

# Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions

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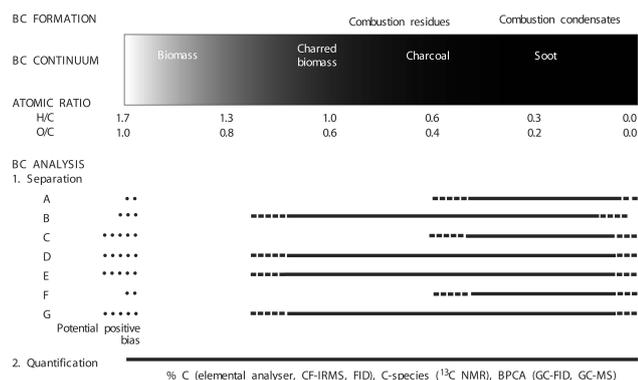
**Abstract.** The carbon (C) cycle in boreal regions is strongly influenced by fire, which converts biomass and detrital C mainly to gaseous forms (CO<sub>2</sub> and smaller proportions of CO and CH<sub>4</sub>), and some 1–3% of mass to pyrogenic C (PyC). PyC is mainly produced as solid charred residues, including visually-defined charcoal, and a black carbon (BC) fraction chemically defined by its resistance to laboratory oxidation, plus much lower proportions of volatile soot and polycyclic aromatic hydrocarbons (PAHs). All PyC is characterized by fused aromatic rings, but varying in cluster sizes, and presence of other elements (N, O) and functional groups. The range of PyC structures is often described as a *continuum* from partially charred plant materials, to charcoal, soot and ultimately graphite which is formed by the combination of heat and pressure. There are several reasons for current interest in defining more precisely the role of PyC in the C cycle of boreal regions. First, PyC is largely resistant to decomposition, and therefore contributes to very stable C pools in soils and sediments. Second, it influences soil processes, mainly through its sorption properties and cation exchange capacity, and third, soot aerosols absorb solar radiation and may contribute to global warming. However, there are large gaps in the basic information needed to address these topics. While charcoal is commonly defined by visual criteria, analytical methods for BC are mainly based on various measures of oxidation resistance, or on yield of benzenepolycarboxylic acids. These methods are still being developed, and capture different fractions of the PyC structural continuum. There are few quantitative reports of PyC production and stocks in boreal forests (essentially none for boreal peatlands), and results are difficult to compare due to varying experimental goals and methods, as well as inconsistent terminology. There are almost no direct field measurements of BC aerosol production from boreal wildfires, and little direct information

on rates and mechanisms for PyC loss. Structural characterization of charred biomass and forest floor from wildfires generally indicates a low level of thermal alteration, with the bulk of the material having H/C ratios still >0.2, and small aromatic cluster sizes. Especially for the more oxidation-resistant BC fraction, a variety of mainly circumstantial evidence suggests very slow decomposition, with turnover on a millennial timescale (in the order of 5–7 ky), also dependent on environmental conditions. However, there is also evidence that some PyC may be lost in only tens to hundreds of years due to a combination of lower thermal alteration and environmental protection. The potential for long-term PyC storage in soil may also be limited by its consumption by subsequent fires. Degraded, functionalized PyC is also incorporated into humified soil organic matter, and is transported eventually to marine sediments in dissolved and particulate form. Boreal production is estimated as 7–17 Tg BC y<sup>-1</sup> of solid residues and 2–2.5 Tg BC y<sup>-1</sup> as aerosols, compared to global estimates of 40–240 and 10–30 Tg BC y<sup>-1</sup>, respectively. Primary research needs include basic field data on PyC production and stocks in boreal forests and peatlands, suitable to support C budget modeling, and development of standardized analytical methods and of improved approaches to assess the chemical recalcitrance of typical chars from boreal wildfires. To accomplish these goals effectively will require much greater emphasis on interdisciplinary cooperation.

## 1 Introduction

Fire is a major driver of ecosystem processes and the carbon (C) cycle in boreal forests and peatlands (Hicke et al., 2003). Globally, it has been estimated that one-third of net primary productivity in boreal forests is consumed by fire (Harden et al., 2000; Wirth et al., 2002), while Bachelet et al. (2005) concluded that 61% of the C gained in Alaska between 1922

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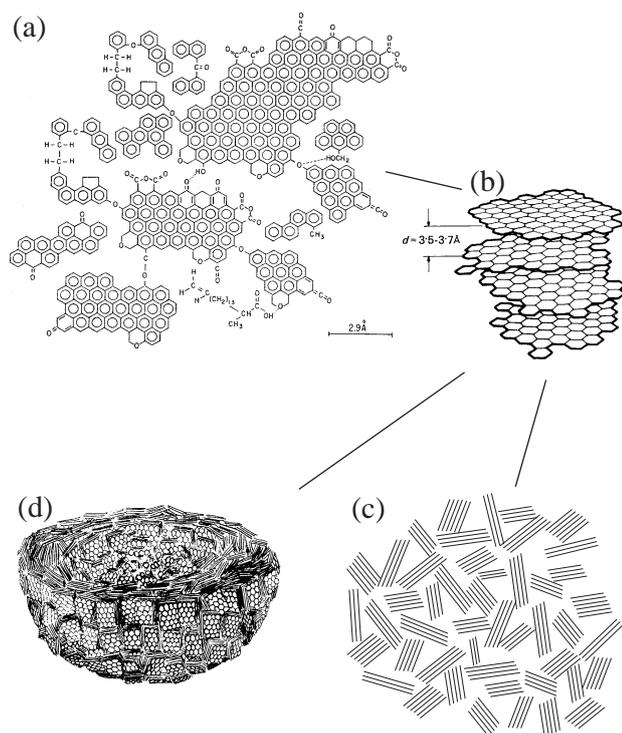
**Fig. 1.** Definitions and analytical windows for PyC from Hammes et al. (2006b)<sup>1</sup>. The upper part represented PyC (here called black carbon BC) plotted along a scale of atomic H/C and O/C ratios, also used in van Krevelen plots (the H/C scale is non-linear). The lower part of the figure is a conceptual summary of the comparative analyses of the seven methods to quantify black carbon. The analysis typically has two steps, separation and quantification. (1) Separation of BC was performed by seven methods A–G. The analytical ranges of separation are conceptual only, visualized by the use of solid and dotted lines. The dotted lines at each end of the solid lines and above “Estimated inaccuracy” next to each method (A–G) indicate the level of inaccuracy – the more dots, the larger the estimated inaccuracy. (2) Quantification of BC in the operationally defined separates includes elemental analysis (to quantify carbon left after separation), <sup>13</sup>C NMR spectroscopy (to identify condensed aromatic C) or the use of gas chromatography to quantify the molecular markers of black carbon.

to 1996 was lost to fires (1 out of 1.7 Pg C). Conard and Ivanova (1997) estimated that boreal forest fires accounted for about 20% of C emissions from global biomass burning. Amiro et al. (2001) estimated that C emission from Canadian forest fires during 1959–1999 amounted to 18% of emissions from all energy sources in Canada, with a similar magnitude of secondary CO<sub>2</sub> emission due to postfire decomposition. The retrospective analysis by Kurz and Apps (1999) indicated that Canada’s forests functioned as a sink for atmospheric C during the period 1920–1990. After 1970 however, increases in fire and insect disturbances have moved the balance closer to neutral or even to C loss. Increasing burn areas are predicted for boreal forests of Canada, Russia and Alaska under warmer and drier conditions resulting from increased atmospheric CO<sub>2</sub> (Stocks et al., 1998, 2000; Bachelet et al., 2005; Flannigan et al., 2001, 2005). One obvious byproduct of forest and peatland fires is black, charred residues from incomplete combustion of biomass and detrital material. Evidence of charred biomass goes back 350 My to the Late Devonian (Schmidt and Noack, 2000; Scott, 2000). The charcoal record preserved in sediment and peat cores has long been used in studies of ecosystem change and fire frequency during the Holocene (e.g., Clark and Royall, 1994; Laird and Campbell, 2000; Flannigan et al., 2001; Sanborn

et al., 2006). Recently, there has been increasing interest in other aspects of charred biomass, or more generally, the whole range of PyC forms (Hedges et al., 2000; Schmidt and Noack, 2000; Schmidt et al., 2001; Masiello, 2004). First, how much does PyC contribute to very stable soil C pools; i.e., what is its sink potential? Second, how does PyC influence soil processes such as microbial activity and nutrient cycling, and third what are the effects of volatile emissions on air quality and atmospheric warming? Despite high interest in these aspects of PyC, and the huge influence of fire in boreal regions, there are few quantitative reports of PyC production and stocks and little direct information on mechanisms and rates of loss in boreal regions, especially for peatlands. We review the current state of knowledge on PyC, including chemical structures, definition of terms, analytical methods and quantitation, formation of PyC including soot aerosols and PAHs, stocks and characteristics of PyC in soil, and loss mechanisms and longevity, and from this background consider the role of PyC in boreal regions, with regard to C cycle, effects on soil processes, and identification of knowledge gaps and research needs. We wish to engage a highly interdisciplinary audience including soil scientists, forest and peat ecologists, fire scientists and C budget modelers, and hope to encourage novel interdisciplinary approaches to address these gaps. While the focus is on boreal regions, we include information from other regions to set the boreal picture in a global context, and also as an aid in interpretation of the inadequate boreal data. We focus on recent and generally available publications providing access to further literature, rather than a comprehensive literature survey.

## 2 What is PyC?

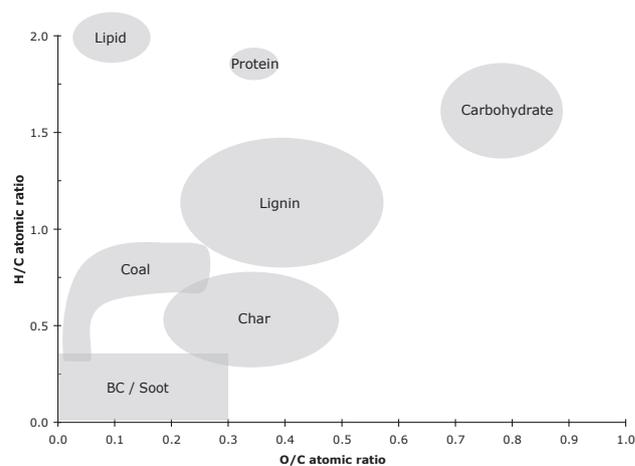
The range of PyC structures is often described as a *continuum* from partially charred plant materials that still retain their physical structure, to charcoal, soot and ultimately graphite (Seiler and Crutzen, 1980). This is visualized in Fig. 1, which also indicates the terminology, the associated chemical properties, and ranges of operationally defined analytical windows. PyC can form in two fundamentally different ways. The solid residues of combustion form char, whereas soot is formed from volatiles formed within and recondensed from flames. The common, defining characteristic of fire-altered biomass is the presence of condensed (fused) aromatic ring structures. As the extent of thermal alteration increases, structures with small cross-linked aromatic clusters (Fig. 2a) give way to larger graphene sheets (Fig. 2b) that tend to form stacks with disordered packing (Fig. 2c). Soot particles that condense from the gas phase typically develop as concentric shells of these graphene stacks (“onion-like” structure, Fig. 2d), which are also sometimes described as micro-graphitic regions. In the limit, graphite (like diamond) is an allotrope of pure C, a highly ordered, electrically conducting structure of parallel graphene sheets of indefinite



**Fig. 2.** Black carbon and soot molecular structures, reproduced with permission from Schmidt and Noack (2000).

size. Its formation from soot, char or other organic precursors requires both heat and pressure and therefore it is not a direct product of fire. Lighter polycyclic aromatic hydrocarbons (PAHs) having structures of 2–7 fused aromatic rings are also produced in the gas phase, although not usually considered part of the PyC continuum.

