures ($\leq 450^\circ\text{C}$). Charcoals formed at low temperatures can be partially or completely oxidized by hypochlorite, because they have a low degree of aromatic ring condensation (≤ 3 fused aromatic rings) and retain substantial polyphenol structure from the original organic matter (Hammes et al. 2006; Schmidt-Rohr et al. 2008).

Cross-polarization (CP) NMR and the molecular mixing model

NMR data were acquired on a 200 MHz Bruker Avance spectrometer (Rice University; Houston, TX, USA) equipped with a 4 mm magic angle spinning (MAS) probe. Approximately 50 mg of untreated soil (dried and pulverized) were packed into a 4 mm (outer diameter) zirconia rotor and sealed with a with Kel-F cap. The rotor spinning rate was 5 kHz. CP spectra were acquired following a 90° ¹H excitation pulse, a 1 ms ¹H–¹³C contact pulse, and with a 3 s delay between acquisitions. The chemical shift frequency was referenced to glycine as an external standard. NMR spectra were processed with 50 Hz line broadening and phase-corrected prior to integrating peak areas in eight spectral regions: 0–45, 45–60, 60–95, 95–110, 110–145, 145–165, 165–190, 190–215 ppm. The peak areas were used as inputs into a molecular mixing model (described in detail by Baldock et al. (2004)) to estimate the relative contributions of charcoal to the total SOC pool. We denote the application of the molecular mixing model to CP and BD NMR data as CP NMR + model, and BD NMR + model, respectively.

Cross polarization NMR is inherently less quantitative than Bloch decay (also known as single pulse, and direct polarization) NMR because ¹³C polarization is generated by the transfer of magnetization from ¹H nuclei to ¹³C nuclei, and the efficiency of the polarization transfer depends, in part, upon the internuclear distances. In highly condensed aromatic domains within the BC structure, ¹³C nuclei can be many bond-lengths removed from the nearest ¹H nucleus. Because of this, CP NMR does not observe the highly condensed or graphitic carbon atoms in the BC continuum as efficiently as carbon located close to protons (Smernik et al. 2002a). Thus, BC values determined by CP NMR + model are likely

a measure of the less condensed aromatic structures typical of low-temperature charcoals.

BD NMR and the molecular mixing model

Bloch decay (DP) NMR spectra were acquired following a 20 degree ^{13}C excitation pulse with a 5 s delay between acquisitions using a MAS frequency of 5 kHz. A background (empty rotor) signal was subtracted from the BD spectra to remove interfering signal from the NMR probe and rotor (see Smernik and Oades 2001). Spectra were processed as described above for the CP analysis, and BC concentrations were calculated using the molecular mixing model (Baldock et al. 2004).

BD NMR is the most quantitative form of NMR spectroscopy and does not underestimate BC relative to other forms of organic carbon. BD NMR routinely detects >90% of the C in black carbon samples (Baldock and Smernik 2002; Skjemstad et al. 1999; Smernik et al. 2002b). Nelson and Baldock (2005) showed that BC concentrations measured using the BD NMR + model approach are slightly higher but linearly correlated to the BC values measured by the UV photo-oxidation technique developed by Skjemstad et al. (1999). The BC concentrations estimated using the BD NMR + model approach are the most inclusive, detecting the widest spectrum of the BC continuum from low temperature charcoals

to highly condensed aromatic structures (accurate to $\pm 5\%$). Therefore, the BD NMR + model approach was used in this study to investigate correlative patterns between key biomolecules and a wide spectrum of the BC continuum. Table 2 reports the BC concentrations measured by all three of the NMR techniques side-by-side with the BC values measured by the chemical and thermal oxidation technique (Kuhlbusch 1995).

Fire frequency and BC accumulation

Four sites were established around small (3–71 ha) isolated lakes. The forest fire history surrounding these lakes had been reconstructed through charcoal particle counts in radiocarbon-dated sediment cores (Jan Lake: Carlson and Finney 2004; Oops Lake: Finney and Krumhardt 2004; Deuce and Dune Lakes: Gregory-Ives et al. 2000; Lynch et al. 2002). Using these data, the number of wildfires reflected in the sediment cores over the last 1000 years was determined when peaks in charcoal count records ($\# \text{cm}^{-3}$) exceeded background conditions by 1.4 times (Lynch et al. 2004). At the four lake margins, we dug eight soil pits (separated by 45° from lake center) encircling the lake. Pit locations were in black spruce forest (occasionally mixed with white spruce (*Picea glauca* [Moench] Voss)) 20–60 m away from the *Alnus* spp. and *Salix* spp. common at the lacustrine border.

Table 2 Comparison of soil BC yields in organic and mineral soil horizons using four different methods (all values expressed as g C g SOC $^{-1}$)

Horizon and soil type	Site name	Aspect	SOC	Thermal and chemical Ox.	Hypochlorite BD NMR	C _{obs} ^a	CP NMR	C _{obs}	BD NMR	C _{obs}
Organic soil (Oe)	MH	South	0.392		0.056	0.94	0.041	0.62	0.030	0.82
	ML	North	0.422		0.030	0.79	0.061	0.39	0.032	0.89
	PH	South	0.423		0.052	0.91	0.077	0.49	0.094	0.95
	PL	North	0.434		0.049	0.95	0.030	0.57	0.025	0.97
Mineral soil (A)	MH	South	0.141	0.148	0.134	1.00	0.197		0.404	
	ML	North	0.156	0.054	0.154	0.98	0.216		0.396	
	PH	South	0.211	0.112	0.122	0.95	0.104		0.313	0.81
	PL	North	0.229	0.104	0.070	0.84	0.009		0.087	0.99
Vertisol	BC reference ^b		0.035	0.153	0.174		0.160			
Mollisol	BC reference		0.019	0.082	0.158					

