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How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor:
Stocks, molecular structure, and conversion to black carbon (charcoal)

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[1] In boreal forests, fire is a frequent disturbance and converts soil organic carbon (OC) to more degradation-resistant aromatic carbon, i.e., black carbon (BC) which might act as a long-term atmospheric-carbon sink. Little is known on the effects of fires on boreal soil OC stocks and molecular composition. We studied how a surface fire affected the composition of the forest floor of Siberian Scots pine forests by comparing the bulk elemental composition, molecular structure (^{13}C-MAS NMR), and the aromatic carbon fraction (BC and potentially interfering constituents like tannins) of unburned and burned forest floor. Fire reduced the mass of the forest floor by 60%, stocks of inorganic elements (Si, Al, Fe, K, Ca, Na, Mg, Mn) by 30–50%, and of OC, nitrogen, and sulfur by 40–50%. In contrast to typical findings from temperate forests, unburned OC consisted mainly of (di-)O-alkyl (polysaccharides) and few aromatic structures, probably due to dominant input of lichen biomass. Fire converted OC into alkyl and aromatic structures, the latter consisting of heterocyclic macromolecules and small clusters of condensed carbon. The small cluster size explained the small BC concentrations determined using a degradative molecular marker method. Fire increased BC stocks (16 g kg^{-1} OC) by 40% which translates into a net-conversion rate of 0.7% (0.35% of net primary production) unburned OC to BC. Here, however, BC was not a major fraction of soil OC pool in unburned or burned forest floor, either due to rapid in situ degradation or relocation. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 1694 Global Change: Instruments and techniques; 1699 Global Change: General or miscellaneous; 9320 Information Related to Geographic Region: Asia; *KEYWORDS:* fire, black carbon, soil organic matter, solid-state ^{13}C-MAS NMR, boreal forests

1. Introduction

[2] Understanding what determines the organic carbon (OC) balance of boreal soils has major implications for the global carbon cycle. Boreal soils store 48–66% (338 to 625 P(10^{15})g C) of the OC present in forest soils worldwide [*Kasischke*, 2000; *Intergovernmental Panel on Climate Change (IPCC)*, 2001]. In boreal forest ecosystems, fire is a frequent disturbance factor which strongly influences the size and molecular composition of the soil OC pool. Fire affects the OC input into the soil by controlling species composition and the amount and structure of forest biomass [*Nalder and Wein*, 1999; *Wirth et al.*, 1999]. Also, fire directly alters the amount and molecular composition of soil OC by distilling, oxidizing, or charring which results in a release of soil OC to the atmosphere as gases, volatiles or aerosols. Simultaneously, during incomplete combustion, fire converts OC to a more degradation-resistant form, i.e., black carbon (BC) [*Goldberg*, 1985; *Gleixner et al.*, 2001].

[3] Fire is a major short-term carbon source to the atmosphere [*IPCC*, 2001]. For the Northern Hemisphere, fire-associated direct OC losses to the atmosphere were estimated to be 0.13 Pg C yr^{-1} during 1977 and 1990 [*Auclair and Carter*, 1993]. An increase in human induced and natural fires within the last decades seems to have converted some boreal forest areas into carbon sources [*Kurz and Apps*, 1999], while the northern extra-tropical regions as a whole acted as a sink [*Schimel et al.*, 2001].

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[4] However, fire may also provide a small long-term carbon sink (globally 0.05 to 0.27 Pg C yr^{-1}) via the conversion of OC to BC [*Kuhlbusch and Crutzen*, 1995; *Kuhlbusch*, 1998]. It is assumed that in soils BC resists microbial degradation due to its highly-condensed molecular structure. Thus, BC is removed from faster cycling carbon pools and accumulates in soils. This assumption is based on the high resistance of BC against oxidation [*Skjemstad et al.*, 1999; *Glaser et al.*, 1998], its observed accumulation in some soils [*Skjemstad et al.*, 1996; *Glaser*, 1999; *Glaser et al.*, 2001; *Schmidt et al.*, 1999], and preservation over long time periods in the geological record (see review by *Schmidt and Noack* [2000]), although some indications for BC degradation exist [*Haumaier and Zech*, 1995; *Bird et al.*, 1999; *Smernik et al.*, 2000].

[5] Estimates of BC formation range globally from 0.05 to 1.7 Pg C yr^{-1} [*Seiler and Crutzen*, 1980; *Crutzen and Andreae*, 1990; *Kuhlbusch and Crutzen*, 1995; *IPCC*, 2001], or for the Northern Hemisphere from 0.005 to 0.013 Pg C yr^{-1} [*Auclair and Carter*, 1993; *Kuhlbusch and Crutzen*, 1995]. Of the BC formed in fires, 80% are considered to remain on the soil surface and to enter the soil OC pool, while 20% are emitted as aerosols to the atmosphere [*Kuhlbusch and Crutzen*, 1995]. These estimates on BC formation are based on a very limited number of studies from the (sub)tropics. At present, there are only a few studies on the conversion rate of OC to BC for aboveground biomass [*Fearnside et al.*, 1993, 1999, 2001; *Kuhlbusch and Crutzen*, 1995; *Kuhlbusch et al.*, 1996; *Graca et al.*, 1999] or for coarse woody debris [*Tinker and Knight*, 2000] from (sub)tropical and temperate ecosystems. Thus far, there have not been any studies on soil BC stocks or the conversion of OC to BC for boreal ecosystems.

[6] Understanding how fire alters stocks and the molecular structure of OC, especially the conversion of OC to BC, may be key in understanding carbon sequestration of boreal soils and their response to a warming climate. This is because fire-induced change in the composition of OC probably results in increased resistance to microbial degradation. Some studies investigated how fire changes soil OC stocks [*Slaughter et al.*, 1998; *Nalder and Wein*, 1999; *Parker et al.*, 2001] or carbon mineralization [*Fernández et al.*, 1999]. Other studies have focused on how the molecular composition of mineral soil OC is affected by recurring fires [*Skjemstad et al.*, 1996, 1999; *Golchin et al.*, 1997a, 1997b; *Schmidt et al.*, 1999; *Smernik et al.*, 2000; *Glaser et al.*, 2001] or during laboratory heating [*Almendros et al.*, 1992; *Fernández et al.*, 2001; *Choromanska and DeLuca*, 2002]. However, few studies exist on how fire affects the soil OC pool of forests with concomitant measurements of OC stocks and the molecular composition [*Fernández et al.*, 1997], especially for the Russian boreal region [*Conard and Ivanova*, 1997; *Schulze et al.*, 1999; *Wirth et al.*, 2002].

[7] Besides the dominant organic elements (OC, nitrogen, and sulfur), the forest floor of boreal forests often contains large proportions of the total plant-available inorganic nutrients stored in the whole soil profile [*Brais et al.*, 2000; *Gower et al.*, 2000]. Fire releases parts of the inorganic elements to the atmosphere as aerosols [*Echalar*

et al., 1998], and of the organic elements as aerosols, volatiles, or gases [*Gleixner et al.*, 2001].

[8] Our study contributes to quantifying and characterizing the effects of surface fires on organic and inorganic elemental composition of the forest floor of Siberian Scots pine (*Pinus sylvestris* L.) forests which cover the largest part (37 area-%) of west Siberian forests [*Shvidenko and Nilsson*, 1994] and are frequently subject to fire. In Russia, 70% of fires occur in Scots pine or larch (*Larix dahurica* Turcz. ex Trautv., *L. gmelinii* (Rupr.) Kuzen.) dominated forests, most frequently as surface fires (80 area-%) [*Conard and Ivanova*, 1997].

[9] In a field study, we took advantage of a naturally occurring fire. We compared burned forest floor with unburned patches as a control by (1) quantifying the bulk stocks of inorganic (Si, Al, Fe, K, Ca, Na, Mg, Mn) and organic (OC, total nitrogen, and sulfur) elements, and by characterizing (2) the molecular composition of the bulk OC (by using solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy), and (3) the composition of the aromatic OC fraction (i.e., by quantifying BC and potentially interfering constituents such as tannins, and calculating the conversion rate of OC to BC).