Functional groups contain mainly oxygen (O) or hydrogen (H), and the degree of functionalization is reflected in the molar ratios O/C and H/C shown as a van Krevelen plot (Fig. 3). The number of functional groups, important for biological degradability, decreases continuously from the initial, thermally unaltered biomass to increasingly thermally-altered structures. Large O/C and H/C ratios indicate the presence of many functional groups, whereas smaller ratios are typical for more condensed structures, with ratios close to 0.0 typical for almost pure carbon. It should be noted that molar ratios are typically used in geochemical studies and in this review, whereas most forestry and soil studies report mass concentration ratios.



**Fig. 3.** van Krevelen plot of molar ratios for typical biopolymers, biomass and pyrogenic materials (adapted from Hammes et al., 2006a).

### 3 Quantitative analysis and chemical characterization of PyC

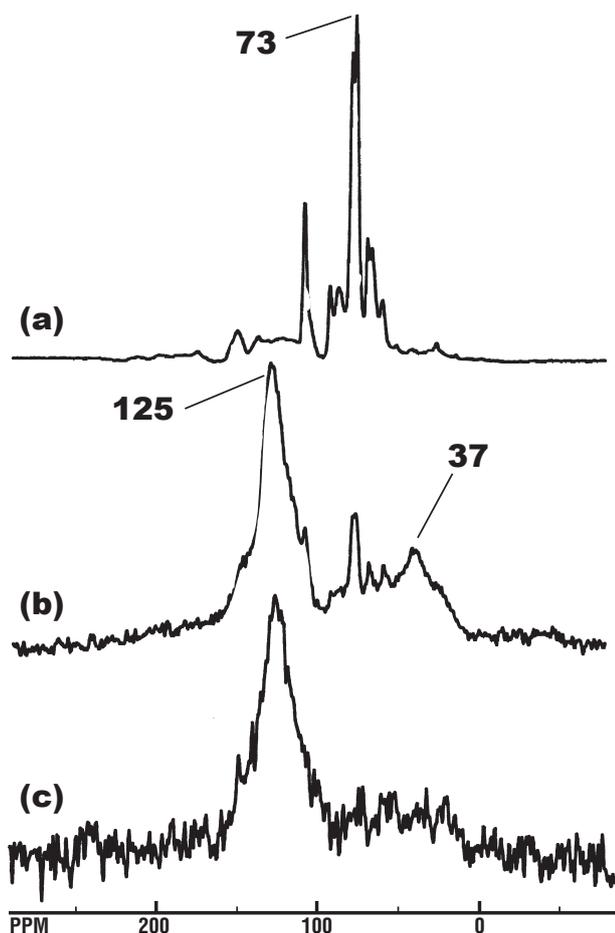
#### 3.1 Quantitative analysis

Figure 1 shows the principal geochemical approaches that have been developed mainly to quantify PyC in soils and sediments. More detailed reviews and comparisons are given elsewhere (Kuhlbusch, 1998; Schmidt and Noack, 2000; Schmidt et al., 2001; Masiello, 2004; Cornelissen et al., 2005; Elmquist et al., 2006; Hammes et al., 2006b<sup>1</sup>).

Analytical techniques for PyC in sediments and soils attempt to differentiate between three forms of C, i.e. inorganic carbonates, thermally unaltered organic C (such as humic substances and plant material) and PyC. Carbonates are released as CO<sub>2</sub> by HCl pretreatment, and the multitude of methods to differentiate PyC from other organic C, essentially all fall into three categories. First, visual or microscopic techniques rely on visual discrimination of charred (i.e. blackened) vs. uncharred plant particles, followed by particle counting or actual physical separation and weighing. This fraction has been traditionally described as charcoal, although it is unclear how much of the charred residues of wildfires and open burning would show the van Krevelen O/C and H/C ratios of 0.4 associated with charcoal in the PyC continuum in Fig. 1 (Schmidt and Noack, 2000; Hammes et al., 2006a).

The second approach uses resistance to laboratory oxidation (induced through heating, exposure to acids or bases, or

<sup>1</sup>Hammes, K., Schmidt, M. W. I., Currie, L. A., et al.: Comparison of black carbon quantification methods using reference materials from soil, water, sediment and the atmosphere, and implications for the global carbon cycle, *Global Biogeochem. Cycles*, in review, 2006b.



**Fig. 4.** Solid-state  $^{13}\text{C}$  NMR spectra of Scots pine wood (a) fresh wood with standard CP acquisition and freshly charred outer layer with (b) CP and (c) quantitative BD acquisition. Sampling site and NMR methods described in Czimczik et al. (2003). Magic-angle spinning rate was 4700 Hz for fresh wood and 12 000 Hz for charred wood.

ultra-violet light, with or without various pre-extractions) to distinguish a BC fraction from other organic matter (summarized by Hammes et al., 2006a). These methods have mainly been developed for soils and sediments, and there are many variations, of which the most vigorous extraction and oxidation treatments leave only graphitic BC (GBC), (Gélinas et al., 2001). Photooxidation is often combined with analysis of the residues by  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy to distinguish BC from other oxidation-resistant organic C. The third approach is based on the release of molecular markers unambiguously related to PyC, namely production of benzenepolycarboxylic acids (BPCAs) after nitric acid oxidation (Glaser et al., 1998; Brodowski et al., 2005b). Levoglucosan which is produced from heating of glucose serves as an indicator for the presence of PyC (Elias et al., 2001) but is not used to quantify BC per se. One problem is that terms are not used consistently. BC has commonly

been used to describe the whole continuum, but it is now more often used to specify the more resistant PyC fraction determined by resistance to laboratory oxidation or by production of BPCAs. The term elemental C (EC) has become more widespread to define the oxidation-resistant fraction in analysis of atmospheric aerosols and soot.

In this paper, we use PyC for the whole continuum of fire-altered biomass and organic matter (sometimes called pyromorphic materials), char for the visually-detected fraction, and BC and GBC for the fractions defined chemically by resistance to oxidation, or by production of BPCAs. We use *charcoal* only where it has been reported as such, based on visual assessment, and similarly, use EC only where it has been reported as such for atmospheric studies. As methods for analysis of PyC are still under development, and definitions are not standardized, readers should check how terms are used in different publications.

Quantification of PyC or BC fractions remains challenging. We reemphasize that PyC constitutes a continuum without clear-cut structural boundaries, and that both visual and oxidation methods are operationally-defined and capture different regions. The BPCA method is a complex multi-step procedure, highly sensitive to operating conditions, and also dependent on the factor used – or sometimes not used (e.g., Rodionow et al., 2006) to convert BPCA yields to BC. It detects only C in larger aromatic clusters, and both oxidation and BPCA procedures hardly detect the bulk of charred biomass or even laboratory-produced char. A recent comparative analysis of soils (Schmidt et al., 2001) showed that BC concentrations obtained by different methods can vary by two orders of magnitude, depending on the type of separation technique used (e.g. Currie et al., 2002). Briefly, particle size, morphology, and the presence or absence of a mineral matrix may lead to an over- or underestimation of the content of pyrogenic organic matter (Masiello, 2004; Elmquist et al., 2006).

A new systematic comparative analysis was started in 2003 (Schmidt et al., 2003; Hammes et al., 2006a; <http://www.geo.unizh.ch/phys/bc/>). Briefly, simple correlation factors between methods and matrices were not apparent, and each method may have limitations and biases, depending on the type of fire-derived carbon and matrix. This study has made clear that future studies urgently need to be calibrated against the set of BC reference materials analyzed by Hammes et al. (2006a).

### 3.2 Characterization of PyC

Once pyrogenic organic matter is separated; e.g., by visual methods or photooxidation, it can be characterized by elemental analysis (e.g., C, N, H, O). While total C and N can be readily determined, H analysis is not routinely available, and total O is often determined by difference. Since the van Krevelen O/C and H/C ratios are so central to the properties of PyC, more application of elemental analysis would be

most useful, especially for freshly charred material uncomplicated by a mineral matrix.

The increasing proportions of aromatic C and loss of oxygen-containing functional groups with charring can be observed directly by  $^{13}\text{C}$  NMR. Spectra of charred biomass and SOM are characterized by a broad aromatic signal with maximum around 125–130 ppm, which can account for up to 100% of the organic C (Baldock and Smernik, 2002; Czimczik et al., 2002, 2003; González-Pérez et al., 2004; Simpson and Hatcher, 2004a, b; Knicker et al., 2005a, b). Condensed aromatic structures are poorly detected by routine solid-state NMR with cross-polarization (CP), so that a more time-consuming quantitative technique (Bloch decay, BD) must be used. The  $^{13}\text{C}$  NMR spectra in Fig. 4 illustrate the effects of charring on Scots pine wood from a wildfire (Czimczik et al., 2003). The CP spectrum of the fresh wood (Fig. 4a) is dominated by the O-alkyl peak of cellulose at 73 ppm. The CP spectrum of the charred wood (Fig. 4b) is dominated by aromatic C at 125 ppm, with small peaks due to residual cellulose, and an increase in alkyl C (37 ppm). The corresponding quantitative BD spectrum (Fig. 4c) has a higher proportion of aromatic carbon than the CP spectrum.

High-resolution transmission electron microscopy actually reveals the condensed aromatic clusters, in both disordered and concentric onion-like structures (Poirier et al., 2000; Schmidt et al., 2002). Other novel approaches to BC characterization include ultra-high-resolution mass spectrometry (Kim et al., 2004; Kramer et al., 2004), and various forms of X-ray spectroscopy (Solomon et al., 2005), which have been coupled with microscopic techniques to produce spatial distribution of BC forms (Brodowski et al., 2005a; Lehmann et al., 2005).

## 4 Production of PyC

### 4.1 Production of PyC from forest biomass burning

#### 4.1.1 Production determined by visually-detected charcoal

As shown in Table 1, very few studies are available, and none that provide a complete accounting of BC or charcoal produced in a boreal wildfire. Three studies determined charcoal production of 235–932 kg ha<sup>-1</sup> from experimental fires with crowning or partial crowning in boreal forests (Clark et al., 1998; Ohlson and Tryterud, 2000; Lynch et al., 2004). These were designed specifically to provide information on how charcoal is transported to, and deposited in nearby sediments, with charcoal yields determined from recovery of particles in surface traps; i.e., particles that were airborne at some point during the fire.