^a NMR observability (C_{obs}), as defined in Eq. 1, is the proportion of soil carbon that is detected by the NMR for a given sample

^b BC reference materials obtained from <http://www.geo.unizh.ch/phys/bc/>, see also Schmidt et al. (1999, 2001), and Hammes et al. (2007)

Four mineral soil BC samples isolated by chemical and thermal oxidation (from the lake margin soils) were analyzed for $\Delta^{14}\text{C}$ content at the Lawrence Livermore National Laboratory (Livermore CA, USA; Center for Accelerator Mass Spectrometry numbers 144800–144803). Sample preparation backgrounds were subtracted, based on measurements of samples of ^{14}C -free wood used as unknowns. Backgrounds were scaled relative to sample size. Analytical error ranged from 3.5 to 4.2%. The quoted age is in radiocarbon years using the Libby half life of 5568 years and following the conventions of Stuiver and Polach (1977); two samples with mean dates more recent than the year 1950 are described as being <54 years old ($\Delta^{14}\text{C}$ of 28.9 and 95.15‰ and fraction modern of 1.04 and 1.10%, respectively).

NMR analysis of SOM molecular composition

The molecular mixing model described by Baldock et al. (2004) was applied to both CP and BD NMR data, for the purpose of estimating the concentrations of four major classes of biochemical compounds: carbohydrate, lignin, lipid, and protein. Charcoal and carbonyl C are also components of the model, which accommodate organic matter altered by fire and oxidation, respectively. Aromatic C is comprised of aromatic structures in lignin and protein. The molecular mixing model determined the best-fit linear combination of NMR integral regions of the six model components that minimized the sum of squares of the differences between measured and predicted integral regions for the acquired soil NMR spectrum while maintaining the measured molar N/C ratio. Note that in the model results, protein-N = $0.275 \times \text{protein-C}$. The NMR peak area distributions used for the 6 model components are given in Table 1 of Baldock et al. (2004).

Quantitation of NMR results

The degree of quantitation in an NMR experiment can be determined by comparing the carbon-normalized signal intensity detected for each sample to the carbon-normalized signal intensity of a well-characterized external standard, a procedure known as spin counting. Pure cellulose (Sigmacell cellulose type 101, Sigma-Aldrich, CAS# 9004-34-6) was used as the spin counting standard, following the convention

of Smernik and Oades (2000). For each sample, the fraction of carbon observed in the NMR spectrum (C_{obs}) was calculated using Eq. 1

$$C_{\text{obs}} = \frac{\text{signal intensity per unit carbon for sample}}{\text{signal intensity per unit carbon for cellulose standard}} \quad (1)$$

The fraction of C observed during each NMR experiment is listed in Table 2. The observability values (C_{obs}) range from 0.3 to 0.6 for CP NMR and 0.5 to 1.0 for BD NMR, comparable to those found in the literature for CP and BD NMR experiments on soils from temperate ecosystems (Keeler and Maciel 2003 and references therein).

Statistics and analysis

Differences in SOC, BC, and biomolecules measured with NMR spectroscopy were tested using one-way analysis of variance (ANOVA) pairwise or between subjects comparisons, by grouping sites by aspect (two north facing and two south facing sites). Where degrees of freedom were seven or less, differences were considered significant at $\alpha = 0.1$ if the effect size (d) was large (difference:standard deviation ratio >0.80 (Urdan 2005)); for all other comparisons $\alpha = 0.05$. Analyses including all 16 sites were conducted at the pedon level so as to preserve the influence of micro-topographic variation in predictor variables (organic layer depth and bulk density) in explaining variation in BC; there was missing profile information from a total of six soil pits (TH, TM, Oop, and PH sites) and therefore total $n = 90$. All data were examined for normality and transformed if necessary. Descriptive statistics were performed with Analyze-it statistical module (Leeds, UK) and regressions were developed (General Linear Model) with PC SAS (version 9.2, SAS Institute, Cary, North Carolina).

Results

Physical characteristics of soils

The depth and mean bulk density of the surface soil organic layers (Oi and Oe horizons) varied among landscape positions (Fig. 1). Organic soil depths

averaged 19.9 ± 0.7 cm at the north-facing and toe-slope forests ($\pm$ standard error; Skewness = 0.28, $p = 0.24$, $n = 100$) and 11.6 ± 0.6 cm at the south-facing and other upland forests (Skewness = -0.38 , $p = 0.16$, $n = 75$) (p values test significant Skewness). Mean bulk densities for the total organic layer were lower on north-facing and toe-slope forests (0.063 ± 0.002 g cm $^{-3}$; Skewness = 1.24, $p < 0.001$) and were higher on south-facing and other upland forests (0.082 ± 0.003 g cm $^{-3}$; Skewness = 1.41, $p < 0.001$). The A horizon mineral soils had a mean thickness of 2.2 ± 0.1 cm (range = 7 cm) across all pits.

Intensive study of landscape effects on soil BC distribution

Organic and surface mineral soil (A horizon) BC concentrations, determined with three different methods employing NMR, were different in two north facing and two south facing forests (mean organic layer depths of 20.5 ± 1.2 and 13.8 ± 0.9 cm, respectively), with variation among methods being much higher for mineral soils than for organic soils (Table 2). Mean BC concentrations were 0.12 ± 0.02 , 0.13 ± 0.05 , and 0.30 ± 0.07 g BC g SOC $^{-1}$ for mineral soils and were 0.05 ± 0.01 , 0.05 ± 0.01 , and 0.05 ± 0.02 g BC g SOC $^{-1}$ for organic soils, as determined by hypochlorite BD NMR, CP NMR + model, and BD NMR + model, respectively (Table 2).