2. Study Area and Sampling

[10] The study area, a permafrost-free glacial-fluvial sand plain, was located about 40 km west of the river Yenisey at the eastern edge of the west Siberian lowland (60°43′N, 89°08′E). Soils are Dystrustepts [*Soil Survey Staff*, 1999], with a homogeneous sandy texture (>90 mass-% > 63 μm, mainly quartz) and spodic features. The vegetation consisted of pristine monotypic Siberian Scots pine forests (*Pinus sylvestris* ssp. *sibirica* Lebed) with an open canopy and a lichen-dominated understorey, surrounded by ''Aapa'' type sphagnum bogs and small rivers. The climate was continental (monthly average air temperature 17.3°C in July, −22.9°C in January, annual precipitation 493 mm, with 70% occurring during summer thunderstorms) [*Wirth et al.*, 1999]. Risk of forest fires was high during the entire growing season (March to September). Periods between thunderstorms, which were the main fire causes, could be very dry and the summer water balance was close to zero [*Kelliher et al.*, 1998]. Average fire return interval was 25 ± 10 years [*Wirth et al.*, 1999].

[11] To study the effect of surface fire on the forest floor, we took advantage of a surface fire which had passed through an approximately 250-year-old forest stand two days before sampling (19 July 2000). The fire had burned major parts of the forest floor and lower forest canopy, but left some unburned patches of forest floor.

[12] We sampled five replicates each from unburned and burned areas of forest floor within an area of flat topography. We collected the whole forest floor in a 0.3 × 0.3 m^2 area including living reindeer lichen, down to the upper boundary of the mineral soil. In addition we took reference samples of living and burned reindeer lichen, the main contributor to the forest floor bulk volume. All samples were taken within an area of a few square meters. It thus could be assumed that unburned samples represented the same forest stand as the burned samples.

[13] Unburned forest floor consisted of two layers that could easily be separated. The upper layer was dominated by living lichen, mixed with slightly decomposed litter (needles and small twigs). The deeper layer consisted of decomposed lichen biomass, litter, and may have contained black carbon, and the degree of decomposition of the material continuously increased with depth. Sampling did not include coarse woody debris (diameter > 2 cm). In the burned areas, forest floor had not burned off completely to the mineral soil and looked completely black (charred). This material was amorphous, although in some cases the structure of burned lichen could still be identified. However, it was not feasible to (1) separate the burned material from the unburned layer below, or (2) identify how deep the fire had burned into the organic layer. For comparison of unburned and burned forest floor, we therefore sampled total forest floor on a constant area basis.

3. Experimental Methods

[14] Prior to analyses, forest floor and lichen samples were dried at $60°C$ and ground in a ball mill (Retsch, Germany). For the forest floor samples, we determined bulk stocks of inorganic elements, OC, total nitrogen and sulfur, the bulk molecular composition of OC, and the composition of the aromatic carbon fraction (BC, and tannins as potentially interfering constituents). For the lichen samples, we determined the bulk molecular composition of OC.

3.1. Elemental Composition

[15] Ash content was quantified by loss on ignition. Samples (0.2 to 0.3 g) were isothermally heated ($1000°C$) in 150 μL Al_2O_3 crucibles filled to one third of volume under oxidizing conditions (oxygen atmosphere) until they reached constant mass after ignition using thermogravimetry (Mettler Toledo TGA/STDA851, Germany; precision 1 μg; 5 scans per second). Al_2O_3 powder served as a blank. To remove evolving gases and aerosols from the sample, the oven interior was permanently flushed with oxygen (20 mL per minute). Sample mass was measured and recorded continuously by the built-in software (Star 6.01).

[16] For analysis of inorganic elements (Si, Al, Fe, K, Ca, Na, Mg, Mn), samples (0.1 g) were digested in a microwave oven ($240°C$, 30 bar; Anton Paar, Austria) using 4 mL of a concentrated $HCl:HNO_3$ solution (3:1 v/v) with 100 μL HF. A certified soil (SRM 2710, Montana Soil, USA) served as quality control. Element ions were quantified via ion-coupled plasma optical emission spectroscopy (Optima 3300 DV; Perkin-Elmer, USA).

[17] Organic carbon (OC), total nitrogen and sulfur were quantified by dry combustion in an elemental analyzer (Vario EL, Germany).

3.2. Bulk Molecular Composition of Soil Organic Carbon

[18] Solid state ^{13}C NMR spectra with magic-angle spinning (MAS) were obtained using a Bruker MSL 300 spectrometer (Bruker Instruments Inc., Germany) operating at 75.47 MHz. Because of the large amount of instrument time required, two samples of unburned and burned forest floor were analyzed from each set of five replicates. For each set we chose the sample that was closest to the mean OC concentration and the sample with the next higher OC concentration. Spectra of unburned forest floor samples 2 and 3, and the unburned lichen sample were obtained at 4.7 kHz MAS rate in a 7-mm outer diameter rotor, and those of burned forest floor samples 2 and 3, the burned lichen sample, and a repeat of the unburned forest floor sample 3 at 8.0 kHz in a 4 mm rotor. A spinning speed of 8000 Hz was chosen as a compromise between reduction of spinning sidebands versus the loss of cross-polarization (CP) efficiency with increasing spinning speeds. The ramped-amplitude (RAMP) method which alleviates this by ramping the ^1H power during contact time [*Dria et al.*, 2002] was not available on our equipment.

[19] Spectra were obtained using CP to transfer magnetization from protons to carbons, the usual method of signal enhancement in routine solid-state ^{13}C spectra. This allows rapid acquisition and detailed examination of spectra features. However, CP signal enhancement is more efficient for carbons in rigid structures with attached protons, whereas other classes of carbons may be underrepresented. These include (1) carbons remote from protons, such as the poly-condensed aromatic structures of black carbon, (2) carbons with some molecular-level mobility in the solid state, such as methyl (CH_3), methoxy (OCH_3) and acetate ($CH_3-CO_2^-$) groups, and methylene (CH_2) in long alkyl chains, and (3) carbons close to paramagnetic centers [*Skjemstad et al.*, 1999; *Smernik et al.*, 2000; *Preston*, 2001; *Preston et al.*, 2002a; *Baldock and Smernik*, 2002; *Czimczik et al.*, 2002].

[20] To obtain further information on carbon structures, we also obtained CP spectra with dipolar-dephasing (DD), where a short delay period without decoupling is inserted between CP and signal acquisition. During the dephasing delay, signal is rapidly lost from carbons with attached hydrogens, although some signal also persists for the more mobile carbons. For equal detection of all carbon we used simple Bloch decay (BD) acquisition without CP, to obtain spectra with lower signal-to-noise ratio and resolution, but quantitative intensity distribution.

[21] The CP spectra were acquired with 1 ms contact time, and 4400 to 19000 scans, with more scans required for spectra of burned samples, and for DD spectra. The relaxation delay was 2 s for unburned samples and 1.5 s for burned samples. DD spectra were obtained with 46 to 47 μs dephasing time. For the unburned samples in the 7-mm rotor, DD was combined with the sequence for total suppression of spinning sidebands (TOSS); this was not used at the with the 4-mm rotor at the higher spinning speed.

[22] BD spectra were obtained with 100-s recycle time and 720 scans (20 hours). These were corrected for spectrometer background (roughly equal to the magnitude of the signal with our equipment) by subtraction of the free induction decay obtained from an empty rotor. To assess the CP efficiency for a sample, we obtained a second CP spectrum of the sample with the same number of scans as the BD spectrum (720 scans).

[23] Spectra were processed with either the PC-based WinNMR, or the original Aspect DISMSL software (Bruker, Germany) using 40 Hz (CP) or 60 Hz (DD, BD) line-broadening and baseline correction. Chemical shifts are

reported relative to tetramethylsilane (TMS) at 0 ppm, with the reference frequency set using the adamantane peak at 38.56 ppm.