No other boreal data could be located, but generally higher yields are reported in the few other studies available. These are mainly from experimental slash-burning after forest clearing: i.e., 7400 kg ha<sup>-1</sup> of forest floor charcoal at a

site in Virginia (Schiffman and Johnson, 1989), and 1140–4540 kg ha<sup>-1</sup> char from four studies in Amazonia (Fearnside et al., 1993, 1999, 2001; Graça et al., 1999). Conversion of 5.1% of initial mass produced 7070 kg ha<sup>-1</sup> of charred particles >1000  $\mu\text{m}$  (8.5% conversion on a C basis) during a slash-pile-and-burn experiment designed to emulate Neolithic practices in temperate deciduous forest (Eckmeier et al., 2006<sup>2</sup>). Much greater increases in site charcoal (<2 mm, to 30 cm depth), of 20 000 and 170 000 kg ha<sup>-1</sup>, were reported by Hopmans et al. (2005) after clearfelling and burning of two eucalypt sites in Australia.

In the only study following forest wildfire, Tinker and Knight (2000) determined 6400 kg ha<sup>-1</sup> of char production on coarse woody debris after an intense crown fire in Yellowstone National Park. For the boreal and Amazonian fires, factors for conversion of fuel to visually-determined char were 0.9–2.2% (mass basis), with higher values for the Yellowstone coarse woody debris and Neolithic-emulation studies (8% and 5.3%, respectively). Using average C concentrations of 500 g kg<sup>-1</sup> for biomass and 700 g kg<sup>-1</sup> for char, these correspond to C conversions of approximately 1.3–3.1%, with 11% for the Yellowstone study, and 7.4% for the Neolithic-emulation burn (close to the 8.5% determined from actual C analysis). The three boreal fire studies were designed to capture only charcoal with potential to be deposited in nearby lake sediments, and comparison with reports from other regions suggests that charcoal production from boreal wildfires is likely to be much higher than 235–932 kg ha<sup>-1</sup>. A full accounting has to include charred material in the forest floor, and on standing and down trees, and could possibly be in the range of 5000–10 000 kg ha<sup>-1</sup>.

Few other data are available, but it is interesting to compare the results discussed so far with charcoal deposition rates estimated from analysis of particles >10  $\mu\text{m}$  in lake sediments (Clark and Royall, 1994). For pre-settlement North America (i.e., before fire suppression), the highest rates (5000 kg ha<sup>-1</sup> y<sup>-1</sup>) were found in prairie/forest border areas, followed by conifer, largely boreal forest, with rates of 500–5000 kg ha<sup>-1</sup> y<sup>-1</sup>. While the highest rates seem improbable, and the authors emphasize the uncertainties and need for further research, these results also indicate that charcoal production rates determined from the three aforementioned boreal experimental burns are probably low. Deposition of 5000 kg ha<sup>-1</sup> y<sup>-1</sup> for 100 y would result in 500 kg m<sup>-2</sup> of charcoal, or a 10 cm layer assuming a density of 0.5 g cm<sup>-3</sup> and no mechanisms for loss (discussed in Sect. 6).

<sup>2</sup>Eckmeier, E., Rösch, M., Ehrmann, O., Schmidt, M. W. I., Schier, W., and Gerlach, R.: Conversion of biomass to charcoal and the carbon mass balance in experimental Neolithic slash-and-burn, Holocene, in review, 2006.

**Table 1.** Production of charcoal and BC from forest biomass burning, on a mass<sup>a</sup> or carbon<sup>b</sup> basis. Based on 500 g C kg<sup>-1</sup> for biomass and 700 g C kg<sup>-1</sup> for char, conversion of 1% of biomass to char on a mass basis is equivalent to 1.4% conversion on a C basis. Conversely, 1% conversion on a C basis corresponds to 0.71% on a mass basis.

Region/site/cause of fire	Method	Char or BC production	Reference
(a) Boreal and Temperate Forests			
Bor Island, Siberia, experimental crown fire in Scots pine ( <i>Pinus sylvestris</i> )	Visual char collected in surface traps	<sup>a</sup> 729 kg ha <sup>-1</sup> (2% fuel conversion)	Clark et al. (1998)
Norway and Sweden, 3 boreal sites, mostly coniferous, experimental fires with partial crowning	Visual char collected in surface traps	<sup>a</sup> 235 kg ha <sup>-1</sup>	Ohlson and Tryterud (2000)
Northwest Territories, Canada, experimental crown fire (ICFME), jack pine ( <i>Pinus banksiana</i> )	Visual char collected in surface traps	<sup>a</sup> 932 kg ha <sup>-1</sup> (2.2% fuel conversion)	Lynch et al. (2004)
Virginia, USA after cutting and slash-burning loblolly pine ( <i>Pinus taeda</i> L.)	Visual char in forest floor	<sup>a</sup> 7400 kg ha <sup>-1</sup>	Schiffman and Johnson (1989)
Germany, to imitate Neolithic agricultural slash-and-burn in deciduous forest, one 8 × 12 m <sup>2</sup> plot	Visual char >2 mm	<sup>a</sup> 7070 kg ha <sup>-1</sup> , 5.3% (8.5% fuel C conversion)	Eckmeier et al. (2006) <sup>2</sup>
Yellowstone National Park, Wyoming, USA, after intense crowning wildfire	Visual char on CWD	<sup>a</sup> 6400 kg ha <sup>-1</sup> (8% CWD conversion)	Tinker and Knight (2000)
Siberia, Yenisey R., Scots pine, mainly surface fire	BPCA in forest floor	<sup>b</sup> 61 kg C ha <sup>-1</sup> (0.7% forest floor C conversion)	Czimczik et al. (2003)
(b) Tropical and Subtropical			
Amazon; Forest clearing; cut, dried 2–3 months, burned, as per local practice.	Visual char on soil or partially burned biomass	<sup>b</sup> 3500 kg C ha <sup>-1</sup> (2.5% fuel C conversion)	Fearnside et al. (1993)
		<sup>b</sup> 1600 kg C ha <sup>-1</sup> (1.3% fuel C conversion)	Fearnside et al. (1999)
		<sup>b</sup> 3200 kg C ha <sup>-1</sup> (1.8% fuel C conversion)	Fearnside et al. (2001)
		<sup>b</sup> 6400 kg C ha <sup>-1</sup> (2.9% fuel C conversion)	Graça et al. (1999)
Australia, slashburning after clearfelling eucalypt stands	Visual char >2 mm, to 30 cm depth	<sup>b</sup> 20 000 and 170 000 kg C ha <sup>-1</sup>	Hopmans et al. (2005)

#### 4.1.2 Production determined by chemically-defined BC

In the single study located (boreal or otherwise), Czimczik et al. (2003) used the BPCA method to determine that a surface wildfire in a Scots pine (*Pinus sylvestris*) stand in Siberia generated 61 kg ha<sup>-1</sup> of BC in forest floor (conversion of 0.7% of prefire forest floor C), adding to the prefire stock of 141 kg BC ha<sup>-1</sup>. Carbon-13 NMR analysis of the same samples showed that estimation of charred biomass as total aromatic C was approximately tenfold higher, as the BPCA method only detects C from large polycyclic aromatic clusters.

Unfortunately, there is limited information on rates of biomass C conversion to chemically-defined BC. Essentially two studies are available (Kuhlbusch and Crutzen, 1995; Kuhlbusch et al., 1996) that used a method based on resistance to thermal oxidation. For savanna fires in South Africa (Kuhlbusch et al., 1996), pre-fire vegetation and litter was approximately 2700 kg ha<sup>-1</sup> from which 90% of C was volatilized. Conversion to BC was 0.5 to 2% (mean 1%)

based on prefire C stocks (defined as the ratio BC/CE, where CE is carbon exposed to fire), or 1.3%, based on BC/CO<sub>2</sub>-C. From laboratory burns of 20 non-woody biomass substrates, Kuhlbusch and Crutzen (1995) found that BC/CE was 0.14–2.2%, or 0.15–2.9% as BC/CO<sub>2</sub>-C. For deciduous wood (mean for two substrates), the values were higher, with BC/CE 3.1%, and BC/CO<sub>2</sub>-C 4%. Despite the differences in methodology, burning conditions, and biomass substrates, these results for BC yields based on chemical oxidation are in a similar range to those in Table 1 based on visual char assessment. This may be because visual assessment of char is chemically inclusive, but is limited by particle-size cutoff. On the other hand, the milder measures of oxidation resistance may exclude less thermally-altered C, but access all sample C. Conversion of C to BPCA-defined BC is likely to produce lower results, as BPCAs are only generated from larger aromatic clusters. Clearly, the limited data on char or BC production from forest fires are an inadequate basis for modelling their role in boreal C budgets, and it is less than satisfactory to compare data derived from various methods

**Table 2.** Estimates of BC (EC) emissions from combustion.

Region, BC Sources	BC or EC estimate	Reference
Global including biomass fuel	5.98 Tg BC y <sup>-1</sup> biomass + 7.96 Tg BC y <sup>-1</sup> fossil fuel	Cooke and Wilson (1996)
Global including biomass fuel, but not boreal and temperate natural fires	5.63 Tg BC y <sup>-1</sup> biomass + 6.64 Tg BC y <sup>-1</sup> fossil fuel	Lioussé et al. (1996)
Global including biomass fuel	4.8 Tg BC y <sup>-1</sup> biomass (late 1990s)	Andreae and Merlet (2001)
Global open vegetation burning	3.3 Tg BC y <sup>-1</sup>	Bond and Sun (2005)
Northern hemisphere open vegetation burning	2–2.5 Tg BC y <sup>-1</sup> (1960–2000)	Ito and Penner (2005)
Canada open biomass burning	0.12 Tg EC y <sup>-1</sup> (1997–2000)	Park et al. (2003)
Canada wildfire, all vegetation types	0.016 Tg BC y <sup>-1</sup> (1960–1969) 0.019 Tg BC y <sup>-1</sup> (1970–1979) 0.038 Tg BC y <sup>-1</sup> (1980–1989) 0.041 Tg BC y <sup>-1</sup> (1990–1997)	Lavoué et al. (2000)
Siberia (experimental surface forest fire)	0.2–1.5 Tg EC y <sup>-1</sup>	Samsonov et al. (2005)

and other regions. However, the rather small range of values for conversion of biomass C to either BC or visual char should be sufficient to allow some initial attempts at modeling their production from boreal wildfire.

#### 4.2 Atmospheric PyC emissions from forest fires

Emissions from forest fires into the atmosphere include a complex mixture of volatile organic compounds (i.e., vapourizing at relatively low temperatures), and poorly-characterized high-molecular-weight substances (Andreae and Merlet, 2001; Friedli et al., 2001; Hays et al., 2002; Duarte et al., 2005), collectively referred to as organic C (OC) or particulate organic matter (POM). These contribute to formation of aerosols, fine particles up to around 100 μm diameter, that remain suspended in the atmosphere. Cooke and Wilson (1996) estimated a lifetime of 7.85 days for BC aerosol particles, during which they increase in hydrophilic character, and are then removed in precipitation with the same efficiency as sulphate. Techniques used to quantify atmospheric BC (often called EC in this context) generally differ from those used for solid soot and char, and will not be discussed here (see e.g., Schmid et al., 2001; Conny and Slater, 2002).