The NMR spectra of Oe and A horizon soils (Fig. 2) showed that the organic matter in each landscape position was dominated by alkyl C (30 ppm), O-alkyl C (70 ppm), O $_2$ -alkyl C (105 ppm), and carboxyl/amide C (165–190 ppm). However, the south-facing

soils had greater relative contributions from aromatic (110–145 ppm) and phenolic (145–165 ppm) carbons compared to the north-facing soils. O-alkyl C and O $_2$ -alkyl C in soils are primarily carbohydrate-derived (see Baldock et al. 1997). Carbohydrate concentrations were lower in the south-facing soils (Table 3), indicating that the organic matter was at a more advanced stage of decomposition than in north-facing soils. The ratio of alkyl to O-alkyl carbon is used here as an index of soil organic matter decomposition extent (Baldock et al. 1997), and mineral soil horizons had higher ratios of alkyl:O-alkyl C than did organic soil horizons (Table 3).

The south facing forests had higher BC stocks (BC SOC $^{-1} \times$ soil bulk density $\times$ depth) in the organic horizons (0.26 ± 0.001 kg C m $^{-2}$) than did the north facing forests (0.14 ± 0.04 kg C m $^{-2}$; Fig. 3). Mineral soil BC stocks were also higher in the south-facing forests than in the north facing forests (0.23 ± 0.003 vs. 0.16 ± 0.08 kg C m $^{-2}$, respectively), though high variability between the two northern forest BC stocks (CV = 70%) rendered this insignificant. BC stocks comprised a higher percentage of total SOC in both organic and mineral soil horizons in the south facing forests than in the north facing forests (Fig. 3c). The concentration of aromatic carbon in the mineral soil horizons tended to increase with the concentration of BC as measured with BD + model and with hypochlorite + BD (Fig. 4a and b). Soil lignin-C was not correlated with aromatic-C (Fig. 4c) or soil BC concentrations in organic or mineral soil horizons ($p > 0.3$ for Bloch Decay methods, respectively). Protein concentrations in organic soil horizons increased with soil BC content as measured by BD + model (Fig. 5). The protein percentage of total

Fig. 2 ^{13}C CPMAS NMR spectra of organic Oe horizon (left, a) and surface mineral A horizon (right, b) soils from north- and south-facing black spruce forest sites in interior Alaska. All spectra are scaled to represent an equal quantity of carbon, so that peak areas can be compared quantitatively

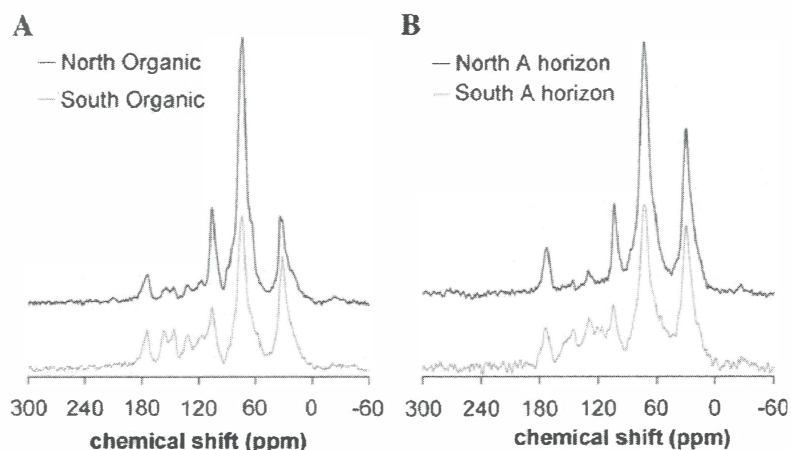
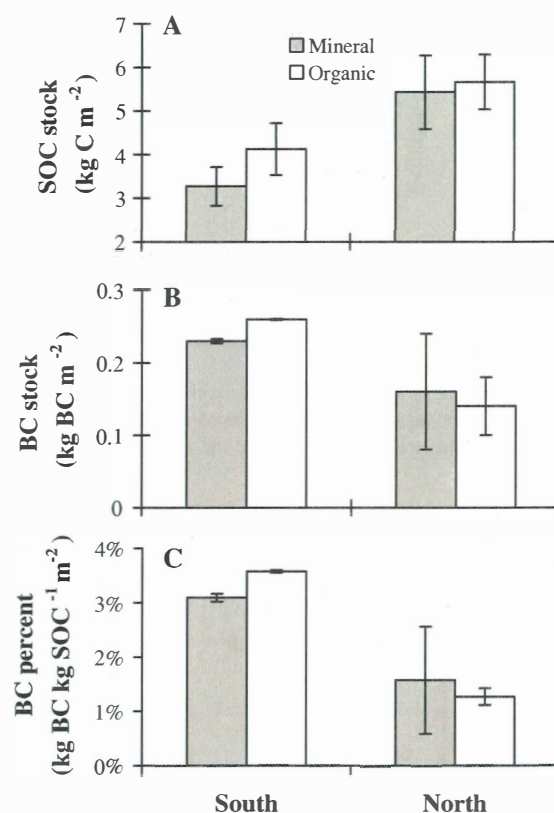