[24] Spectra were divided into the following chemical-shift regions for carbon: alkyl (0–50 ppm), O-alkyl (50–93 ppm), di-O-alkyl (93–112 ppm), aromatic and phenolic (112–165 ppm), and carboxyl and carbonyl (165–215 ppm). These boundaries were adjusted slightly as required to retain correspondence with the natural minima in the spectra. The region from 50–60 ppm is associated with methoxy carbon, especially from lignin, and N-alkyl carbon of proteins. This region was not quantified separately, as it was generally weak and poorly resolved from the much larger O-alkyl signal. The relative areas (percentage of total intensity) were calculated after corrections were made for spinning sidebands by assuming equal intensity for the upfield and downfield sidebands [*Preston*, 2001].

[25] For the spectra of the burned samples, especially with BD, the large, broad aromatic signal clearly extended into the di-O-alkyl region. Its contribution was estimated by sketching in the wing of the aromatic signal, and dividing the integrated intensity accordingly (typically assigning half to di-O-alkyl and half to aromatic for the CP spectra). For the BD spectra, there was often no distinct di-O-alkyl signal, in which case the whole region was assigned to aromatic carbon.

[26] To estimate the overall CP efficiency of a sample, CP and BD spectra (both with 720 scans) were compared by plotting with the "absolute intensity mode" (MSL 300 Aspect computer), and the total integral heights compared. Integral heights were also compared to determine CP efficiency of individual chemical-shift regions. For the 720-scan CP spectrum, the total integral height was divided according to the relative intensity data from the normal CP spectrum with many more scans and much better signal-to-noise ratio. For calculating CP efficiencies, the O- and di-O-alkyl regions were combined.

3.3. Tannins

[27] Tannins were analyzed using the proanthocyanidin assay [*Preston et al.*, 1997; *Lorenz et al.*, 2000], in which the condensed tannin is depolymerized by an acid catalyst (HCl) in *n*-butanol to give an anthocyanin product (a flavylium ion), with an intense red color whose adsorbance is determined.

[28] The assay was standardized against purified condensed tannin from balsam fir needles (*Abies balsamea* (L.) Mill.) [*Preston et al.*, 1997]. Aliquots (0.05 to 0.25 mg) from a standard solution of 0.5 mg mL^{-1} in methanol were pipetted into screwcap 10 mL Pyrex centrifuge tubes and dried at 70°C. Forest floor samples (0.4 g) were weighed into the tubes. Five mL of reagent (5% concentrated HCl in *n*-butanol (v/v), with a total water content of 5% (v/v) and 200 mg L^{-1} Fe^{2+} as FeSO$_4$ × 7 H$_2$O) was added to the tubes. Samples and standards were hydrolyzed in a water bath at 95°C for 1 hour with vortex mixing before and after 30 min of heating. The tubes were then centrifuged (4000 rpm, Hermle Z382, Germany) for 20 min, decanted into disposable cuvettes and scanned from 430 to 650 nm using a UV-vis-spectrophotometer (Milton Roy 1001 Plus, USA).

Adsorbances were determined at the peak maximum at 555 ± 2 nm, with allowance for sloping baseline. Tannin concentrations were determined from the calibration curve established for balsam fir tannin.

3.4. Black Carbon

[29] Black carbon (BC) was quantified using benzenepolycarboxylic acids (BCAs: hemimellitic, trimellitic, trimesic, pyromellitic, prehnitic, mellophanic, benzoepentacarboxylic, and mellitic acid) as molecular markers. We extended the method developed by *Glaser et al.* [1998] to detect the lower BC concentrations (16–44 compared to 50–140 g BC kg^{-1} OC) by enhancing cation removal using different filters and cation exchange resin. Polyvalent cations form complexes with BCAs, preventing derivatization needed for gas-chromatographic quantification. Samples (0.05 g) were oxidized in 2 mL HNO$_3$ (65%, p.a., 170°C, 8 hours, pressure apparatus, Seif, Germany), filtered into 10 mL flasks (ashless cellulose filter), rinsed with deionized water and filled up to 10 mL.

[30] Polyvalent cations were removed from the samples by using cation exchange resin (Biorad, Germany, AG 50 WX8, 200–400 mesh, fill height 6, diameter 1 cm), with the base of the column plugged by glass wool (prewashed with 2 M HCl (ultra pure) followed by water). Resin columns were conditioned using 18 mL 2 M HCl, and subsequently rinsed with water until the solution was neutral.

[31] Two mL of sample, plus 100 μL of internal standard (citric acid, 25 mg per 50 mL in water), were percolated through the column and collected in 100 mL flasks. Columns were rinsed twice with 18 mL water, then once with 9 mL water. Combined solutions were freeze-dried, transferred into 3 mL Teflon-lined screwcap vials using 4 times 750 μL methanol (p.a.) and dried under N$_2$. Samples were derivatized with 100 μL dried pyridine and 100 μL *N*, *O*-bis (trimethylsilyl)-triflouroacetamide at 80°C for 2 hours. Derivatized oxidation products were separated using a Hewlett Packard 19091S-433 gas chromatograph, Germany (carrier gas: He, capillary column HP-5ms: 34 m × 250 μm, 0.25 μm film thickness) and detected by an atomic emission detector. After injection (2 μL, split ratio 2.5:1), the temperature program was the following: 110°C for 1 min, 110 to 200°C at 10°C min^{-1}, 200 to 250°C at 5°C min^{-1}, 250° to 300°C at 20°C min^{-1}, and 300°C for 5 min.

[32] Individual BCAs were quantified by comparison of their retention times with those of commercially available BCAs (external standards), and response factors were calculated using citric acid as internal standard and external standards in three different concentrations. The response factor for pyromellitic acid was used to quantify prehnitic and mellophanic acid which were not accessible commercially. BC concentrations were calculated by dividing the sum of BCAs by 0.441 as revealed from a set of BC standards by *Glaser* [1999].

4. Results and Discussion

[33] We took advantage of a naturally occurring surface fire to study the effects of fire on the forest floor of Siberian Scots pine forest. Of the unburned and burned samples, we (1) determined mass, inorganic and organic element con-

Table 1. Concentrations (g kg^{-1} soil) of Inorganic Elements in Unburned and Burned Forest Floor of Siberian Scots Pine Forests

Concentrations	Ash Content	Si	Al	Fe	K	Ca	Na	Mg	Mn
Unburned	520 (108)	6.0 (1.28)	5.9 (0.78)	3.3 (0.38)	2.2 (0.44)	1.4 (0.50)	0.5 (0.10)	0.3 (0.03)	0.1 (0.03)
Burned	454 (83)	7.5 (0.72)	6.9 (0.68)	3.5 (0.27)	2.6 (0.37)	2.1 (0.48)	0.7 (0.12)	0.4^b (0.03)	0.2 (0.07)
Unburned - burned	−66	+1.5	+1.0	+0.2	+0.4	+0.7	+0.1	+0.1	+0.1
Percent unburned[a]	−13	+25	+17	+6	+18	+50	+20	+33	+100

[a]Calculated as (burned-unburned) × 100/unburned; standard deviation in parentheses; n.d not determined.
[b]$p < 0.05$, Student's unpaired, two-tailed t-test.

centrations, and calculated the corresponding stocks, (2) characterized the bulk molecular composition of OC using ^{13}C-MAS NMR, and (3) quantified the aromatic carbon fraction (BC stocks, and potentially interfering aromatic constituents such as tannins), and from this, we calculated the conversion rate of OC to BC.

4.1. Elemental Composition

[34] To quantify inorganic and organic element stocks in the unburned and burned forest floor, we determined dry mass and element concentrations for each sample.

4.1.1. Mass

[35] The dry mass of the unburned forest floor (3.4 ± 0.9 kg m^{-2}, Table 3 in section 4.1.3) was similar to earlier measurements for the studied region (4.3 kg m^{-2}) [FIRE-SCAN Science Team, 1996]. Fire reduced forest floor dry mass by 2.0 kg m^{-2} or 60% which was similar to earlier findings for the same region (2.4 kg m^{-2}) [FIRESCAN Science Team, 1996], and to Canadian jack pine (Pinus banksiana Lamb.) stands (40 to 60%) [Brais et al., 2000].