Smoke aerosols affect air quality locally, such as demonstrated for the Missoula Valley, Montana (Ward and Smith, 2005), but can also be transported over long distances. For example, smoke plumes from Siberian forest fires in 2003 affected air quality over Korea (Lee et al., 2005), and Canadian forest fires have been associated with events of elevated CO<sub>2</sub>, BC and OC over the USA (Wotawa and Trainer, 2000; Park et al., 2003). Boreal forest fires contribute substantially to atmospheric BC in the Arctic (Cooke and Wilson, 1996), and soot deposition reduces the albedo of Arctic sea ice (Kim et al., 2005); even Antarctica receives BC from biomass burning in the tropics (Wolff and Cachier, 1998).

In addition to impacts on visibility and health, atmospheric BC produced from fossil fuel and biomass combustion has been identified as a contributor to global warming due to its direct absorption of solar radiation (Jacobson, 2002), and there have been calls for its control to mitigate this effect (Hansen et al., 2000; Bond and Sun, 2005). This is opposite to the effect of sulphate aerosols that tend to mitigate the greenhouse effect by reflecting solar radiation; secondary effects of atmospheric BC and other aerosols are discussed elsewhere (Jacobson, 2002; Menon et al., 2002).

As shown in Table 2, global atmospheric emissions from biomass burning, including biomass fuels, are estimated at 5–6 Tg BC y<sup>-1</sup>, almost as high as those from fossil fuels (Cooke and Wilson, 1996; Lioussé et al., 1996; Andreae and Merlet, 2001). Excluding biomass and fossil fuel consumption, global emissions were estimated as 3.3 Tg BC y<sup>-1</sup> by Ito and Penner (2005), and northern hemisphere emissions as 2–2.5 Tg EC y<sup>-1</sup> by Park et al. (2003).

A detailed spatial and monthly inventory of carbonaceous particle emission from boreal and temperate wildfires in forests, shrublands and grasslands for 1960–1997 was produced by Lavoué et al. (2000). One key result was the very high interannual variability: fires in boreal and temperate regions accounted for 4%, on average, of global biomass burned, but ranged up to 11.5% of biomass burned, with emissions up to 8.8% of BC and 19.4% of POM, due to less complete combustion than in other ecosystems. They noted that particle emissions from boreal fires may have especially high impact in Arctic regions that are highly sensitive to climate change. As shown in Table 2, BC emissions from Canadian forest fires, mainly from boreal regions, have been increasing from 0.016 Tg BC y<sup>-1</sup> in 1960–1969, to 0.041 Tg BC y<sup>-1</sup> in 1990–1997. This is consistent with trends of increasing fire disturbance and declining total ecosystem C in Canadian forests (Kurz and Apps, 1999).

Park et al. (2003) estimated  $0.12 \text{ Tg EC y}^{-1}$  emission from Canadian fires for 1997–2000. The discrepancy between this and the lower value of  $0.04 \text{ Tg BC y}^{-1}$  for 1980–1997 in Lavoué et al. (2000) is mainly due to the different EFs used:  $2 \text{ g EC per kg dry mass}$  by Park et al. (2003) compared to  $0.75$  by Lavoué et al. (2000).

These analyses of global and regional BC emissions rest on many assumptions and uncertain estimates, highlighting the need for more direct measurements of BC emissions from boreal forest fires, of emission factors, and of atmospheric BC concentrations and deposition rates. Estimated or measured EFs for BC production are generally within the range of  $0.5\text{--}2 \text{ g BC kg}^{-1}$  biomass, consistent with EFs recently determined by Hays et al. (2002) for six foliar fuels under open burning to simulate natural events.

Until recently, there was little direct information on aerosols and gases produced by boreal wildfires. Studies carried out near Fort Providence, NWT, Canada, in jack pine (*Pinus banksiana*) as part of the International Crown Fire Modelling Experiment (ICFME) determined particle production and size distribution in smoke plumes in 2000 (Payne et al., 2004), gases and total nonmethane hydrocarbons in 1997 (Cofer et al., 1998), and BC and OC in aerosol particles in 1998 (Conny and Slater, 2002). In the latter study of particles up to  $2.5 \mu\text{m}$  diameter, the BC/TC ratio was found to be  $0.085$  for the flaming stage and  $0.0087$  for the smouldering stage, but EFs were not determined. However, more information is recently available from experimental fires in three Scots pine sites of central Siberia (Samsonov et al., 2005). Aerosol emissions corresponded to  $1\text{--}7\%$  of the mass of fire-consumed biomass, with EC constituting  $7\text{--}15\%$  of total aerosol mass. This was scaled up to an estimated  $3\text{--}10 \text{ Tg}$  aerosol mass per year for boreal Russia from  $12\text{--}14$  million ha burned, or  $0.2\text{--}1.5 \text{ Tg}$  of EC, in line with previous estimates.

### 4.3 PAHs from forest fires

The products from incomplete combustion of carbon-based fuels include polycyclic aromatic hydrocarbons (PAHs), having structures of 2–7 fused aromatic rings. The natural background of PAH deposition from wildfires is preserved in sediments, which also record the recent increases from fossil fuel combustion, industrial pulping and direct contamination with oil and coal (Yunker and Macdonald, 2003). In urban areas, atmospheric PAHs originate largely from fossil fuel combustion, but extensive use of wood for home heating was responsible for half the atmospheric PAHs at a semirural forested Swedish site (Mandalakis et al., 2005). PAHs can be transported long distances, especially the lighter ones (Bucheli et al., 2004), and they are deposited in Arctic regions far from their sources (Yunker et al., 2002; Hung et al., 2005).

PAHs are produced in the gas phase during combustion, but at lower temperatures they rapidly condense onto ash particles (Kim et al., 2003). Therefore PAHs formed in for-

est fires may be emitted as volatiles or deposited on the soil surface with the ash. We did not locate any direct measurements of PAH emission from forest fires, but the previously noted study of Hays et al. (2002) on open burning of foliar fuels found that PAHs constituted  $0.2$  to  $2 \text{ g kg}^{-1}$  of  $\text{PM}_{2.5}$  (fine particulate matter with aerodynamic diameter  $<2.5 \mu\text{m}$ ) which itself was formed with an EF of  $15\text{--}35 \text{ g kg}^{-1}$ . Kim et al. (2003) measured changes in PAH concentrations in  $0\text{--}5 \text{ cm}$  soil after forest fires at three sites in Korea. On average, soil PAH concentrations (sum of the 16 US Environmental Protection Agency (EPA) priority PAHs, denoted  $\Sigma 16\text{PAH}$ ) were  $1200$ ,  $200$  and  $300 \mu\text{g kg}^{-1}$  at one, five, and nine months after fire, compared to  $50 \mu\text{g kg}^{-1}$  in control sites. The decline in the first few months was attributed to loss of ash by wind and rain erosion. The same 16 PAHs were determined in  $0\text{--}10 \text{ cm}$  soils of the Swiss soil monitoring network (Bucheli et al., 2004), with median  $\Sigma 16\text{PAH}$  values increasing in the order of arable soils ( $66 \mu\text{g kg}^{-1}$ ), grassland and pasture ( $142 \mu\text{g kg}^{-1}$ ), forests ( $164 \mu\text{g kg}^{-1}$ ) and urban soils ( $451 \mu\text{g kg}^{-1}$ ). Wilke and Amelung (2000) found similar values for the sum of 20 PAHs in North American native grassland sites ( $63\text{--}321 \mu\text{g kg}^{-1}$ ). No data were located in a literature search for information on PAHs in boreal forest soils, but these surveys indicate the general range that could be expected under natural conditions.

There is an interaction of PyC and PAHs in the environment; not only are they co-produced but compared to non-pyrogenic OM in soils and sediments, BC has a much higher ability to adsorb PAHs and other hydrophobic organic compounds. This has been the subject of much recent research, especially concerning the fate and bioavailability of these compounds in BC-containing harbour sediments (e.g., Accardi-Dey and Geschwend, 2003; Cornelissen et al., 2005; Jonker et al., 2005; Lohmann et al., 2005). Laboratory-produced biomass chars (Chun et al., 2004; Zhu and Pignatello, 2005) also showed high affinity for aromatic compounds, depending on the degree of carbonization and oxygen loss. The influence of soil and sediment BC on the fate of organic pollutants is not likely of immediate concern for boreal regions which are mostly affected by natural fires. Studies of PAH deposition in peatlands of eastern Canada (Dreyer et al., 2005), and of PAHs in precipitation in Atlantic Canada (Brun et al., 2004) indicated that emissions were predominantly from coal and fossil fuel combustion rather than forest fires.

## 5 Characteristics and stocks of soil PyC

### 5.1 How fire affects soil properties and development

In addition to obvious charring or increases in chemically-defined BC, fire causes other general changes in soil organic matter (SOM) properties, and wider-ranging effects on soil development, although the information available is mainly from grasslands and agriculture in temperate and tropical regions. As recently reviewed (Certini, 2005; González-Pérez et al., 2004), the effects of fire on soil organic matter (SOM) include a relative decrease in the proportion of humic acid (the fraction obtained by extraction with base and subsequent precipitation with acid), with increase in the insoluble humin fraction. There is a loss of carbohydrates and oxygen-containing functional groups. The proportion of alkyl C may increase, and this is often associated with development of hydrophobicity in the upper mineral soil, which contributes to soil erosion, landslides and flooding in mountainous territory (Neary et al., 1999; DeBano, 2000). The loss of carbohydrates (indicated by reduction of O-alkyl C in the  $^{13}\text{C}$  NMR spectra) also contributes to loss of aggregate stability (Kavdir et al., 2005). Thus, fire generally causes the remaining organic matter to become less soluble and more resistant to oxidation and biological decomposition.

Charring often results in only small changes (Czimczik et al., 2003; Knicker et al., 2005a) or a decrease (Baldock and Smernik, 2002; Harden et al., 2004; Neff et al., 2005) in the C/N ratio, and an increase in more recalcitrant organic N forms (González-Pérez et al., 2004; Castro et al., 2006). In SOM unaffected by fire,  $^{15}\text{N}$  NMR indicates that amide is the predominant form of soil N, whereas an increase of pyrrole-type N is found in fire-affected soils, and has been suggested as a molecular marker of fire (Knicker et al., 2005a).

Reported effects of charring on  $\delta^{13}\text{C}$  are generally small and somewhat erratic (Bird and Gröcke, 1997; Czimczik et al., 2002; Rumpel et al., 2006). With increasing thermal alteration, biomass should become isotopically lighter with preferential loss of cellulose, and greater contribution of more-depleted lignin to formation of condensed aromatic structures, as was recently demonstrated for wood samples (Turney et al., 2006). In general, char retains the signature of its C3 or C4 plant origin (Hiradate et al., 2004), although much greater depletion has been observed for char derived from some C4 grasses, especially for natural rather than oxygen-limited laboratory burns (Turekian et al., 1998; Krull et al., 2003). Measurement of changes in  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  is one of the approaches used to quantify  $\text{CO}_2$  emissions from forest fires (Langenfelds et al., 2002; Schuur et al., 2003; Randerson et al., 2005).