Table 3 Mean biomolecule percentages of soil organic carbon in organic (Oe) and mineral (A) soil horizons from 4 forests on north- and south-facing aspects (standard errors of the mean values are in parentheses)

Horizon and aspect	Carbohydrate	Protein-C	Lignin-C	Lipid-C	Alkyl:O-Alkyl	Aromatic-C	Hypochlorite BC
Oe south	34.45 (0.75)	4.95 (0.65)	34.60 (5.62)	14.75 (1.05)	0.66 (0.04)	27.63 (2.65)	5.40 (0.22)
Oe north	49.55 (10.28)	4.80 (0.30)	22.95 (7.77)	12.70 (0.70)	0.44 (0.08)	20.49 (1.69)	3.94 (0.96)
A south	32.15 (2.16)	9.75 (2.16)	20.85 (2.76)	18.15 (2.26)	0.85 (0.01)	46.16 (0.24)	12.77 (0.58)
A north	45.71 (11.45)	10.41 (1.82)	10.44 (3.67)	19.54 (4.35)	0.68 (0.02)	31.75 (20.04)	11.22 (4.22)
Differences (F, p value) ^a							
By aspect	4.92, 0.07				4.44, 0.08		
By horizon		18.80, 0.01	4.41, 0.08	5.51, 0.06	5.51, 0.06	15.14, 0.01	5.51, 0.06

All values were obtained from cross-polarization NMR spectra processed through the molecular mixing model, with the exception of aromatic-C and hypochlorite bleached BC, which were determined from Bloch decay NMR spectra (accurate to $\pm 5\%$)

^a only significant values shown ($\alpha = 0.10$); ANOVA 1-way pairwise; F, p value; $DF_{1,7}$

**Fig. 3** Stocks of soil organic carbon (SOC) (a) and BC (b) for organic and mineral soil horizons, as well as the percentage of total SOC stocks made up of BC (c) in organic and mineral soil horizons. Error bars represent standard errors of the mean values by soil type

soil nitrogen (N) concentrations also increased with soil BC content (BD + model) in organic horizons ($R^2 = 0.44$, $p = 0.05$; with logarithmic transformation). As expected, there were strong correlations between protein concentrations and soil N percentages of SOC in the mineral and organic soils ($R^2 = 0.73$, $p = 0.007$ and $R^2 = 0.93$, $p < 0.001$, respectively; Fig. 5).

Extensive study of landscape effects on mineral soil BC

Mineral soil BC concentration measured (in 90 soil pits) with a chemical and thermal oxidation method (Kuhlbusch 1995) declined with increasing organic layer depths (Table 4). Mineral soil BC concentrations were lower in north facing and flat toe-slope ($<5\%$) forests (0.08 ± 0.005 g BC g SOC⁻¹) than in south facing and other upland forests

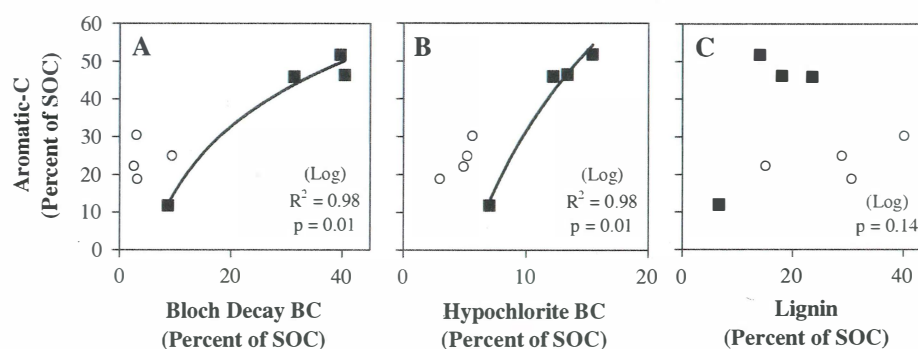


Fig. 4 The percentage of aromatic soil organic carbon in mineral soil horizons (*squares*) increased as the percentage of BC increased (a and b). The percentage of aromatic c in the

soil was not correlated with lignin (c) or with BC in the organic soil horizons (*circles*). Logarithmic regression lines are through mineral soil horizon data

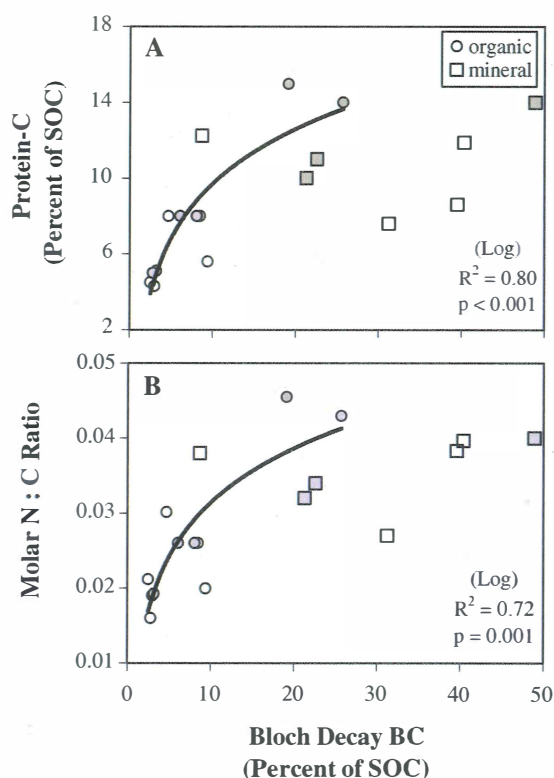


Fig. 5 The percentage of protein SOC increased with BC concentrations in organic soil horizons (*circles*), but not in surface mineral soil horizons (*squares*) (a). This pattern is in agreement with the increase in N:C commonly observed with depth in a soil profile (b), and illustrates that protein is a dominant component of soil nitrogen concentrations, especially within the surface mineral soil. Shaded symbols denote data from a complementary study of other interior Alaskan black spruce forest soils (Hockaday et al. 2009). Logarithmic regression lines are through organic soil horizon data