4.1.2. Inorganic Elements

[36] The ash content of the unburned forest floor was about 50% of the mass, and was predominantly Si and Al, with lesser amounts of Fe, K and Ca, and minor amounts of Na, Mg, and Mn (Table 1). Compared to jack pine forest stands of the northern American BOReal Ecosystem Atmosphere Study (BOREAS) sites [Gower et al., 2000], Ca concentrations were 2 orders of magnitude, and Mg concentrations one order of magnitude higher. Stocks of inorganic element showed a similar composition as concentrations (Table 2). Compared to Canadian jack pine forests [Brais et al., 2000], stocks of Ca and Mg were one order of magnitude, and of K 2 orders of magnitude smaller.

[37] Differences between studies in proportion, concentration, or stocks of inorganic elements are probably due to differences in soil parent materials, vegetation, and analytical techniques applied to quantify inorganic element composition.

[38] Concentrations of Si and Al indicate the incorporation of mineral soil into the forest floor. This may result from windthrow of trees, bioturbation, or transport through the biological mycorrhiza-root pump [Vogt et al., 1987; van Breemen et al., 2000]. Furthermore, some mineral soil might have originated from our sampling approach where the sampling depth for each individual forest floor sample was adjusted to coincide with the upper part of the mineral soil. Transitions between forest floors and mineral soils were a continuum and so some mineral soil might have been included into the forest floor samples. However, the similar total inorganic element concentration within the unburned sample set indicates that our sampling approach was successful and reproducible.

[39] The ash content of the burned forest floor decreased slightly whereas inorganic element concentrations increased by 18 to 100% (Table 1). The increase in K, Ca, Mg, and Na concentrations probably will have increased the pH value, as frequently reported after fire [Ahlgren and Ahlgren, 1960]. Fire reduced inorganic elements stocks by 40 to 50 mass-% (Table 2). Losses of K, Ca, and Mg stocks were similar to findings from Canadian jack pine forests, where severe burning reduced stocks by 50, 30, and 40%, respectively [Brais et al., 2000]. K, Ca, Mg, and Na are commonly lost during biomass burning and emitted to the atmosphere as aerosols [Trabaud, 1994; Echalar et al., 1998]. In this study, we also found losses of Si, Al, and Fe which are usually not attributed to fire, but to erosion of mineral soil [Echalar et al., 1998]. Apparent differences in Si, Al, and Fe might also reflect different sampling depths between unburned and burned sample sets, although similar values within each set point at least toward a reproducible sampling per set.

4.1.3. Organic Elements

[40] The average OC concentration of the unburned forest floor was 250 g kg^{-1} (Table 3) and thus similar to results from Canadian jack pine forests (226−318 g kg^{-1} [Preston et al., 2002b]). Total nitrogen concentration was 5.2 g kg^{-1}, which was smaller than those reported from

Table 2. Stocks of Inorganic Elements (g m^{-2}) in Unburned and Burned Forest Floor of Siberian Scots Pine Forests

Stocks	Si	Al	Fe	K	Ca	Na	Mg	Mn
Unburned	19.7 (3.4)	19.6 (4.2)	10.9 (2.3)	7.1 (1.2)	4.9 (2.5)	1.8 (0.3)	0.9 (0.3)	0.3 (0.1)
Burned	10.7^b (2.6)	9.8^b (2.2)	4.9^b (1.1)	3.6^b (0.7)	2.9 (0.7)	0.9^b (0.2)	0.6 (0.1)	0.2 (0.0)
Unburned - burned	−9.0	−9.7	−6.0	−3.4	−1.9	−0.8	−0.3	−0.1
Percent unburned[a]	−46	−50	−55	−49	−40	−47	−37	−26

[a]Calculated as burned-unburned) × 100/unburned; standard deviation in parentheses; n.d. not determined.
[b]$p < 0.05$, Student's unpaired, two-tailed t-test.

Table 3. Concentrations of Organic Elements, BC, and Tannins in Unburned and Burned Forest Floor of Siberian Scots Pine Forests

Sample	Dry mass[a] kg m^{-2}	Carbon					Total Nitrogen g kg^{-1} soil	Total Sulfur g kg^{-1} soil	C:N- Ratio
		Organic Carbon g kg^{-1} soil	Black Carbon		Tannins				
			g kg^{-1} soil	g kg^{-1} OC	g kg^{-1} soil	g kg^{-1} OC			
Unburned									
1	4.6	311.1 (1.0)	3.7 (0.3)	12.0 (1.1)	0.26 (0.02)	0.8	6.2 (0.02)	0.3 (0.1)	50
2	3.9	279.9 (1.1)	5.3 (0.1)	18.9 (0.2)	0.05 (0.02)	0.2	6.6 (0.1)	0.2 (0.03)	43
3	3.3	253.6 (17.0)	6.2 (0.5)	24.3 (2.1)	0.18 (0.02)	0.7	5.7 (0.4)	0.2 (0.01)	44
4	2.9	202.5 (0.4)	3.5 (0.04)	17.3 (0.2)	0.10 (0.02)	0.5	4.6 (0.01)	0.1 (0.01)	44
5	2.3	193.5 (3.4)	1.1 (0.1)	5.7 (0.5)	0.05 (0.02)	0.3	3.2 (0.1)	0.1 (0.00)	61
Average[b]	3.4 (0.9)	248.1 (50.2)	4.0 (1.9)	15.6 (7.1)	0.13 (0.1)	0.5 (0.3)	5.2 (1.4)	0.2 (0.1)	49 (8)
Burned									
1	1.7	352.6 (2.6)	11.6 (0.01)	32.9 (0.02)	0.51 (0.02)	1.4	5.6 (0.02)	0.4 (0.05)	63
2	1.7	308.7 (1.6)	21.1 (0.8)	68.2 (2.6)	0.19 (0.02)	0.6	7.6 (0.1)	0.3 (0.01)	41
3	1.6	342.9 (2.1)	16.2 (0.8)	47.2 (2.3)	0.05 (0.02)	0.1	8.0 (0.1)	0.3 (0.05)	43
4	0.9	293.0 (4.2)	11.6 (0.4)	39.6 (0.4)	0.02 (0.02)	0.1	5.7 (0.1)	n.n	51
5	1.3	255.9 (3.5)	7.7 (0.2)	30.1 (0.8)	0.00 (0.02)	0.0	4.6 (0.1)	0.1 (0)	56
Average[b]	1.4[c] (0.4)	310.6[c] (39.1)	13.5[c] (0.6)	43.6[c] (15.3)	0.15 (0.2)	0.5 (0.6)	6.3 (1.4)	0.3 (0.1)	51 (9)

[a]Dry mass: 60°C, 0.09 m^{-2}.
[b]Arithmetic mean; standard deviation in parentheses; n.n below detection limit;.
[c]$p < 0.05$, Student's unpaired, one-tailed t-test.

Canadian jack pine forests (7 g kg^{-1} [*Preston et al.*, 2002b]). Our concentrations translate into OC stocks of the unburned forest floor (0.9 kg m^{-2}, Table 4) that were smaller than reported for northern American boreal forests (1.35 kg m^{-2}) [*Slaughter et al.*, 1998; *Nalder and Wein*, 1999], but within the range reported from Canadian jack pine forests (0.3–0.9 kg m^{-2} [*Preston et al.*, 2002b]). Also, total nitrogen stocks (19 g m^{-2}, Table 4) were within the range reported from Canadian jack pine forest stands (5–20 g m^{-2}) [*Preston et al.*, 2002b]. Low OC and nitrogen stocks in the investigated Scots pine forest with an open canopy may be explained by the low litter input caused by the low tree density and the lichen-dominated soil surface vegetation.