There is increasing evidence that pyrogenic C can make a substantial contribution to SOM in fire-prone ecosystems, and can influence pedogenesis. The isolation of highly aromatic humic acids from SOM has long been considered an indicator of BC inputs (Haumaier and Zech, 1995; Golchin

et al., 1997; Zech et al., 1997; Almendros et al., 2003; Benites et al., 2005), as is development of stable humus forms highly resistant to decomposition (Almendros et al., 2003; Benites et al., 2005). Highly aromatic humic acids (Shindo et al., 1986; Hiradate et al., 2004) and charred plant fragments constituting 3–33% of SOC (Shindo et al., 2004, 2005) were found in volcanic ash soils from Japanese grasslands subject to frequent burning.

Charcoal inputs have been proposed to account for the development of dark Chernozemic soils in the Canadian prairies (Ponomarenko and Anderson, 2001), and the Russian steppe (Rodionov et al., 2006) and also the patchy, relict Chernozems in Europe, especially where there were Neolithic settlements (Schmid et al., 2002; Schmidt et al., 2002; Kleber et al., 2003). Black carbon is a defining property of the South American anthropogenic soils (*Terra Preta*) developed by native populations before European contact. They are dark in colour and still high in fertility compared to the surrounding highly weathered and infertile Oxisols (Glaser et al., 2000, 2001, 2002). In the deep A horizons (40–80 cm), BC (BPCA method) typically constitutes 20% or more of SOC. It has also been suggested that podzolization processes are inhibited by frequent fires that destroy the forest floor and C available for translocation (Mokma and Vance, 1989), including one study in Siberian Scots pine forest (Czimczik et al., 2005).

### 5.2 Quantitative analysis of PyC – non-forest soils

Table 3a summarizes literature data for soil BC from mainly non-forest sites, as percentage of total SOC if available. None of these sites are boreal, but there are sufficient data to allow some comparison of results from different techniques. The values obtained from photo-oxidation and  $^{13}\text{C}$  NMR of the  $<53\ \mu\text{m}$  fraction (Skjemstad et al., 1999a, 2002, 2004), up to 35% of SOC, are in general higher than those from other thermal and chemical measures of oxidation resistance (Schmidt et al., 2001). Even higher-ranging values were found by Ponomarenko and Anderson (2001), who determined BC by mass remaining after photo-oxidation. These higher values are likely because the residues from photooxidation still contain other resistant or protected C structures that can be distinguished by subsequent NMR analysis; also some of the highest values (up to 80%) came from samples with visible charred particle content. Generally lower results (1.7–18%) were found using the BPCA method (Glaser and Amelung, 2003; Dai et al., 2005; Rodionov et al., 2006), and the lowest range (1–7%) by thermal and chemical oxidation techniques (Bucheli et al., 2004; Rumpel et al., 2005).

**Table 3.** Soil BC or charcoal in soil for (a) non-forest and (b) forest sites. Unless otherwise stated, results given as percentage of total soil organic carbon (SOC). Abbreviations: NMR (nuclear magnetic resonance), OX (oxidation), BPCA (benzenepolycarboxylic acids).

Region/site	Method	BC or Char quantities	Reference
(a) Non-forest sites			
Australia, 8 surface soils	Photo OX + NMR of <53 $\mu\text{m}$	< 1 to 30%	Skjemstad et al. (1999a)
Australia, 2 long-term agriculture sites, 0–30 cm	Photo OX + NMR of <53 $\mu\text{m}$	10 to 27% (4–15 Mg C ha <sup>-1</sup> )	Skjemstad et al. (2004)
USA, surface soils (4 cultivated, 1 prairie)	Photo OX + NMR of <53 $\mu\text{m}$	10–35%	Skjemstad et al. (2002)
Canada, Black Chernozem, aspen parkland native and cultivated	Photo OX	20–60% (whole soils), 10–80% (size fractions)	Ponomarenko and Anderson (2001)
North American great plains, 18 native grassland sites, 0–10 cm	BPCA	4–18%, average 9% (1–15 Mg C ha <sup>-1</sup> )	Glaser and Amelung (2003)
Texas grassland fire study, 0–20 cm	BPCA	5–13%	Dai et al. (2005)
Russian steppe soils	BPCA	3.5–12.1% (0–10 cm); 1.5–17.2 (50–60 cm)	Rodionov et al. (2006)
Switzerland, 23 monitoring sites including forests, 0–10 cm	Thermal OX	1–6%, median 2%	Bucheli et al. (2004)
Thailand, slash-and-burn agriculture	Chemical OX	3–7%	Rumpel et al. (2006)
China, Loess Plateau, very deep profiles	Chemical OX	0.41–5.7 g C kg <sup>-1</sup> soil	Wang et al. (2005)
(b) Forest sites			
(i) Forest floor/humus only			
Sweden, 12 lake islands, 1–350 y after fire	Visual Char	984–2074 kg ha <sup>-1</sup>	Zackrisson et al. (1996)
Canada, 6 stands, southern Quebec, 75 y after fire,	Visual Char >2 mm	343–1295 kg ha <sup>-1</sup>	Bélanger et al. (2004) and personal communication
(ii) Mineral soil or whole soil profile			
France, Alpine conifer forests	Visual Char >0.4 mm	0.1–20% (10–30 000 kg ha <sup>-1</sup> )	Carcaillet and Talon (2001)
Corsica (France), <i>Pinus/Quercus</i> forests		9800–148 000 kg ha <sup>-1</sup>	Carcaillet and Talon (2001)
Australia, 3 eucalypt forest management sites, to 30 cm depth	Visual char >2 mm	15–32% (15 000–140 000 kg C ha <sup>-1</sup> )	Hopmans et al. (2005)
Siberia, Yenisey R., 215-y <i>Pinus sylvestris</i>	Thermal OX	20–24% in forest floor + 0–75 cm; 13% for 75–300 cm	Schulze et al. (1999)
Siberia, Yenisey R., <i>Pinus sylvestris</i> fire chronosequence study	BPCA	≤3.5% in organic layer (up to 720 kg C ha <sup>-1</sup> ) 0.01–0.02% (0.16 to 0.2.5 g m <sup>-2</sup> ) for 0–100 cm mineral soil	Czimczik et al. (2005) More detail in Fig. 5
Siberia, Yenisey R., forest tundra	BPCA (sum of BPCAs; no conversion factor used)	0.7–5.7 % (higher values in permafrost sites)	Rodionow et al. (2006)

### 5.3 PyC in forest soils

#### 5.3.1 Qualitative characterization

Few studies have characterized the BC component of forest soils, especially for boreal regions. Solid-state <sup>13</sup>C NMR was used to elucidate changes in organic matter composition after wildfires in Spain (Knicker et al., 2005a) and Turkey (Kavdir et al., 2005), and after prescribed fire in eucalypt plantations in Australia (Guinto et al., 1999). The general results are similar to trends noted above (Sect. 5.1) and for a moorland site (Haslam et al., 1998), mainly a relative decrease in O-alkyl C and increase in alkyl and aromatic C. While individual charred particles may be very high in aromatic C, there may actually be little change in aromatic C in bulk forest floor or surface mineral horizons of fire-affected sites. This can be the case where organic matter is consumed by fire,

leaving ash rather than char, with little alteration of underlying material, or if new organic matter quickly accumulates from the pulse of detritus from fire-killed biomass and litter from regrowing vegetation.

Preston et al. (2002b) found evidence for BC in coastal temperate forest sites of southern Vancouver Island, British Columbia. Solid-state <sup>13</sup>C NMR showed that several samples of the 2–8 mm water-floatable fraction from mineral soil were high in aromatic C characteristic of BC; all of these samples were from the drier east side of Vancouver Island, where fire was historically more prevalent than from the cooler, wetter west coast.

Although sparse, information on boreal forests includes two studies on the Boreal Forest Transect Case Study (BFTCS) in northern Saskatchewan and Manitoba. Preston et al. (2002a) separated mineral soil from two jack pine and

one black spruce (*Picea mariana*) sites into water-floatables and three size fractions. Solid-state  $^{13}\text{C}$  NMR spectra suggested a small BC contribution to the  $<63\ \mu\text{m}$  fraction of the A horizon of the jack pine sites, but not to the B horizon samples. For the black spruce site, the broad aromatic peak in the  $250\text{--}63\ \mu\text{m}$  fraction of the A+B horizon also indicated possible incorporation of BC into mineral soil OM. In a survey of forest floor chemistry along the BFTCS transect, Preston et al. (2006) found high aromatic intensity from charcoal in some of the samples from jack pine sites, but not from black spruce sites. No attempt was made to quantify BC, as the studies were not designed with this objective.

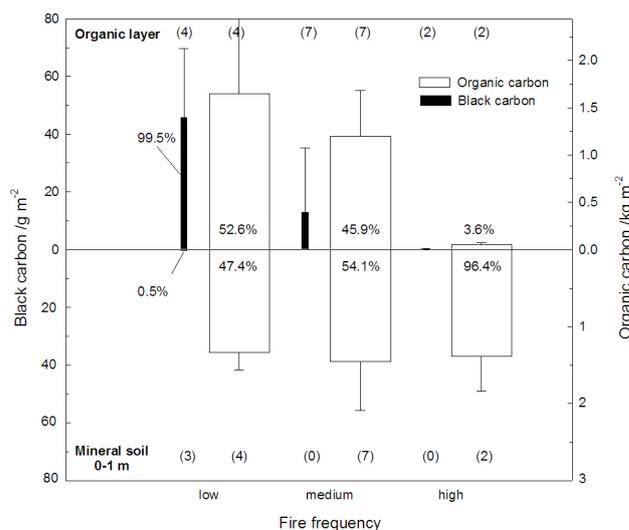
Also using  $^{13}\text{C}$  NMR, Czimczik et al. (2003) characterized the changes in organic composition of forest floor, by sampling burned and unburned patches shortly after a wildfire in Scots pine in central Siberia. The highly aromatic structures produced from fire were underrepresented by routine CP, and quantitative spectra required the Bloch decay (BD) method.

Harden et al. (2004) used thermogravimetry in  $\text{O}_2$  to characterize fire effects on organic horizons as part of the FROST-FIRE experimental burn study in black spruce in Alaska. With burning, the proportion of mass loss at the first peak ( $280^\circ\text{C}$ ) decreased and that at the second peak ( $400^\circ\text{C}$ ) increased, and there was lower total mass loss up to  $1000^\circ\text{C}$ . These changes indicate loss of labile C, mainly carbohydrates, and increase in lignin and/or black C. Similar changes in organic composition were found following wildfire in Alaska (Neff et al., 2005). Although peatlands comprise large areas of the boreal forest, and are also vulnerable to fire (Zoltai et al., 1998; Benscoter and Wieder, 2003; Turetsky et al., 2004), we found no information on BC characteristics or stocks. Analyses of char in peat profiles to investigate paleobotany and peat development (e.g., Kuhry, 1994; Laird and Campbell, 2000; Flannigan et al., 2001) are not generally designed for this purpose.

As part of their studies of C cycling in the BOREAS Old Black Spruce study area near Thompson Manitoba, Harden et al. (1997) and Trumbore and Harden (1997) concluded that charred material was an important input to deep organic layers in black spruce-feathermoss. In a later study, Manies et al. (2005) estimated that 10 to 60% of C in deep organic horizons is derived from wood biomass, specifically from fire-killed trees (i.e., data were only used from buried wood with evidence of charring). However, charcoal was not specifically quantified in any of these three studies.

