Biogeochemistry (2007) 85:91–118
DOI 10.1007/s10533-007-9104-4

ORIGINAL PAPER

How does fire affect the nature and stability of soil organic nitrogen and carbon? A review

Heike Knicker

Received: 6 February 2006 / Accepted: 3 November 2006 / Published online: 15 March 2007

Abstract After vegetation fires considerable amounts of severely or partly charred necromass (referred to here as char) are incorporated into the soil, with long-term consequences for soil C and N dynamics and thus N availability for primary production and C and N transport within the soil column. Considering results reported in the pyrolysis literature in combination with those obtained from controlled charring of plant material and soil organic matter (SOM), it has become clear that common models claiming char as a graphite-like material composed mainly of highly condensed polyaromatic clusters may be oversimplified. Instead, I suggest a concept in which char is a heterogeneous mixture of heat-altered biopolymers with domains of relatively small polyaromatic clusters, but considerable substitution with N, O and S functional groups. Such a concept allows fast oxidation facilitating both microbial attack and dissolution. Although, char is commonly believed to degrade more slowly than litter, over the long term and under oxic conditions, char may degrade to an extent that it becomes indistinguishable from naturally formed SOM. Oxygen depletion or environments with low microbial activity may be necessary for char to survive without major chemical alteration and in considerable amounts for millennia or longer.

Keywords Pyrolysis · Charcoal · Black carbon · Black nitrogen · Aromatic · Alkyl

Introduction

Soil organic matter (SOM) is highly heterogeneous. For modeling purpose, it can be divided into a young or active fraction that responds to recent environmental changes (i.e. management practices or reforestation), an intermediate pool with turnover times of years and decades, and a recalcitrant or passive pool with at least several 100–1,000 years of residence time (Smith et al. 1997). Both quality and quantity of these pools are affected by vegetation fires. Burning of biomass releases from 2×10^{15} g to 6×10^{15} g carbon per year as CO_2 (Crutzen and Andreae 1990; Wittenberg et al. 1998), a part of which returns to the biosphere via rain and photosynthesis (Johnson and Curtis 2001). Further, between 50×10^{12} g and 270×10^{12} g of so-called ''Black Carbon'' (BC) are annually produced by partial combustion of biomass (Kuhlbusch and Crutzen 1995). Because of its high chemical resistance and its survival potential in sediments and some soils (Hopkins et al. 1990; Masiello and Druffel 1998), char is often assumed to reside in

---

H. Knicker (✉)
Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising-Weihenstephan, Germany
e-mail: knicker@wzw.tum.de

the passive SOM pool (Kuhlbusch 1995; Kuhlbusch and Crutzen 1995; Schmidt and Noack 2000) and, thus, to represent an important global sink for C (Kuhlbusch 1998). Fire has complex effects on size and quality of many ecosystem C pools. These effects range from reduction or elimination of aboveground and topsoil biomass, with a subsequent shift in plant and microbial populations, to alterations of physical and chemical properties of the soil. These changes can have long-term effects on microbiologically and biochemically mediated processes and therefore can alter the humification processes. Here, humification describes the formation of SOM with high recalcitrance and involves degradation and modification of organic precursors but also the mechanisms that are responsible for the stabilization of the respective products.

Soil organic matter transformation and stabilization by fire continue to receive attention (Neary et al. 1999; González-Pérez et al. 2004; Certini 2005), but reports on SOM alteration due to fire often lead to divergent conclusions, which makes it difficult to postulate a generalized model about the lasting effects of fires on SOM. Thus, the intention of the present review is to synthesize present literature and to extract a possible common pattern describing the impact of fire on SOM composition and stabilization.