[41] OC, and total nitrogen concentrations of the burned forest floor increased by 25 and 20%, respectively (Table 3), not leading to a net-change in C:N-ratio. Total sulfur concentration did not change after fire, as typically observed [*Kuhlbusch et al.*, 1996]. Stocks of OC, total nitrogen, and sulfur decreased by 40 to 50% (Table 4), typical for vegetation fires [*Dyrness et al.*, 1989; *Lobert and Warnatz*, 1993; *Brais et al.*, 2000]. Loss of OC was similar to findings for northern American boreal forests (0.4 kg C m^{-2}) by *Slaughter et al.* [1998], but lower than findings for Canadian jack pine forests (0.95 ± 0.4 kg m^{-2}) by *Stocks and Kauffman* [1997]. In the studied region, OC stocks in Scots pine forests are strongly affected by fire. Typically, OC stocks were lowest shortly after fire (0.6 kg C m^{-2}), and then increased with time (2.3 kg C m^{-2} at 50 years since fire) [*Wirth et al.*, 2002]. Differences in fire-induced losses between forest types or stands occur, because forest floor consumption during fire is extremely variable, for example, for surface fires in Russia ranges from 10 to 50% of mass [*Shvidenko and Nilsson*, 2000], depending on fuel type and load, fire intensity, and soil moisture content [*Gleixner et al.*, 2001].

4.2. Bulk Molecular Composition of Soil Organic Carbon

[42] Knowledge of the molecular composition of the soil OC pool is crucial in understanding its decomposition dynamics [*Preston et al.*, 2000; *Kögel-Knabner*, 2002;

Table 4. Stocks of Organic Elements, BC, and Tannins in Unburned and Burned Forest Floor of Siberian Scots Pine Forests

	Carbon					Total Nitrogen g m^{-2}	Total Sulfur g m^{-2}	C:N-Ratio
	Organic Carbon g m^{-2}	Black Carbon		Tannins				
		g m^{-2}	% OC	g m^{-2}	% OC			
Stocks								
Unburned	875.0 (396.3)	14.1 (7.7)	1.6	0.5 (0.4)	0.05	18.6 (8.7)	0.7 (0.5)	48.6
Burned	450.3[b] (148.8)	20.2 (11.0)	4.5	0.3 (0.4)	0.05	9.2[b] (3.7)	0.4 (0.2)	50.7
Alterations in Stocks, g m^{-2}								
Unburned - burned	−424.7	+6.4		−0.2		−9.4	−0.3	-
Percent Unburned								
As a fraction of unburned[a]	−49	+43		−46		−51	−43	-

[a]Calculated as (burned-unburned) × 100/unburned; standard deviation in parentheses.
[b]$p < 0.05$, Student's unpaired, one-tailed t-test.

Baldock and Smernik, 2002]. To study the bulk composition of OC in the forest floor and lichen samples, we used ^{13}C-MAS NMR, a nondestructive spectroscopic method.

4.2.1. Quantitative Reliability of Cross Polarization Measurements

[43] The quantitative reliability and efficiency of CP were determined for one sample of unburned forest floor (sample 3). The BD spectrum is shown in Figure 1, but not the corresponding 720-scan CP spectrum as it was similar to the normal CP spectrum (Figure 2), only with a lower signal-to-noise ratio and resolution due to the lower number of scans. The BD and CP spectra showed a similar intensity distribution, but in the BD spectrum, intensities were slightly lower in the O-alkyl carbon region, and higher in the aromatic plus phenolic, and carbonyl plus carboxyl carbon region. This is a result of higher CP efficiency for alkyl and di-O- and O-alkyl carbon, compared to the aromatic and phenolic, and carboxyl and carbonyl regions (Table 5). The maximum signal enhancement by CP is a factor of 4, but values closer to 2 are more typical [*Dria et al.*, 2002], similar to the overall CP efficiency of 1.7 for this sample.

[44] We tested the CP efficiencies for both burned forest floor samples and the burned lichen sample. The CP efficiencies for the aromatic and phenolic region, of 0.3 to 0.4 (Table 5) are similar to those found for our previous study of laboratory-charred wood samples (0.4 to 0.5 [*Czimczik et al.*, 2002]). This low CP efficiency probably could be explained by a combination of remoteness from protons for carbons in condensed aromatic structures, plus reduction of ^1H $T1_\rho$ values by organic free radicals in these same structures and paramagnetic cations [*Pastorova et al.*, 1994; *Smernik et al.*, 2000; *Preston*, 2001; *Baldock and Smernik*, 2002]. Our values are also in reasonable agreement with reported CP efficiency of 0.3 to 0.4 for BC in soils or laboratory charred wood [*Smernik et al.*, 2000; *Baldock and Smernik*, 2002]. Direct comparison is complicated because the latter two studies were done at a lower spinning rate, with correction for the effects of $T1_\rho H$ relaxation, and with CP visibility determined against a spin-counting standard, rather than by direct comparison with the BD spectrum, which may still not detect all of the carbon.

[45] Precise determination of CP efficiency for BC samples is difficult, as previously outlined [*Golchin et al.*, 1997a, 1997b; *Skjemstad et al.*, 1999; *Smernik et al.*, 2000; *Preston et al.*, 2002a, *Czimczik et al.*, 2002]. Also, our CP efficiencies are estimates rather than precise values. With 720 scans, the signal-to-noise ratio of both BD and CP spectra is poor (the CP spectra in Figure 2 resulted from several thousand scans). The BD spectra are further affected by a broad background signal similar in total integrated intensity to that of the sample, which originates mainly from probe components [*Smernik and Oades*, 2001]. The subtraction of the background signal, and the detection of very broad signals by the BD sequence also results in varying difficulties with phasing and baseline correction. However, there is no doubt that the aromatic structures of BC generated in laboratory-charred wood or by wildfire in a forest are poorly detected by conventional CP, and this
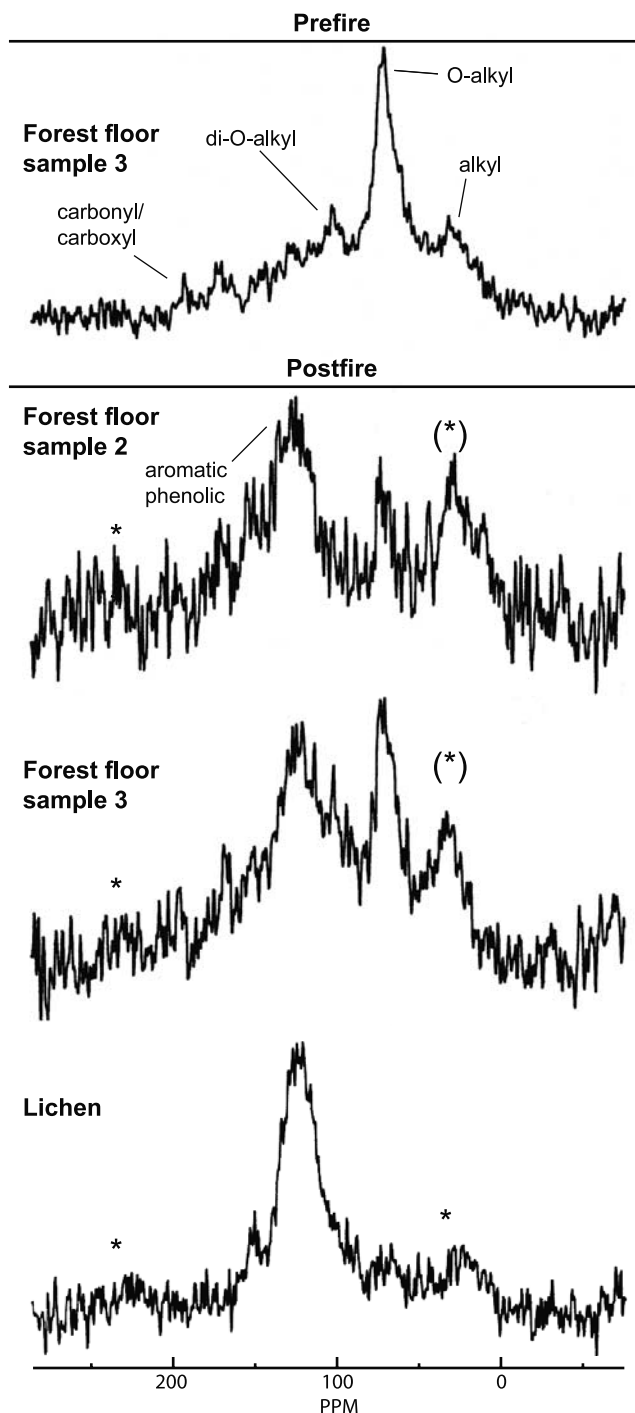

Figure 1. Bloch decay ^{13}C-MAS NMR spectra of unburned forest floor sample 3, and burned forest floor samples 2 and 3, and reindeer lichen from a Siberian Scots pine forest (asterisk indicates spinning sidebands).

underestimation is exacerbated in matrices incorporating aliphatic structures with much higher CP efficiency.