### 5.3.2 PyC in forest soils – quantitative analyses

Again, there are few studies from boreal regions. For studies limited to organic horizons, only two studies were found, based on visual assessment of charcoal (Table 3b). Higher amounts ( $984\text{--}2074\ \text{kg ha}^{-1}$ ) were found by Zackrisson et al. (1996) in boreal Sweden than in the temperate Quebec forest ( $343\text{--}1295\ \text{kg ha}^{-1}$ ) by Bélanger et al. (2004 and personal communication). This is probably due to several fac-



**Fig. 5.** Distribution of PyC above and below ground in a Siberian Scots pine site, reproduced as permitted from Czimczik et al. (2005).

tors, including low intensity of the fire, low biomass of the stands, and no quantification of charcoal fragments smaller than 2 mm.

Studies of mineral soils and whole soil profiles can be divided into those based on visual assessment of charcoal vs. those using chemical analyses of BC. Carcaillet and Talon (2001) determined charcoal stocks in soil profiles along altitudinal transects in dry valleys in the French Alps. In the current conifer-dominated forest belt (1700 to 2200 m a.s.l.) charcoal C accounted for 0.1 to 20% of SOC, corresponding to 10 to 30 000  $\text{kg ha}^{-1}$  of charcoal. The high variability likely resulted from both local spatial variation in fuel type (e.g., log vs. twigs or shrubs), and variation in fire frequency throughout the Holocene.

A recent Australian study (Hopmans et al., 2005) produced high estimates of both charcoal generated in slash-burning (Sect. 4.1.1, Table 1) and soil charcoal C stocks ( $>2\ \text{mm}$ , to 30 cm depth). Charcoal accounted for 15–32% of total soil C, or 15 000–140 000  $\text{kg ha}^{-1}$ . A similar result was found for Corsican forests, with 9800 to 148 000  $\text{kg ha}^{-1}$  of soil charcoal (Carcaillet and Talon, 2001).

Three studies from Siberia determined BC by chemical methods. Two studies of Scots pine stands in Siberia produced widely differing results. For a 215-y-old stand (Schulze et al., 1999), BC determined by a thermal method amounted to 20–24% of total C in forest floor plus 0–75 cm mineral soil, and 13% for 75–300 cm. Using the BPCA method, however, Czimczik et al. (2005) found much lower soil BC stocks for a fire chronosequence in the same study area, with 99% of the BC found in the organic layer (Fig. 5). This study also suggested that BC could be lost in subsequent fires: for sites with low fire frequency, BC stocks in the

organic layer were up to  $720 \text{ kg ha}^{-1}$ , but much lower values ( $<50 \text{ kg ha}^{-1}$ ) were found for stands subject to intense fires that had previously consumed the whole organic layer. A recent study of permafrost soils further north along the Yenisey River found that BC was up to 5.7% of SOC (Rodionow et al., 2006), using the BPCA method, but without multiplying the BPCA yields by the commonly-used factor of 2.27.

Estimates of PyC stocks as BC or charcoal are very limited, especially for boreal regions, and very difficult to compare, due to the variations of sampling and analysis. However, the estimates of forest floor charcoal stocks in the order of  $1000\text{--}2000 \text{ kg ha}^{-1}$  for boreal forest sites likely underestimate total site charcoal, including that in mineral soil, coarse woody debris, and very fine particles. For the mineral soil/soil profile studies using chemical methods, with results available as percent of SOC, the value determined by Schulze et al. (1999) may not be reliable, due to early development of the thermal oxidation method, and results from only one profile. For the other studies, generally higher values are found for charcoal C as percent of total SOC, rather similar to those derived from photo-oxidation plus NMR for the non-forest sites in Table 3a, while the two BPCA studies produced lower results.

## 6 What happens to PyC?

### 6.1 Mechanisms for transformation and transport of PyC

Although PyC is generally assumed to be relatively inert to degradation (especially the BC fraction that is oxidation-resistant), it must degrade eventually (Schmidt and Noack, 2000). There is ample evidence that char, or highly aromatic carbon structures, are decomposed more slowly than other plant residues. Studies of C-depleted plots from long-term bare fallows showed that the remaining soil C was enriched in aromatic structures (Kiem et al., 2000). Similar results were found in two Australian studies of agricultural soils (Skjemstad et al., 1999b, 2004). The Terra Preta anthropogenic soils of South America have retained their higher C and BC contents centuries after being abandoned (Glaser et al., 2001).

There is increasing evidence, however, that BC is susceptible to losses, especially over longer time scales. One possible mechanism for BC loss is oxidation by subsequent fires. This hypothesis has not yet been tested directly, but based on measurements of charcoal production, stocks in forest floor, and fire return intervals, Ohlson and Tryterud (2000) concluded that charcoal stocks in boreal forests should be approximately ten times higher than actually observed. To explain this discrepancy, they suggested that some charcoal is consumed by subsequent fires, a hypothesis also suggested by Czimeczik et al. (2005, Sect. 5.3.2).

Second, there is evidence for the role of slow chemical oxidation and solubilization of soil BC, as already demonstrated

for atmospheric BC (Decessari et al., 2002). The surfaces of BC particles aged in soils for decades to millennia become increasingly oxidized (Schmidt et al., 2002, Brodowski et al., 2005b), characteristically exhibiting more carboxylic and phenolic groups (Lehmann et al., 2005). Fourier-transform ion-cyclotron-resonance mass spectrometry showed that a humic acid from a dark Japanese soil with frequent burning of crop residues was high in heavily-carboxylated, hydrogen-deficient condensed aromatic structures, consistent with oxidized BC (Kramer et al., 2004). Oxidation increases water solubility, and similar BC-derived structures have also been detected in dissolved organic matter from the Delaware and Amazon River systems (Kim et al., 2004), and from a fire-affected forest soil (Hockaday et al., 2006).

Third, pyrogenic carbon is susceptible to biological degradation. Even graphite is not immune, with 2% oxidation reported for a 96-day incubation of artificial graphite in soil (Shneour, 1966). Other incubation studies are discussed in Sect. 6.2. Compared to the PyC formed from fossil fuel combustion, however, PyC formed from biomass burning has a relatively low degree of thermal transformation (Fernandes et al., 2003; Knicker et al., 2005b), with higher polarity, and small and less-ordered aromatic regions. Similar to laboratory-produced chars from wood (Baldock and Smernik, 2002; Czimeczik et al., 2002), BC found in boreal forest floor after wildfire had small cluster size with many functional groups (Czimeczik et al., 2003). Such PyC would probably fall in the intermediate region termed charcoal in Fig. 1. Small cluster size combined with a relatively high degree of functionalization would probably make these particles more susceptible to chemical degradation than more highly condensed structures. Finally, PyC is also susceptible to physical fragmentation and transport from its site of origin (Sects. 6.4, 6.5).

### 6.2 Incubation studies

The few incubation studies show very low rates of decomposition in a laboratory setting. Shindo (1991) used charred plant residues from an experimental fire in a grassland (mainly *Miscanthus sinensis* A.), and qualitatively reported hardly any decomposition after 40 weeks incubation in volcanic ash soil. Baldock and Smernik (2002) used red pine (*Pinus resinosa*) wood charred at different temperatures. After 120 days incubation in sand, 20% of C was mineralized from wood heated at  $70^\circ\text{C}$  (essentially unaltered). Carbon mineralization decreased to 13% for wood heated to  $150^\circ\text{C}$ , and to less than 2% for chars produced at  $200\text{--}350^\circ\text{C}$ , with increasing proportions of aromatic C. Incubation of wheat and rice chars (produced at  $350^\circ\text{C}$  for 2 h) with soil and quartz showed a rapid initial loss of 5–50% of the initial BC (determined by the BPCA method) within the first 6 months, but this levelled off in the following 1.5 years (Brodowski, 2004). No changes in BC content were found in the sterile

controls, consistent with microbial rather than abiotic processes.

The importance of an additional source of more readily-available C (co-metabolism) for the breakdown of PyC was shown by Hamer et al. (2004), in a study of charred maize (*Zea mays* L.), rye (*Secale cereale* L.) and oak wood incubated in sand for 60 days. For the charred substrates, carbon mineralization of 0.3%–0.8% was increased to 0.6%–1.2% by glucose additions at 0 and 26 days. However, glucose mineralization was also enhanced by addition of charcoal, suggesting that its high surface area and porous structure may promote growth of microorganisms. Similar effects have also been found in field studies, as discussed in Sect. 7.2. Hamer et al. (2004) suggested that small molecules may not be stabilized by sorption into charcoal pores, but could actually become even more susceptible to microbial activity.

The possibilities for microbial degradation of charred biomass are likely to be similar to those occurring in forest sites that have shown microbial utilization of C from lignite combustion ash (Machulla et al., 2004), and from lignite in soils developed after open-pit coal mining (Rumpel and Kögel-Knabner, 2002, 2004). The latter studies also showed increasing oxidative transformation of lignite into humic acids and the importance of co-metabolism for decomposition of lignite.

### 6.3 Information from degradation of geological and sedimentary substrates

Studies using a variety of techniques indicate that the resistance of BC and char to mineralization is relative, and while the rates may be slow, they appear to be affected by similar factors that inhibit or enhance loss of other organic substrates. The results of short-term incubations would mainly represent the less-condensed fraction, so rates would be expected to decline with time. However, most incubation studies measure decomposition by CO<sub>2</sub> evolution, and especially in the short term would not capture incomplete oxidation of BC and its incorporation into SOM. Additionally, decomposition in field settings could be enhanced by other factors such as photooxidation, leaching, and variable availability of nutrients and more readily-available C. While these have not been investigated for charcoal and BC in forest or peatland settings, some information can be gathered from studies of other recalcitrant organic substrates such as coal, shale and kerogen.

At geological timescales, chemical weathering of ancient organic matter plays a role in the global C cycle. These slow processes consume oxygen, release CO<sub>2</sub>, and generate dissolved and solid oxidation products (Mackenzie et al., 2004a). Recent studies of coal (Chang and Berner, 1998, 1999) and black shale (Petch et al., 2000, 2001) have highlighted the importance of contact with oxygen-rich surface waters. The laboratory coal oxidation studies of Chang and Berner (1998, 1999) show that while chemical oxida-

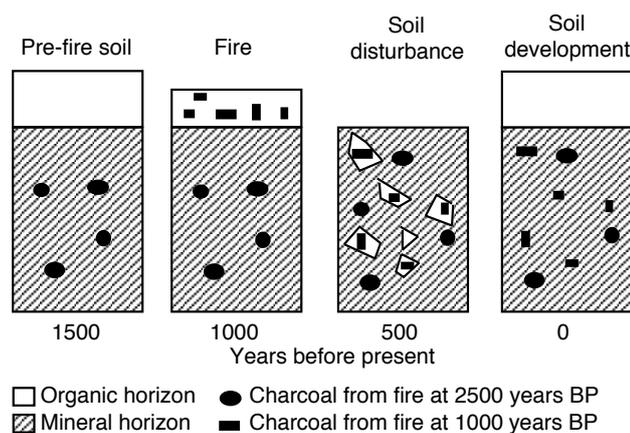
tion rates are low, they are significant on a geological time scale. Chang and Berner (1999) estimated lifetimes of 8000 and 80 000 y for coal with grain sizes of 10 μm and 100 μm diameter, respectively. The coal and shale studies also show that CO<sub>2</sub> production accounts for only 30–50% of oxygen consumption, with the rest producing partially oxidized solids and a small fraction of DOC. Thus similar to aging of PyC in soil, the residues become enriched in oxygen-containing functional groups such as carboxylic acid, esters, aldehydes and ketones, enhancing their water-solubility and initiating their transformation into humic fractions of SOM. Keller and Bacon (1998) determined that Cretaceous-age till kerogen in the vadose zone would be consumed in 10 000 y or less with oxygen exposure.