Ecological importance of vegetation fires past and present

Over geological times natural vegetation fires have shaped regional ecology (Jones and Chaloner 1991; Bird 1995; Schmidt and Noack 2000). Even the global soot layer at the boundary between the Cretaceous and Tertiary periods has been attributed to global wildfire caused by a meteorite impact (Wolbach et al. 1988; Venkatesan and Dahl 1989), which was estimated to have burned about 25% of the worldwide aboveground biomass (Ivany and Salawitch 1993). With the development and the spread of hominids using fire to gain land suitable for hunting and agriculture, the importance of anthropogenic fires for changing environments increased continuously (Caldararo 2002; Carcaillet et al. 2002). Although grasslands, savannahs and fire-adapted vegetation existed long before the Pleistocene, humans promoted the expansion of savannahs by burning the forest margin and by depleting the populations of large herbivores that had previously helped reduce fuel loads. The increasing human influence during the Neolithic age supported the expansion of evergreen sclerophyllous trees in the Mediterranean basin (Willcox 1999) and of conifers in cold temperate forests (Björkman and Bradshaw 1996). Currently, approximately 10–15 × 10^6 ha of boreal and temperate forest, 20–40 × 10^6 ha of tropical forests, and up to 500 × 10^6 ha of tropical and subtropical savannahs, woodlands and open forests are burnt every year (Goldammer 1993), mostly due to human activity (90–97% in USA, Siberia and Mexico) (Zhukov 1976; Caldararo 2002).

Fire severity spectrum and temperature regime

The impact of fire on SOM depends largely on the chemical and physical properties of the soil, the nature of the biological communities of the respective ecosystem, and the severity of the fire. Prescribed fires are controlled and commonly initiated at moderate soil moisture levels. Generally they show low severity. Wildfires, on the other hand, occur uncontrolled in the presence of an abundant and dry fuel load and can be very severe. However, due to high variation in local factors, their severity is highly variable (Kutiel et al. 1995).

Fire intensity, an integral part of fire severity, refers to the rate at which a fire produces thermal energy. Resulting temperatures can range from 50°C to 1,500°C and heat release can vary between 2.1×10^3J kg^{-1} and 2.1×10^6 J kg^{-1} of fuel (Neary et al. 1999). Rates of fire spread can vary from 0.5 m week^{-1} in smoldering peat fires to as much as 7 km h^{-1}. Fast moving fires on grass may be intense in terms of energy release per unit area, but do not transfer the same amounts of heat to mineral soil or soil organisms as do slow-moving fires in moderate to heavy fuels (Rollins et al. 1993).

Threat of wildfire is exacerbated by long warm and dry seasons. The danger is more pronounced if the previous season was highly productive, resulting in a high fuel load. At dry and sandy soils, low water supply fosters flammability. Such sites are dominated by surface fires, consuming mostly only the litter layer and the above ground vegetation. Here, the heat radiation commonly affects only the upper 30–40 mm of the topsoil. Depending on the thickness of their bark, increasing fire intensity results in the death of trees. To develop a crown fire, fuel load must be large enough for the flames to reach the canopy.

Draining peat bogs and swamps can increase fire frequency as dried peat is easily ignited and provides a large fuel load. In contrast to surface fires in which the rooting mats are usually not attacked, peat fires can burn down several meters below the surface and can smolder indefinitely. They are even capable of surviving several centimeters of rainfall and can destroy the rooting systems of most plant species. The loss of organic material due to peat burning can be so dramatic that the peat surface sinks noticeably with respect to its surroundings (Haslam et al. 1998; Rollins et al. 1993).