4.2.2. OC Composition of Unburned Forest Floor

[46] CP spectra of the unburned forest floor samples 2 and 3 were similar in overall features and dominated by di-O-
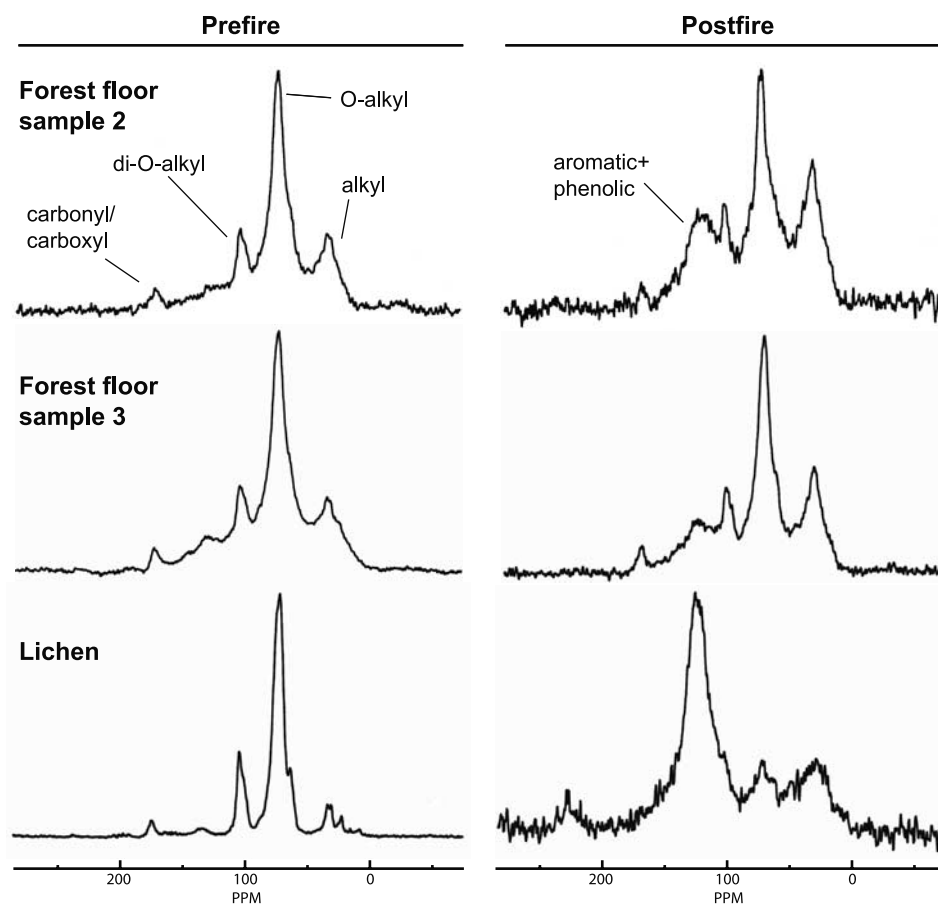
Figure 2.   Cross-polarization ^{13}C-MAS NMR spectra of unburned and burned forest floor samples 2 and 3, and reindeer lichen from a Siberian Scots pine forest.

Table 5. Molecular Composition of Unburned and Burned Forest Floor as Revealed by Solid-State Cross-Polarization (CP) or Bloch Decay (BD) ^{13}C-MAS NMR Spectroscopy[a]

		Relative Intensity of −C Region,[b] %					CP Efficiency (CP Versus BD)[c]			
Technique	Sample	0−50 ppm Alkyl	50−93 −112 ppm Di-O- and O-Alkyl	112−165 ppm Aromatic and Phenolic	165−215 ppm Carboxyl and Carbonyl	Ratio Alkyl to O-Alkyl	0−50 ppm Alkyl	50−93−112 ppm Di-O- and O-Alkyl	112−165 ppm Aromatic and Phenolic	165−215 ppm Carboxyl and Carbonyl
					Unburned					
CP	2	18.0	70.3	7.9	3.8	0.3	n.d.	n.d.	n.d.	n.d.
CP	3	20.3	63.2	11.6	5.0	0.4	1.7	2.1	1.1	0.9
BD		20.3	52.1	18.0	9.6	0.5				
CP	Lichen	13.0	79.2	5.7	2.1	0.2	n.d.	n.d.	n.d.	n.d.
					Burned					
CP	2	28.4	42.7	24.7	4.2	0.8	1.3	3.6	0.3	0.4
BD		17.4	9.1	65.2	8.3	1.9				
CP	3	24.0	48.8	21.7	5.5	0.6	2.0	2.8	0.4	0.6
BD		12.8	18.8	59.0	9.4	0.7				
CP	Lichen	16.4	10.6	69.0	4.6	2.0	1.6	1.1	0.4	0.4
BD		5.3	4.9	83.7	6.2	1.1				

[a]Not determined: n.d.
[b]Integral of region × 100/total integral of spectrum.
[c]Plotted in absolute intensity mode: (integral height of region of 4400- to 19000-scan.
CP spectrum/total integral of 4400- to 19000-scan CP spectrum × total integral of 720-scan CP spectrum)/height of integral of region in BD spectrum.
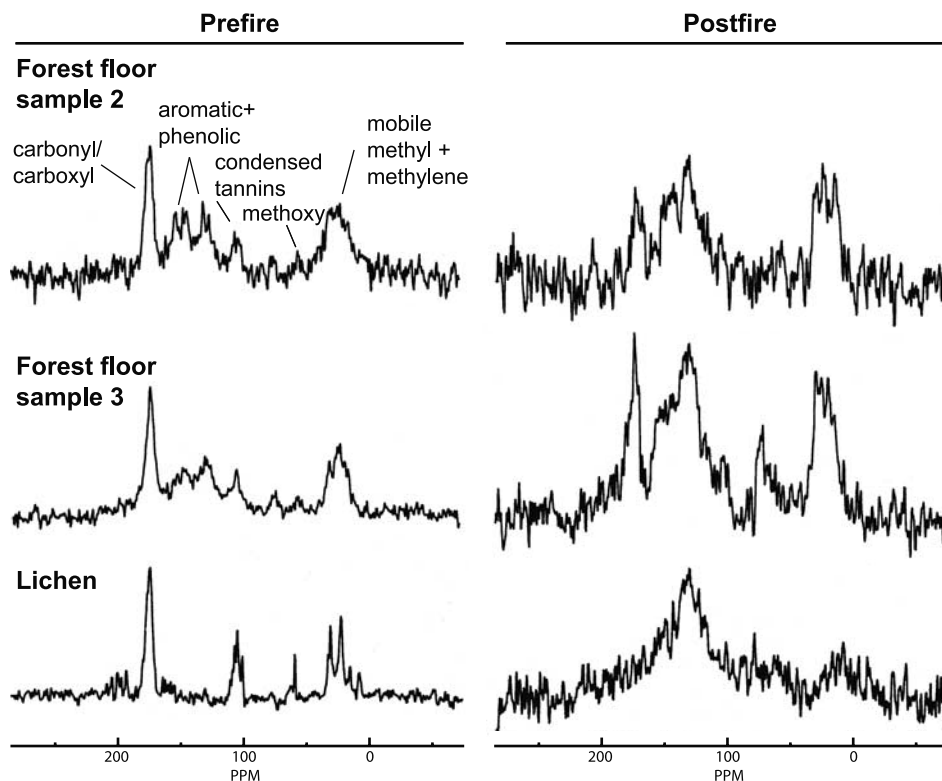
Figure 3.   Dipolar-dephasing ^{13}C-MAS NMR spectra of unburned and burned forest floor samples 2 and 3, and reindeer lichen from a Siberian Scots pine forest.