(0.10 ± 0.008 g BC g SOC⁻¹; 1-way ANOVA between subjects; $F_{1,89} = 6.51$, $p = 0.01$). Landscape position, parsed into four class variables (north facing, south facing, other uplands, and flat toe-slope forests), and organic layer depth were both significant in explaining variation in mineral soil BC concentrations (Table 4). The decline in mineral soil BC concentrations with increasing organic layer depth was more evident when means were investigated at the site level ($R^2 = 0.36$, $p = 0.01$; Fig. 6). Mean BC declined as the standard deviation in organic soil depths increased across sites ($R^2 = 0.49$, $p = 0.004$), indicating that variations in organic soil depth are also influential in BC accumulation.

Organic soil bulk density did not explain variation in BC concentrations at the pedon level ($F_{1,82} = 1.53$, $p = 0.22$; logarithmic transformation), but it did

Table 4 General linear model results explaining variability in mineral soil BC concentrations (using a chemical and thermal oxidation procedure) across all soil pits

Source	DF	SS	MS	F	p value	R ²
Landscape position ^a	3	0.028	0.009	5.67	0.0014	
Organic layer depth	1	0.008	0.008	5.12	0.0263	
Model	4, 89	0.036	0.009	5.53	0.0005	0.21
Bulk density $\times$ landscape position						
Model	4, 69	0.018	0.006	5.18	0.003	0.23

DF degrees of freedom (source, model total); SS sum of squares; MS mean square error

^a Grouped by four class variables: north facing slopes, south facing slopes, flat uplands, or flat lowlands and toe-slopes

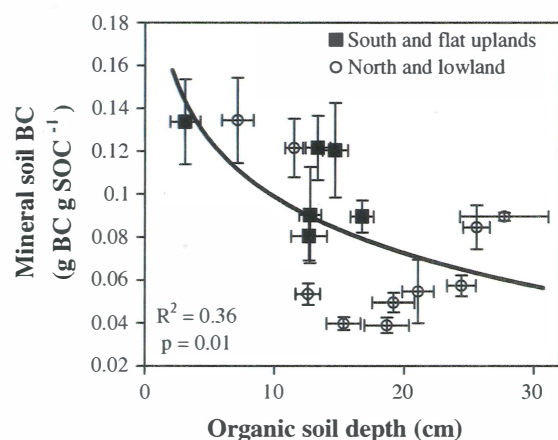


Fig. 6 Mineral soil BC (determined using a chemical and thermal oxidation procedure; Kuhlbusch 1995) decreased as organic horizon depths increased in black spruce forests in interior Alaska. Coefficients describing the logarithmic regression line are $\beta_0 = 0.186 \pm 0.036$, $\beta_1 = -0.0379 \pm 0.0134$

interact with landscape position in explaining variation in mineral soil BC (Table 4). Mean mineral soil BC increased with mean organic soil bulk density ($R^2 = 0.25$, $p = 0.05$) and decreased with increasing A horizon SOC concentrations across sites ($R^2 = 0.30$, $p = 0.03$).

Fire frequency effects on mineral soil BC stocks

There was no clear trend between mineral soil BC concentrations (measured at four sites located around small lake basins for which long-term sediment records reflected the frequency of fire over the last 1000 years) and fire frequency ($F = 0.33$, $p = 0.6$), and there was no trend between soil BC stocks and fire frequency across these four sites (Fig. 7a). Radiocarbon ages for BC isolated from the surface mineral soil at these four sites ranged from relatively modern (<54 years) to approximately 400 years (Fig. 7b). $\Delta^{14}\text{C}$ of soil BC samples was not correlated with fire frequency ($F = 0.13$, $p = 0.76$).

Discussion

Interactions among landscape position and SOC properties

The alkyl:O-alkyl C ratio is higher in both organic and mineral soil horizons from the south facing

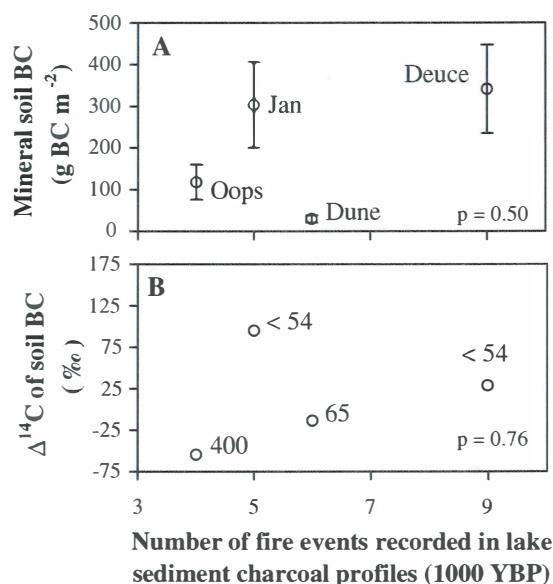


Fig. 7 Mineral soil BC stocks (determined using a chemical and thermal oxidation procedure; Kuhlbusch 1995) (a) and $\Delta^{14}\text{C}$ of soil BC (b) were not correlated with estimated fire frequency. Inset numbers in (b) are radiocarbon years using the Libby half life of 5568 (Stuiver and Polach 1977)