Results in the same range have been found for loss of BC in ocean sediments. Middelburg et al. (1999) estimated 64% BC degradation in marine sediments with 10–20 ky of oxygen exposure. By comparing radiocarbon ages of BC and concurrently deposited non-BC organic matter Masiello and Druffel (1998, 2003) estimated BC residence times of 2400 to 13 900 y with oxygen exposure. Recalcitrant substrates such as coal, shale, kerogen and BC in sediments can be oxidized in the order of 10–20 ky, and similar results might be expected for the more recalcitrant PyC from forest fires, depending on structure and oxygen exposure.

### 6.4 Movement and fragmentation of PyC

There is much evidence for fragmentation and movement of PyC down into mineral horizons, although most is from non-boreal regions. Movement of fine char particles or BC down through mineral soil was demonstrated for sugar cane fields in Australia (Skjemstad et al., 1999b), native grassland in Texas (Dai et al., 2005), slash-and-burn soils in Thailand (Rumpel et al., 2006), and steppe soils of Russia (Rodionov et al., 2006). As noted previously, Ponomarenko and Anderson (2001) found high proportions of charcoal C in aspen parkland sites. They also used scanning electron microscopy to show the importance of pedoturbation and mechanical processes that cause downward movement, and fragmentation and rounding of charcoal particles, especially the more fragile combustion products of herbaceous plants compared to those of woody origin.

Little information is available for forested regions, although some studies have been undertaken to deal with the effects of charcoal movement on reconstruction of Holocene vegetation and disturbance regimes. For an altitudinal transect in the French Alps, Carcaillet (2001a, 2001b) showed that fragmentation by freeze-thaw processes, bioturbation by soil fauna, and profile disturbance by tree uprooting and surface erosion following fires all contribute to downward migration of charcoal. This study concluded that “the minimum time for a charcoal particle to migrate down the soil profile to a depth of 100 cm is less than 500 y at 2000 m a.s.l., but most of the charcoal production of the last two millennia remains



**Fig. 6.** Schematic showing how charcoal could be transported from organic to mineral horizons in Podzols (Vancouver Island, British Columbia). Charcoal from a fire 1000 years before present (BP) is deposited in the organic horizon and mixed into the mineral soil at 500 yBP. A new charcoal-free organic horizon has developed by 0 yBP. Reproduced with permission from Gavin (2003).

in the upper 30 cm. After 2500–6000 y, the major part of the charcoal mass was buried at a depth of 40–70 cm for elevations below 2000 m.”

Tree uprooting was considered to be the main cause of charcoal movement for a coastal temperate rainforest of Vancouver Island (Clayoquot River watershed), where cryoturbation, bioturbation and landslides were of minor importance (Gavin, 2003; Gavin et al., 2003). Figure 6 from Gavin (2003) shows how charcoal could be transported from organic to mineral horizons from fires at 2500 y and 1500 y before present. The importance of charcoal burial by tree uprooting also shown by Talon et al. (2005), who used the charcoal fragments in podzolic soils to reconstruct fire history in an old-growth deciduous forest in southern Québec. On steeper slopes of British Columbia interior rainforest, charcoal is transported and buried mainly by shallow earth landslides resulting from loss of root strength after wildfires (Sanborn et al., 2006). A recent study of Alaskan soils (Ping et al., 2005) noted that charcoal particles typically accumulated at the base of the O horizon, and throughout the A and upper B horizons, and that profile development can be influenced by gelifluction and cryoturbation. Therefore, charcoal movement and fragmentation in boreal regions may occur by several mechanisms, including tree uprooting, mass wasting, gelifluction and cryoturbation.

### 6.5 Transfer of PyC to marine sediments

For even the most recalcitrant organic substrates, the only long-term shelter from mineralization is burial in anoxic marine sediments which accumulate one mole of organic C for every 500–1000 fixed by photosynthesis (Hedges and Oades, 1997). PyC is delivered by atmospheric deposition, and dis-

solved, colloidal and particulate organic matter of rivers to marine sediments, where it constitutes up to one-third of organic C (Gustafsson and Gschwend, 1998; Masiello and Druffel, 1998, 2001; Middelburg et al., 1999; Mitra et al., 2002; Golding et al., 2004). In addition to BC from biomass combustion, sedimentary BC includes petrogenic graphite (GBC) which can be weathered out of rock, transported and reburied in ocean sediments (Dickens et al., 2004a, b) and soot from fossil fuel combustion (Masiello and Druffel, 2003).

Pyrogenic organic matter and its breakdown products have been suspected to be exported from boreal forests to rivers and ultimately to the Arctic Ocean (Schmidt, 2004). For estuarine sediments in the Siberian Arctic, the proportion of BC (chemothermal oxidation method) increased from 1% to 15% of TOC from west to east (Guo et al., 2004). The  $^{14}\text{C}$  ages of sediment C also increased from 2570 to 13 050 yBP, supporting the idea that BC is more resistant than other soil organic carbon. It appeared that the BC was mostly derived from old organic matter released by permafrost thaw and riverbank and coastal erosion, rather than recent forest fires. For the Canadian Arctic, Gōni et al. (2005) found that ancient organic C (radiocarbon age exceeding 7000 y) accounted for ~70% of the particulate organic matter delivered by the Mackenzie River to the Mackenzie Delta/Beaufort Shelf region. It was suggested to originate from a combination of fossil C (bitumen and/or kerogen) eroding from sedimentary rocks, and old soil C released from permafrost deposits. It is possible that the former category could include graphite, and the latter BC from ancient fires, but certainly data are lacking to assess the flux of BC from boreal fires to Arctic sediments.

### 6.6 How long does PyC last in soils?

There is remarkably little field data on the longevity of PyC that is not consumed in a subsequent fire, or transported down through the soil profile or off-site. Soils of temperate rainforests in coastal British Columbia contain charcoal fragments dating back to deglaciation, approximately 13 000 y (Lertzman et al., 2002). For one site, Gavin et al. (2003) plotted charcoal mass vs. time since last fire determined by  $^{14}\text{C}$  dating of individual charred particles, and found that charcoal mass decreased exponentially with increasing time since the last fire. From their data we calculate an average half-life of 6623 years, assuming that all fires initially produced similar amounts of BC. This is similar to the time-scale for BC loss in sediments, and for geological substrates, and also to results for charcoal buried by landslides in interior British Columbia (Sanborn et al., 2006). Soil charcoal radiocarbon ages ranged up to nearly 10 000 y BP, but only a few samples were older than 6000 y. Schmidt et al. (2002) found radiocarbon ages of charred particles in a similar millennial range (1160–5040 y BP, up to 3990 y older than bulk SOC) for relic European chernozems.

The rapid decomposition (<100 years at 0–5 cm) found in Bird et al. (1999) could be due to higher temperatures, good aeration and stronger photooxidation, and also because char produced from savanna vegetation is finer than from wood. By contrast, in the British Columbia studies (Gavin et al., 2003; Sanborn et al., 2006), decomposition would be much slower due to colder temperatures, larger size of char fragments produced from wood, burial in soil and moss layers, and especially in coastal sites, wet conditions in winter. Even slower decomposition may be expected in colder boreal forests, especially for poorly-drained sites, and permafrost-affected soils (Rodionow et al., 2006). Except for anoxic peats or permanently frozen soil, the high end for the half-life of PyC may be expected to be in the kY region (maybe 5–7 ky), for cold, wet environments, and for the PyC fraction with more recalcitrant structure. At the other extreme, a half-life in the order of 100 y (Bird et al., 1999) may be not unrealistic for some fraction of PyC from boreal wild-fire, with less thermal alteration and especially with surface exposure (unpublished field observations from Canadian and Siberian boreal forest sites).

## 7 Towards understanding and quantifying the PyC cycle in boreal regions

### 7.1 How much PyC is produced in boreal regions?

Kuhlbusch and Crutzen (1995) estimated annual release of 90–180 Tg C as CO<sub>2</sub>-C from boreal and temperate fires. Using their BC/CO<sub>2</sub>-C ratio of 5–7% for boreal and temperate forest fires gives a range of 4.6–12.6 Tg BC y<sup>-1</sup>. Lynch et al. (2004) calculated fuel consumption and charcoal production for the boreal regions of Canada and Alaska for 1959–1995, based on 2% conversion of fuel mass to charcoal mass (Sect. 4.1.1). For Canada, fuel consumption was 46.86 Tg y<sup>-1</sup>, resulting in 0.94 Tg charcoal annually. For Alaska, fuel consumption was 8.51 Tg y<sup>-1</sup>, corresponding to 0.17 Tg charcoal. Assuming charcoal C concentration of 700 g C kg<sup>-1</sup> gives 0.66 Tg charcoal C for Canada and 0.12 Tg charcoal C for Alaska, totaling production of 0.78 Tg C y<sup>-1</sup> as charcoal particles that were airborne at some point during the fire.

Comparison is difficult because of the different methods and approaches. Kuhlbusch and Crutzen (1995) define BC as C remaining after pre-extraction and chemical oxidation. It would be expected that production of this oxidation-resistant BC fraction would be lower than conversion to C as visually-determined char. However, the 5–7% ratio of BC/CO<sub>2</sub>-C corresponds to the upper range of char C yield (Table 1). On the other hand, the 2% mass conversion reported by Lynch et al. (2004) is probably low, as it only includes charcoal particles collected in surface traps.