and O-alkyl carbon, such as polysaccharides (Figure 2). By contrast, signals in the aromatic and phenolic region were less intense and poorly resolved. In particular, the phenolic region lacked the distinct peaks characteristic of lignin (148–152 ppm) and of condensed tannins (144 and 154 ppm) [*Preston et al.*, 1998; 2002a; *Almendros et al.*, 2000]. Consistent with this, the spectra also lacked even a shoulder for the methoxy carbon of lignin at 57 ppm. Unburned sample 3 showed a slightly higher degree of decomposition than sample 2, as indicated by a lower proportion of di-O- and O-alkyl carbon, a higher ratio of alkyl to O-alkyl carbon, a higher proportion of aromatic and phenolic carbon (Table 5), and broader features (Figure 2) [*Baldock et al.*, 1992].

[47] The DD spectra of unburned forest floor samples 2 and 3 (Figure 3), were dominated by a distinct carboxyl carbon peak (173 ppm), and a broader signal from more mobile methyl and methylene carbon (centered around 21 ppm). As in the CP spectra, the aromatic and phenolic regions were weak and poorly resolved, consistent with the almost complete absence of a distinct methoxy carbon signal at 57 ppm (lignin). However, both DD spectra showed a broad, weak signal at 105 ppm that is a characteristic and persistent marker peak for condensed tannins. It is often observed in forest floor DD spectra, despite the absence of other distinct tannin signals at 144 and 154 ppm [*Lorenz and Preston*, 2002; *Preston et al.*, 2002a].

[48] We also obtained ^{13}C-MAS NMR spectra of unburned reindeer lichen, because lichens account for the major proportion of forest floor volume in the investigated forest type, and could not be separated from the burned forest floor material. The CP spectrum of unburned lichen (Figure 2) was similar to the unburned forest floor samples, but even more dominated by di-O- and O-alkyl, and alkyl carbon, and correspondingly lower in other regions, indicating a very high polysaccharide content. We found no indications for chitin, a N-containing polysaccharide common in many lichens. This is consistent with the observation that fungi associated with green algae in reindeer lichen have typically low nitrogen concentrations (here 3 to 7 g N kg^{-1}) [*Palmqvist et al.*, 1998]. The spectrum is similar to that of reindeer lichen shown by *Preston et al.* [2000], except for a somewhat better resolution.

[49] The DD spectrum of unburned lichen (Figure 3) had several sharp peaks for alkyl, carboxyl and carbonyl carbon, some sharp, very weak signals in part of the phenolic region (153–164 ppm), but no signals for aromatic carbon. Lichen may contain a variety of phenolics from secondary metabolites unique to lichens, such as dipsides and depsidones [*MacGillivray and Helleur*, 2001]. The sharp but very weak methoxy signal (58 ppm) typical for lignin probably indicated some contamination by other plant material, because lichens do not contain lignin [*Wilson et al.*, 1989]. Contamination might occur because individual lichens were usually rooted in the lower part of the forest floor which includes partly decomposed tree litter. The peaks in the di-O-alkyl region (100–106 ppm) cannot be attributed to tannin, because there is no corresponding intensity in the

aromatic or phenolic regions. These peaks are likely due to slightly slower dephasing rate of the anomeric C1 compared to the other carbohydrate ring carbons, but a more detailed study would be required to confirm this [*Wilson et al.*, 1989].

[50] Compared to our findings, the forest floor of temperate forests often contains lower proportions of O-alkyl carbon structures, such as carbohydrates, and alkyl carbon, mainly from proteins. These structures are thought to undergo rapid decomposition by microorganisms, as they are part of the energy metabolism or transformed into microbial biomass [*Baldock et al.*, 1992; *Gregorich et al.*, 1996; *Gleixner et al.*, 2001, 2002]. On the other hand, there is often accumulation of alkyl carbon from plant waxes, suberin and cutin and of aromatic and phenolic carbon structures from lignin and tannins [*Preston et al.*, 1997; *Lorenz et al.*, 2000; *Quideau et al.*, 2001].

[51] The indicators of low inputs or preservation of lignin, tannins, and BC from earlier fires are probably related to the dominant influence of lichen, a nonvascular plant that lacks these structures, and the type of fires associated with this forest type, as discussed above.

[52] There have been few NMR studies of the forest floor in boreal forest ecosystems, and the unburned forest floor spectra are in good agreement with those from two jack pine sites in Canada [*Preston et al.*, 2002b] with high moss and lichen inputs. Similar low and poorly resolved signals for aromatic and phenolic carbon were observed for other situations dominated by inputs from lower plants, such as wetlands [*Krosshavn et al.*, 1992; *Preston et al.*, 2002b] and the moss/grass stage of a sand dune vegetation succession [*Nierop et al.*, 2001].

4.2.3. OC Composition of Burned Forest Floor

[53] Little is known about the immediate changes in forest soil OC composition during wildfires. Compared to the unburned forest floor, CP spectra of burned forest floor (Figure 2) were higher in alkyl and aromatic carbon, and lower in di-O- and O-alkyl carbon. This is typically observed as a result of burning [*Czimczik et al.*, 2002]. Burned forest floor sample 2 showed a greater effect of burning than sample 3: For sample 2 the aromatic signal was broader, although the aromatic and phenolic signal was only slightly higher, and the alkyl-to-O-alkyl ratio was higher (Table 5). The effect of burning and the higher degree of burning for sample 2 could also be seen in the DD spectra (Figure 3). The signal for nonprotonated aromatic and phenolic carbon were higher in the spectra of the burned than in the unburned forest floor.

[54] The higher degree of burning for sample 2 was, however, not accompanied by a higher OC concentration compared to sample 3 (Table 3). The forest floor samples represented the whole layer down to the mineral soil, and thus probably incorporated a gradient of burning intensity, decreasing from the uppermost material. Molecular structural alteration, mass loss, and OC concentration during burning (assuming a similar moisture content), is mainly controlled by temperature, while burning time has less influence [*Czimczik et al.*, 2002].

[55] The contrast between CP and BD spectra was greater for burned forest floor than for unburned forest floor

samples (Figures 1 and 2): The BD spectra of the burned forest floor had less O-alkyl and more aromatic and phenolic carbon, and the distinct di-O-alkyl peaks shown in the CP spectra, could not be detected in the BD spectra against the larger aromatic peak. Comparison of integrals for CP versus BD showed only low CP efficiencies for the aromatic and phenolic region (Table 5). The CP efficiencies generally increased from aromatic to carboxyl and carbonyl, to alkyl, to di-O- and O-alkyl carbon, with the highest value of 3.6 for burned sample 2 probably being an outlier.

[56] The burned lichen sample showed even greater transformation during burning than the forest floor. The CP and DD spectra of the burned lichen (Figure 2 and 3) had a much lower proportion of di-O- and O-alkyl and a higher proportion of aromatic and phenolic carbon than of the unburned lichen. The BD spectrum was dominated by alkyl, aromatic, and phenolic carbon (Figure 1). The CP efficiency of the aromatic and phenolic region was low and similar to that found for the burned forest floor. However, the under-representation of aromatic carbon in the burned lichen sample was not as severe, simply because it was such a high proportion of the total.