forests than in north facing forests. A higher alkyl:O-alkyl ratio is consistent with the increased decomposition extent commonly observed in warmer, south facing soils in boreal black spruce forests (Van Cleve et al. 1981, 1983; Kane et al. 2005; see also Wickland and Neff 2008). The greater extent of decomposition in south-facing soils was also reflected in higher organic layer bulk densities and shallower organic layer depths (Fig. 1; see also Yi et al. 2009). Deeper organic layers are formed in cooler forests with slower rates of decomposition and greater proliferation and coverage of mosses at the forest floor. Therefore, the chemical properties of organic soils from north facing forests more closely resemble those of mosses in early stages of decomposition. In an independent analysis of the molecular composition of a mixture of surface mosses and lichens (*Pleurozium sherberi*, *Hylocomium splendens*, *Stereocaulon spp.*, and *Peltigera spp.*) from an acidic black spruce forest using CP NMR (Masiello and Hockaday, unpublished data), the alkyl:O-alkyl ratio was 0.20. Most of the surface moss C was attributed to carbohydrates (70.7%) and lignin (17.6%). It is therefore not surprising that the concentrations of carbohydrate C were higher and alkyl:O-alkyl C were lower in the

cooler, north facing forests (Table 3; see also Czimczik et al. 2003).

Previous studies have also concluded that aromatic C increased with increased decomposition in boreal spruce forests (e.g., Hannam et al. 2005), which could be due in part to increases in the concentration of aromatic C as carbohydrate and lignin C is preferentially decomposed. In our study, all measures of BC were correlated with total aromatic C in the mineral soil, and lignin C was not correlated with any measure of soil BC (Fig. 4). Other studies using ^{13}C NMR have revealed that aromatic C accumulates during early diagenesis but then disappears as lignin structures are degraded, leaving residues high in alkyl-C (Baldock et al. 1992, 1997). The lack of a relationship between lignin C and aromatic C in the soil may suggest that lignin structures did not contribute substantially to the pool of aromatic C in the soil. Thiffault et al. (2008) found increased concentrations of aromatic C in mixed black spruce forests of Canada that had burned ~20 years previously, compared to harvested forests with no fire in recent decades. The data presented and discussed herein suggest that the accrual of aromatic carbon in boreal black spruce forest soils results from the accumulation of a form of aromatic carbon other than lignin, and is most likely attributed to black carbon created by wildfires.

BC quality differs by soil horizon

The three NMR techniques used in this study isolate different types of BC formed in the pyrolysis continuum. The BD NMR + model technique is the most inclusive—detecting highly condensed BC structures in addition to charcoals formed under less severe pyrolysis conditions (Nelson and Baldock 2005). On the other hand, the hypochlorite technique is selective for BC formed under more severe pyrolysis conditions and detects little charcoal formed at low temperatures ($<450^\circ\text{C}$) (Hammes et al. 2007). While there were no significant differences in BC measured among the different methods in organic soil horizons, there were considerable differences among the three methods in BC measured in the shallow mineral soil horizons (Table 2). The close agreement between hypochlorite BC and the BC detected by BD NMR + model suggests that most of the BC in organic soil horizons was

composed of highly condensed aromatic structures, as found in soot and high-temperature charcoals. In the mineral soil, BD NMR + model detected higher BC concentrations than the hypochlorite BC technique, indicating that BC in the mineral soil contains a mixture of highly condensed graphitic BC and partially charred material that likely formed at low temperatures. The greater relative abundance of low temperature char in the mineral horizons may suggest that it originates from a different fire event, or different types of BC have different transport properties. Alternatively, differences in BC decomposition rates in the organic and mineral soil horizons may alter the BC in situ. In this case, the presence of less extensively charred material could suggest that BC in the mineral soil is more protected from decomposition (or burning) than in the organic soil horizons.

The quantification of different types of BC in the organic and mineral horizons also has important ecological and biogeochemical consequences. There is mounting evidence that differences in the physicochemical properties of BC (e.g., degree of aromatic ring condensation, surface area, surface oxidation, nitrogen content, alkalinity, etc.) originating from variations in pyrolysis conditions can influence soil microbial activity (Steiner et al. 2008; Thies and Rillig 2009), and soil pH and ion exchange capacity (Liang et al. 2006; Lehmann et al. 2006; Lehmann 2007). In turn, these properties likely affect soil microbial activity and exchange capacity differently in organic and mineral soil horizons.

Soil physical properties affect BC accumulation

In boreal black spruce forests, the physical properties of organic soil horizons, which change with topography, explained significant amounts of variation in mineral soil horizon BC concentrations. Two possible mechanisms for this are: (1) higher bulk density soils foster greater charcoal conversion rates (more charcoal produced per unit of SOC combusted in the organic layer) and (2) more complete consumption of organic layers in warmer, south facing forests (with relatively shallow organic layer depths) allowed for more incorporation of BC with the mineral soil. In a recent review of BC accumulation in soils, Czimczik and Masiello (2007) similarly nominated appropriate combustion conditions and physical mixing with

mineral soil as dominant controls over soil BC storage. An examination of mechanistic controls over organic matter combustion or charcoal conversion was outside the scope of this study, but the BC distribution patterns we observed provide clues to how soil physical properties influence BC accumulation through the interplay of formation and preservation mechanisms. For example, the higher BC stocks observed in south-facing soils in this study suggest either high BC formation rates or a unique mechanism that preserves BC in this landscape position. The smoldering combustion conditions necessary for BC production (low O_2) are more likely to occur in soils with higher bulk density (lower porosity) found in south-facing organic soils (see also discussion by Miyanishi and Johnson 2002). The organic layers of cooler north-facing forests had lower bulk densities near the surface and therefore it was more likely that flaming combustion patterns occurred near the soil surface during dry periods when fires are more common. The deeper organic layers in north-facing forest soils also harbor more moisture (Kasischke and Johnstone 2005; Kane et al. 2007), making them more resistant to burning (Shetler et al. 2008). The higher flaming potential and wetter conditions suggest that BC formation rates would be lower in north facing forests than in south facing forests when surficial organic horizons burn, given similar fire weather conditions.