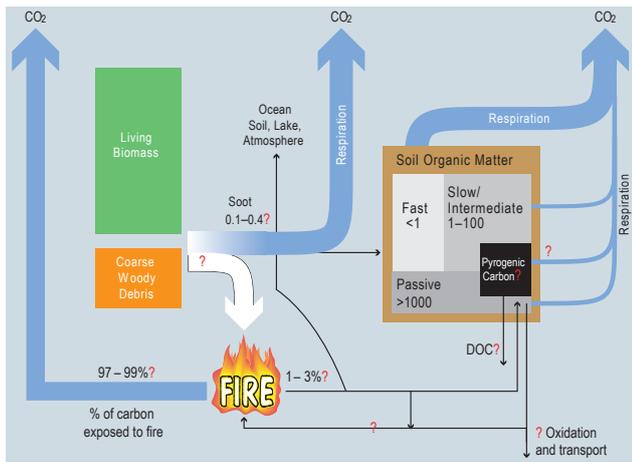
Kasischke et al. (2005) recently modeled boreal fire emissions for 1992, and 1995–2003, including detailed con-

sideration of flaming vs. smouldering combustion stages, and extent of forest floor consumption. For the whole high Northern Hemisphere (HNH), emissions were 162.9, 225.8 and 265.5 Tg C y<sup>-1</sup> for low-, moderate- and high-severity fire scenarios, respectively, based on depth of forest floor consumption. For Canada, the corresponding emissions were 35.3, 58.2 and 64.1 Tg C y<sup>-1</sup>. Combining the emissions range from Kasischke et al. (2005), with a general estimate of 90% conversion of C to CO<sub>2</sub> and 5–7% BC/CO<sub>2</sub>-C (Kuhlbusch and Crutzen, 1995), results in 7.3–16.7 Tg BC y<sup>-1</sup> from fires in the HNH, and 1.6 to 4.0 Tg C y<sup>-1</sup> for Canada. Using the more conservative 46.86 Tg estimate of annual boreal fuel consumption in Canada from Lynch et al. (2004), and assuming 500 g C kg<sup>-1</sup> in fuel, 90% conversion of C to CO<sub>2</sub>, and 5–7% BC/CO<sub>2</sub>-C results in 1.2 to 1.6 Tg BC y<sup>-1</sup>. This is in the low range predicted by Kasischke et al. (2005), but higher than the 0.66 Tg charcoal C calculated above, using 2% conversion of mass to charcoal. This is mainly due to higher consumption of forest floor in the work of Kasischke et al. (2005), especially by smouldering combustion.

Further refinements of these estimates are really beyond the scope of this review, and our expertise. These preliminary estimates, however, provide a starting point to consider the significance of BC as a component of the very stable soil C pool. Recently modeled estimates of soil C for north of 50 degrees (White et al., 2005) were 514 Pg C for forests and peatlands and 26 Pg C for grasslands, plus another 230 Pg C for tundra, totaling 870 Pg C. Bhatti et al. (2003) report 207 Pg C in boreal forest soil and detritus plus 415 Pg C for peat, totaling 622 Pg C. For Canada, the amounts were 65 Pg C in forest soil and detritus, and 113 Pg C in peat. Boreal production of the order of 7 to 17 Tg BC y<sup>-1</sup> is therefore a small input to some global 600 Pg C in boreal forest, peatland and grassland soils. However, much of the soil C in boreal regions is in poorly-decomposed forest floor and peat, protected from rapid decomposition mainly by environmental conditions of cold, waterlogging or permafrost (e.g., Preston et al., 2006; Harden et al., 1997). Future predictions of warmer temperatures, lower precipitation, loss of permafrost, and increased fire could enhance soil and detrital C loss, and increase the relative importance of the BC sink. It would also be useful to consider annual boreal BC production in relation to detrital inputs, in particular, that proportion of detrital C transferred to more stable soil pools.

### 7.2 How do fire, charcoal and vegetation influence boreal forest soil function?

In addition to the general effects of fire on SOM discussed earlier, there are interacting effects of fire, charcoal and vegetation in boreal forests. In some boreal ecosystems, stands that have not experienced fire for many years develop thick forest floor derived from feathermoss (mainly *Pleurozium schreberi*); over time there is increasing cover of ericaceous



**Fig. 7.** A preliminary concept for pools and fluxes of PyC in boreal forests.

plants, higher concentrations of forest floor phenolics and tannins, and lower N mineralization and nutrient availability, with N increasingly sequestered in poorly-available organic forms. Ericaceous species are better able to utilize organic N (Read et al., 2004; Treseder et al., 2004), and late-successional increase in N-fixation by feathermoss in association with cyanobacteria may mainly benefit ground vegetation rather than trees (Zackrisson et al., 2004). Decomposition is further impeded by lower growing-season temperatures in the thick feathermoss layer, and sometimes by excessive moisture, with development of impermeable layers or sphagnum growth and incipient peat profile development. Fire consumes the insulating moss layer, producing warmer surface soil temperatures, and increasing the depth of the active layer in permafrost-affected soils. The ash from forest floor and biomass provides nutrients and increases pH. Reduction of competition and allelopathy from ericaceous plants improves germination and growth of tree seedlings. These general concepts of the role of fire in ecosystem function have been developed through many studies, notably of black spruce in North America (Richter et al., 2000; Kasischke and Johnstone, 2005), and Norway spruce (*Picea abies* (L.) Karst.) and Scots pine in Scandinavia (DeLuca et al., 2002; Zackrisson et al., 1996, 2004). A similar trajectory of ecosystem development after fire was found for conifer forests in Montana (MacKenzie et al., 2004b, 2006).

Nitrogen losses from fire are highly variable and soil N may even increase from inputs of canopy necromass (Dryness et al., 1989; Harden et al., 2004). As discussed earlier, fire generally reduces the biological availability of organic N. However, thermal ammonification of organic N, increased microbial activity after reduction of thick forest floor, and inputs of freshly killed litter may result in increased availability of  $\text{NH}_4^+$  for 2–5 y (Choromanska and DeLuca, 2002).

In addition to direct effects of fire on forest soils and vegetation succession, Zackrisson et al. (1996) proposed that charcoal in boreal forests may itself influence microbial activity and nutrient cycling in soils. This mainly derives from its porous structure that can sorb organic molecules and provide microbial habitat (Harvey et al., 1976; Pietikäinen et al., 2000; Hamer et al., 2004). Charcoal produced from laboratory heating of twigs and stems adsorbed phenolics and reduced their phytotoxic effects on germination (Zackrisson et al., 1996; Keech et al., 2005), and increased growth of birch (*Betula pendula*) seedlings in pots (Wardle et al., 1998). However studies using activated carbon (Wallstedt et al., 2002; Naydenov et al., 2006) produced less clear benefits to seedling germination and growth. Increased nitrification was found with addition of wildfire-produced charcoal (DeLuca et al., 2006) and with activated carbon, although results for field studies were weaker than for laboratory incubations (DeLuca et al., 2002; Berglund et al., 2004). This is likely because charcoal addition is not a complete surrogate for the effects of fire on soil, and also, activated charcoal has different physical and chemical characteristics, mainly much higher surface area than wildfire- or laboratory-produced chars (Brown et al., 2006; Hille and den Ouden, 2005). It also appears that the sorptive power of wildfire-produced charcoal persists up to around 100 y (Zackrisson et al., 1996).

Apart from these specific studies of boreal and temperate forest soils, charcoal amendment has been associated with general improvement and sustainability of soil fertility in fire-prone native grassland sites in the North American Great Plains (Glaser and Amelung, 2003), and from charcoal amendment of tropical soils (Glaser et al., 2000, 2001, 2002; Topoliantz et al., 2005). While studies thus far support a positive influence of charcoal on boreal forest soils, more extensive studies are required to test its substantive consequences in the field, and especially to disentangle the direct effects of charcoal from those mainly resulting from postfire effects on soil temperature and moisture, and on plant succession.

### 7.3 The boreal PyC cycle – filling the knowledge gaps

Figure 7 shows our initial view of the BC cycle, on a C basis, with many question-marks. Fuel conversion to solid char in forest fires is probably in the range of 1–3% on a C basis, although higher values around 8–10% may be found where there are large stocks of coarse woody debris. Conversion to volatile soot is much lower, around 0.1–0.4% of fuel C, and deposition data are lacking. The solid char may be consumed in a subsequent fire, or slowly lost by photochemical, chemical and biological oxidation, whose rates and mechanisms are poorly known. Partially degraded and modified BC structures are likely to contribute to DOC, and to C deposited in ocean sediments. As part of SOM, the more labile char may turn over within tens or hundreds of years, whereas the less degradable and better-protected PyC may require several

millenia. The persistence of char and BC is affected by similar factors as other forms of SOM. First, its recalcitrance to oxidative degradation increases with increasingly condensed polyaromatic structures with lower H/C and O/C ratios, and in particular with increasing soot content (Elmquist et al., 2006). Second, it appears that BC can become stabilized by association with mineral particles, and third, persistence is enhanced by colder and less-oxic conditions, so that BC is well-preserved in peat bogs and sediments. For boreal regions, there are essentially no direct field measurements of the turnover time or rates of PyC loss by chemical, biological, thermal or photochemical oxidation, or quantitative studies of its movement. These are obviously key requirements for modeling the PyC cycle in boreal regions, especially its role as a long-term sink of stable soil C. However, the data gathered from other regions on PyC loss and transformation should provide reasonable expectations of its behaviour for boreal regions.

While analytical problems persist, and methodologies for BC are still under intense development and discussion, this should not be an impediment to acquiring some basic information on PyC in boreal regions, especially as required for C budget modelling. Techniques for visual assessment of char are well-established, but there appear to be no studies with a complete accounting of char in any boreal forest site, and we found no quantitative information on BC storage in boreal peatlands. Integrated projects and interdisciplinary approaches are required, so that, for example, measurements of PyC production could be integrated into experimental fire studies such as the ICFME (Stocks et al., 2004) and FIRE BEAR (Samsonov et al., 2005), and the painstaking efforts to assess char abundance in peat cores could also be used to develop estimates of area-based char stocks. Increased application of  $^{14}\text{C}$  dating is also necessary to assess the turnover time of different fractions of PyC. Char height on stems has been used to predict tree mortality after fire (Hély et al., 2003), and there are assessments of stocks of downed coarse woody debris and snags in Canadian boreal regions (Lee, 1998; Greif and Archibold, 2000; Pedlar et al., 2002), but only one study (Manies et al., 2005) has linked fire-killed wood (but not wood-associated char) to soil C storage.

Analysis of BC by thermal or chemical oxidation resistance, BPCA production or photochemical oxidation plus NMR is expensive and time-consuming, and it is unlikely that any one method will prove suitable for all samples. Valuable information has come from the BC comparative analysis ring trial (Hammes et al., 2006b<sup>1</sup>). Urgently needed are rapid and inexpensive analytical tools capable to analyze large numbers of char and BC produced in boreal fires. It would also be useful to develop more capacity for routine analysis of H concentration as well as C, as the H/C ratio is a good indicator of aromatic condensation. Radiocarbon dating of char fragments and soil fractions is essential to understanding the long-term sink potential of BC, including its contribution to marine sediments.

Efforts should be made to acquire more field data on production and stocks of visually-defined char in boreal regions, while analysing a subset of samples for BC by several methods. This approach should allow development of a two-component model for PyC, and a conversion factor to estimate what fraction of visually-determined char has the more recalcitrant structures that will likely contribute to a long-lasting BC sink. For mineral soils, char may be less visible and chemical and spectroscopic methods essential to assess adequately the BC contribution to SOM. Information on the atmospheric component is also inadequate, and requires measurement and tracking of volatile C emission from fires, and monitoring of atmospheric BC concentrations and deposition rates.

Despite the impact of wildfire in boreal regions, there has been little study of stocks, production, characteristics or longevity of BC in boreal forests and even less for peatlands. We still lack much basic information required to assess the role of BC as a C sink in boreal forest soils and Arctic sediments, or whether it substantively influences soil processes by sorption of phenolics and provision of microbial habitat. It seems equally urgent to quantify boreal soot production, transport, and potential for atmospheric warming.

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