[57] It became clear from ^{13}C-MAS NMR analysis that fire strongly affected the OC composition. With increasing burning intensity, the proportion of di-O- and O-alkyl carbon structures decreased, while that of aromatic carbon increased, and the proportion of alkyl carbon first increased and then decreased. These findings agree with laboratory studies indicating the formation of aromatic condensed structures from biomass high in cellulose or other carbohydrates by dehydration and condensation of O-alkyl structures [*Almendros et al.*, 1992; *Pastorova et al.*, 1994; *Knicker et al.*, 1996; *Czimczik et al.*, 2002]. Also, increasing amounts of aromatic and phenolic structures may reflect a preferential loss of nonaromatic carbon structures.

[58] For the aromatic carbon region, the very broad peak centered around 130 ppm found in our burned forest floor suggests that not only highly condensed BC was formed, but a variety of condensed and O- or N-substituted macromolecules. The spectra further indicate that the BC produced mainly consists of relatively small clusters of condensed carbon, lacking a high proportion of bridgehead carbon, or graphitic structures, as found for laboratory-charred woods [*Czimczik et al.*, 2002]. In ^{13}C NMR spectra, due to their high electrical conductivity, graphitic structures lead to severe broadening and a downfield shift of the aromatic carbon signal [*Solum et al.*, 1995; *Freitas et al.*, 2001]. Accumulation of alkyl carbon structures during early stages of combustion may be due to condensation of hydrocarbons and amino acids or fatty acids into macromolecular material [*González-Vila et al.*, 2001; *Poirier et al.*, 2002].

4.3. Tannins

[59] In ^{13}C NMR spectra of bulk soil, the signal typical for BC (at 130 ppm) overlaps with other aromatic components, such as lignins and tannins. Thus, to quantify the conversion of OC to BC and to further characterize the composition of the aromatic carbon fraction, we quantified BC and tannins by wet-chemical analyses. The low proportion of lignin in the investigated forest OC was already

Table 6. Rates of Organic Carbon (exposed OC) Conversion to Black Carbon (in the Residue) From Various Ecosystems

Ecosystem	Conversion Rate, Percent Unburned OC	Fuel Type	Method
Tropical forest, savannah, agricultural land[a]	1.0 to 2.0 2.5 to 3.5	non-woody biomass woody biomass	review of gravimetric field studies, model
Tropical rain forest[b]	2.2 (1.3 to 4.1)	aboveground biomass, coarse woody debris, litter (woody and non-woody)	gravimetric
Subtropical savannah[c]	0.6−1.5	aboveground biomass (non-woody)	chemical-thermal oxidation/gravimetric
Temperate coniferous forest[d]	8.0	coarse woody debris	volumetric
Boreal forest[e]	0.7	soil organic layer, excluding coarse woody debris	benzenepolycarboxylic acids as molecular markers (GC-AED)

[a]*Kuhlbusch and Crutzen* [1995].
[b]*Fearnside et al.* [1993, 1999, 2001] and *Graca et al.* [1999].
[c]*Kuhlbusch et al.* [1996].
[d]*Tinker and Knight* [2000].
[e]This study.

indicated by ^{13}C NMR (see above). Tannins may account for an important fraction of aromatic carbon in plants and are considered stable toward biogeochemical degradation [*Wilson and Hatcher*, 1988], but their role in the stabilization of OC is a matter of debate [*Harrison*, 1971; *Fierer et al.*, 2001; *Lorenz and Preston*, 2002].

[60] In this study, tannin concentrations (Table 3) and stocks (Table 4) were very low compared to findings from forest floors of tannin-rich vegetation like spruce (1 to 7% OC) [*Lorenz et al.*, 2000] or oak forests (10 g kg^{-1}) [*Kuiters and Denneman*, 1987]. Fire had no significant effect on tannin concentrations or stocks. Thus, wet-chemical analyses and ^{13}C NMR showed that tannins were only a minor proportion of the aromatic carbon fraction in the investigated forest soil. Low tannin stocks may be caused by low input, or rapid leaching [*Kuiters and Denneman*, 1987].

4.4. Black Carbon

[61] Black carbon (BC) determined by using molecular markers was only a small fraction of unburned OC (2%, Table 4) and only about one tenth of the amount of aromatic and phenolic carbon detected by using BD (^{13}C-MAS NMR). It was previously shown that the quantification of BC is strongly influenced by the techniques applied [*Schmidt et al.*, 2001]. This is because BC is not a single substance with a well-defined molecular structure, but exists as a continuum from partly charred material to highly graphitized soot particles. The technique applied in this study is thought to trace highly condensed carbon in larger clusters, i.e., the highly oxidation-resistant fraction of the BC continuum [*Glaser et al.*, 1998; *Glaser*, 1999]. Low BC concentrations detected here using an oxidative technique are consistent with our ^{13}C NMR results which indicate that the investigated fire produced relatively small clusters of condensed carbon, and a variety of O- or N-substituted macromolecules, typical for low-temperature fires and smoldering combustion [*Gleixner et al.*, 2001].

[62] Compared to the amount of BC (30 to 60% OC) found in the mineral soil of some ecosystems [*Skjemstad et al.*, 1996; *Schmidt et al.*, 1999; *Glaser et al.*, 2001], BC stocks detected here were extremely small and may be explained by (1) low conversion rate of OC to BC, (2) relocation of BC to greater depth, (3) surface erosion, or (4) in situ degradation.

[63] First, in this study, fire increased forest floor BC concentrations by 240% (Table 3) and stocks by 40% (Table 4) which corresponds to a conversion rate of 0.7% unburned OC (exposed OC) into BC (Table 6). Assuming a net primary production (NPP) of 70 g C m^{-2}yr^{-1} [*Wirth*, 2000], the conversion into BC accounted for 0.35% of NPP (0.25 g C m^{-2}yr^{-1}). Comparable data for the conversion of OC to BC for the boreal region do not exist. However, the conversion rate found here was slightly lower than earlier measurements for non-woody biomass from the tropics, but within the range measured in a savannah ecosystem (Table 6). This is in line with the ^{13}C-MAS NMR results showing that the unburned forest floor was dominated by di-O- and O-alkyl carbon (mainly polysaccharides), which are typical for nonwoody biomass (e.g., lichen). The close agreement of our BC conversion rates with earlier estimates is, however, surprising, since theses earlier estimates were obtained with methods that would have detected more BC (Table 6), as discussed above.

[64] Second, relocation of BC from the forest floor into the mineral soil probably could not explain the low BC stocks in the forest floor, because >90% of total BC stocks (including forest floor and the first meter of the mineral soil) are located in the forest floor (C. Czimczik et al., unpublished results, 2002).

[65] Third, surface erosion of BC seems unlikely to explain low BC stocks in the forest floor, because the topography was flat and no strong winds or rain occurred until we sampled two days after the fire.

[66] Fourth, in situ degradation of BC may occur through oxidation during recurring fires or microbial degradation. Detailed studies on in situ degradation of BC and studies on the long-term stability of BC in boreal ecosystems, however, do not exist.

[67] Summarizing, to quantify the role of BC as a potential long-term OC sink in boreal forests, further studies on stocks and dynamics of BC within forest soils are needed. Differences in conversion rates for non-woody or woody biomass underline the need of also quantifying BC formation from aboveground biomass and coarse woody debris. In forest ecosystems with surface fire regime, like Siberian Scots pine forests, fire is the major factor reducing the amount of lying coarse woody debris (about 70%) [*Wirth et*

al., 2002], but the conversion rates for coarse woody debris OC to BC are not known.

5. Conclusions

[68] Our results suggest that the composition of OC in the forest floor of Siberian Scots pine forest was strikingly different from OC in temperate forest soils, probably mainly reflecting the predominant input of lichen biomass. BC was not a major fraction of the soil OC pool in the forest floor. These low BC stocks seemed to reflect low formation rates (0.7% of unburned forest floor OC), and low stability against degradation (the aromatic carbon fraction consisted mainly of heterocycles and small clusters of condensed carbon). Clearly, further studies are required to study the fate of BC in boreal forest soils.

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