We suggest that differences in organic soil physical properties (thickness and density) largely determined the observed patterns in mineral soil BC stocks in interior Alaskan black spruce forests. BC deposited within the thick organic soil horizons on N-facing aspects would be more susceptible to combustion in subsequent fires than BC incorporated with the mineral soil (c.f., Czimczik et al. 2005), largely because of reduced flammability and physical protection. Therefore, an increase in organic layer depth offers a parsimonious explanation for the patterns of lower mineral soil BC concentrations measured across sites (Fig. 6; Table 4).

In a small catchment in northern Siberia, Guggenberger et al. (2008) also determined that the amount of BC harbored in organic soil horizons relative to surface mineral soil horizons (0–20 cm) was higher in north-facing forests with shallow active layer depths than in warmer south facing forests (ratios of 0.26 and 0.10, respectively). In contrast to our

findings, however, the north-facing forests harbored significantly more BC (measured by benzene polycarboxylic acid molecular markers) in organic and surface mineral soil horizons ($325 \pm 58 \text{ g BC m}^{-2}$) than did south facing forests ($91 \pm 39 \text{ g BC m}^{-2}$). Proposed mechanisms for increased BC stocks in colder, north facing forests were the preservation of BC owing to permafrost, anoxia, and retarded decomposition within the active layer. While discontinuous permafrost was also common to the north facing forests in this study, we observed less BC in the surface mineral soil of these forests than in warmer, south facing forests lacking permafrost. These differences may be explained in part by changes in fuel type and organic layer characteristics. The Alaskan field sites had mean organic layer SOC stocks that were approximately 2–5 times greater than those reported for the north and south facing Siberian forests, respectively, which corresponds to thicker organic horizons (e.g., Yi et al. 2009). The deeper organic layers present in the Alaskan study could impede the incorporation of burn residues with the mineral soil. This would be especially evident in early season wildfires occurring on north facing aspects, as seasonal ice would still likely be present in deep organic layers. The ground layer fuel types available in the Alaskan forests were also different than those in the Siberian study. Surface organic layers were comprised of mosses and black spruce detritus in various stages of decay in this study, whereas the Siberian study also included sites dominated by grasses in the ground layer, and had changing sources of tree litters (pine, larch, and birch species). Therefore, the nature of wildfires and the types of BC produced within pine and larch ecosystems may be quite different than within black spruce ecosystems. Gaining a mechanistic understanding of controls over the products of burning (especially charcoal conversion rates) within stand and organic layer components would help clarify differences in patterns of BC accumulation between these different ecosystem types.

Finally, the results of our study can be contrasted with that of Fang et al. (2009). Working in cultivated Iowa Mollisols, Fang et al. (2009) used BDMAS NMR to assess variation in soil aromaticity with landscape position. Using the nonprotonated fraction of aromatic carbon as a proxy for BC content, Fang et al. (2009) found increases in BC content in soil

from a poorly drained, low-lying landscape position. The authors attribute this landscape effect to either (a) preferential transport of BC to lower landscape positions, and/or (b) poor decomposition of BC in anoxic soils. Although the landscape-scale BC distribution patterns described by Fang et al. (2009) are different from those of our study, they support the broader hypotheses that landscape position and physical properties of the fuel load play an important role in BC production and storage, in concert with fire frequency and soil mineralogy, to produce ecosystem-specific patterns of soil chemistry.

Fire frequency and BC accumulation

Recent studies have suggested that pyrogenic C is susceptible to re-burning in subsequent fires (Czimczik et al. 2005; see also Johnstone 2006). This could explain in part why there was no trend between BC stocks and estimates of fire frequencies across these sites (Fig. 7a). At the sites with the highest fire frequencies (Deuce, Dune, and Jan), radiocarbon ages of mineral soil BC samples isolated using the Kuhlbusch (1995) method confirmed that the majority of pyrogenic C in the surface mineral soil horizon was derived from recent wildfire activity (Fig. 7b). In fact, the age of the BC pool in the surface mineral soil closely matched the mean age of the black spruce stand (listed in Table 1) at sites of high fire frequency. Therefore, the BC pool at the surface of the mineral soil was dominated by BC generated during the most recent stand-replacing fires which occurred in the last 100 years. These observations suggest that “old” BC from historic fires was subject to (i) extensive consumption by recent fires, (ii) extensive and rapid decomposition, and/or (iii) extensive physical transport from the fire site.

Previous research in other ecosystems has also found relatively young ages for soil BC (220–545 years), using multiple fractionation techniques to isolate soil BC (Krull et al. 2006). While it is possible that older BC particles may have been lost in the chemical oxidation process used to isolate BC in this study (c.f., Krull et al. 2006), other recent research has also found relatively young ages (mean of 652 years) for soil charcoal particles isolated by washing and sieving (not by chemical oxidation) in boreal forest soils (Ohlson et al. 2009). Nevertheless,

BC is likely the dominant source for aromatic SOC in these fire-prone forest ecosystems (Thiffault et al. 2008), and further research is needed to determine the relationship between BC concentrations and the residence time of discrete SOC pools. Taken together, these findings suggest that soil BC concentrations and stocks may be more dependent on recent fire severity and its interactions with topography (particularly aspect and drainage) than the frequency of past fire events.

Charcoal records from lake sediments are well suited for reconstructing the incidence of past fire events, but changes in local micro-topographical factors can substantially affect fire activity within a lake margin, even over long periods (as reviewed by Gavin et al. 2007). For example, the fire return intervals (110–250 year) reflected over the 1000 year record within the lake margins in this study were longer than previous reports for upland black spruce forests of interior Alaska (~100 year; Yarie 1981). Changes in local micro-topographical features, such as the presence of deep sphagnum (Benscoter and Wieder 2003; Shetler et al. 2008), organic layer depth, soil moisture, and depth to permafrost (Kasischke and Johnstone 2005; Harden et al. 2006) exert considerable control over the depth of burning (fire severity) and the interaction of burn residues with the mineral soil (Gavin 2003; Kane et al. 2007; Czimczik and Masiello 2007). Therefore, we suggest that local topographical features (organic layer depth, landscape position, and bulk density) are at least as important as fire frequency in mediating the accumulation of BC in soils.

Implications of BC for organic matter quality and nitrogen cycling

Soil BC concentrations increased while SOC concentrations declined across sites, which is likely due to the relative recalcitrance of BC and the preferential mineralization of labile forms of SOC (e.g., carbohydrate-C). The relative stability of BC was confirmed by its co-occurrence with high alkyl:O-alkyl ratios, a common index for the extent of organic matter decomposition (Table 3). Surprisingly, protein concentrations were also higher in the surface mineral soil. Proteins and amino acids are widely viewed as labile materials (e.g., Jones 1999), rapidly used in soils (Persson and Nasholm 2001; Kielland

et al. 2007), and therefore would not be expected to increase in relative abundance in mineral soils with more advanced SOC decomposition than in organic horizons (as indicated by alkyl:O-alkyl ratios). However, N:C ratios typically increase from organic to mineral soils, with increased N:C generally being attributed to active clay adsorption or occlusion within mineral soil aggregates with higher particle density and less organic matter (Sollins et al. 2006; Kleber et al. 2007). Therefore, the fact that protein and charcoal concentrations increase concomitantly could be caused by a shared preservation mechanism (mineral adsorption or occlusion). However, this is unlikely because the incipient, loess-derived mineral soil of interior Alaska has few active clay minerals and nutrient retention and ion exchange capacity are more closely linked to SOC content (Van Cleve et al. 1993; Ping et al. 1995; Michaelson et al. 2008). In this study, the relative increase in protein-C and N:C from organic to mineral soil horizons (Fig. 5) likely reflects the loss of carbohydrate and lignin as decomposition increases with depth (Table 3). However, the stabilization mechanisms of protein, as a dominant component of the soil N pool, are not well understood.

Within organic horizons, protein-C concentrations increased with increasing BC, from 3 to 26% BC. The maximum BC% in organic soils was approximately equal to the mean BC% measured for all mineral soil horizons (Fig. 5a). This pattern observed within the organic soil horizons cannot be explained by changes in particle density or mineral occlusion of N, because large changes in particle density are not likely and there are no clay minerals to occlude N. The correlation between BC and protein C observed in this study is consistent with previous research that has demonstrated a link between soil charcoal and the retention of amino acids (e.g., Pietikainen et al. 2000; DeLuca et al. 2002; Berglund et al. 2004). It is possible that proteins and amino acids are physically/chemically stabilized and/or biologically immobilized within BC particles owing to their increased surface area, reactivity, and interior protected space (Rillig et al. 2007). Though certainly not exhaustive, these data suggest that soil concentrations of BC (particularly the low temperature charcoals detectable by BD NMR + model) could serve a role in the stabilization of soil proteins, and highlight the need for more research.

Conclusions

Interactions among landscape position, organic layer depth, and bulk density explained most of the variance in soil BC across sites. Contrary to our hypothesis, soil BC stocks did not increase with increasing frequency of fire, as determined by lake sediment charcoal records (representing a 1000 year period) at four sites. Cooler, north facing forests (deep organic layers) harbored the lowest soil BC, and more BC was harbored in shallow mineral soil horizons than in the organic soil horizons. These findings suggest that (i) BC in organic horizons is more vulnerable to burning (and increased frequency of burning) in subsequent wildfires than is BC incorporated within the shallow mineral soil, and (ii) the conversion of surface organic material into BC may be higher in warmer, south facing forests. The concentrations of different forms of BC, reflecting changing pyrolysis conditions from different wildfires or burning conditions, were correlated with the concentration of aromatic-C in the surface mineral soil horizons. Moreover, the positive relationship between BC (BD NMR + model) and soil protein concentrations, while within a limited dataset, suggests that BC may contribute to the retention of amino acids, which certainly deserves further investigation.

The patterns of climatic warming and drying predicted for North American boreal forests are likely to increase the extent of wildfires in the region (e.g., Flannigan et al. 2005). Our results imply that soil and site characteristics occurring with changes in topography could modulate the conditions for soil organic matter combustion in warmer conditions predicted for the future, and therefore exert considerable control over the patterns of BC accumulation in surface organic and mineral soil horizons.

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