In fire-prone scrublands temperatures between 700°C und 1,000°C were observed (Rundel 1983). During forest fires, maximum ground temperatures are typically in the range of 200–300°C. On the other hand, under heavy fuels like slash, instantaneous temperatures can exceed 1,500°C, but the measured soil-surface temperatures at such sites peak at only 500–700°C (Neary et al. 1999 and references therein). Those temperatures are in agreement with temperatures found in organic layers during experimental burns (Savage 1974; Raison 1979; Campbell et al. 1995). Fires in grassland with fuel loadings of <1 Mg ha^{-1} usually have ground-level temperatures of <25°C although higher instantaneous temperatures have been measured (Raison 1979). With low-severity soil heating, mineral soil temperatures typically do not exceed 100°C at the surface and 50°C at 5-cm depth (Campbell et al. 1995). For example, during a grass fire in Papua and New Guinea (Scotter 1970) a rapid increase of the surface temperature to 300°C was observed, but temperatures above 100°C lasted only 80 s. At 2-cm depth the temperature did not exceed 35°C and at 4 cm no change in temperature was observed. Similar results are reported by Raison (1979). The degree of heating at any soil depth depends on factors such as intensity and duration of heat transfer, heat conductivity of the mineral phase, soil porosity, and soil moisture. In general, in dry soils below-ground temperatures will rise very slowly because they are very good insulators (DeBano et al. 1998). Heat is transported faster and penetrates deeper in moist soils than in dry soils. However, because of evaporation, temperatures do not exceed 95°C until the water content drops below 0.02 m^3 m^{-3} (Campbell et al. 1995). Due to a higher content of air-filled coarse pores, sandy soils are better insulated against heat transfer than loams.

Temperatures between 40°C and 70°C are high enough to start biological tissue disintegration. Between 48°C and 54°C, roots can be desiccated or killed. Between 70°C and 90°C seed mortality begins, and mortality of microbes occurs between 50°C and 121°C (Hernández et al. 1997; Neary et al. 1999). Although considerable C can be lost at lower temperatures, organic matter is commonly volatilized at temperatures between 200°C and 315°C (Lide 2004). Between 130°C and 190°C, lignin and hemicellulose begin to degrade (Chandler et al. 1983). Above 200°C the carbonization processes starts (Freitas et al. 1999). Under oxic conditions at around 460°C almost all unprotected SOM is combusted. At 200°C nitrogen (N) starts to volatilize and above 500°C half of the N in organic matter is lost to the atmosphere. Temperatures of more than 760°C are needed to vaporize potassium (K) and phosphorus (P). Sulfur (S) and sodium (Na) volatilize above 800°C and 860°C, whereas magnesium (Mg) and calcium (Ca) are lost only at temperatures above 1107°C and 1240°C, respectively (Lide 2004).

Impact of fire on soil properties

Liming effect

The physical and chemical properties and processes of soils have direct effects on biomass productivity and SOM dynamics. Thus, their alteration during fire can substantially affect SOM quality and quantity both in the short and the long term.

After combustion of vegetation and organic horizons during a fire, nutrient-rich ash remains, the fertilizing effect of which has been known since the beginning of agriculture (Pyne 2001). The increase in pH, the so-called liming effect, has a positive impact on the biological recovery of soils after fire (Baath and Arnebrant 1994; Chambers and Attiwill 1994). However, significant pH increases occur only at high temperatures (>450°C). In acid top soils, increases of up to three pH units were observed immediately after burning (Ulery 1993). This rise can be attributed to the accumulation of K- and Na-hydroxides, Mg- and Ca-carbonates, but also to destruction of acid groups in the organic matter (Giovannini et al. 1990; Kutiel and Inbar 1993; Dumontet et al. 1996). The latter effect was shown to persist even 3 years after burning and to maintain a moderately alkaline soil pH. The other mineral elements are eventually solubilized and leached during the wet season resulting in concentrations that can be less than levels observed for unburned control soils. Carbonates resist temperatures up to 1,000°C, thus fire-induced increase in pH is negligible in carbonate-rich soils.

The release of inorganic ions from combusted organic matter leads to a considerable increase in electrical conductivity of the soil solution (Kutiel and Inbar 1993; Hernández et al. 1997), but soil ion exchange capacity was found to decrease due to loss of adsorption sites with destruction of SOM (Badìa and Martí 2003).

Nutrient availability

The effect of burning on soil N presents a paradox that has been debated for years (Neary et al. 1999). Beside N losses to the atmosphere, biological and non-biological processes after and during low-intensity burning transform organic N forms into more available ammonium and nitrate N and dissolved organic matter (DOM) (Prieto-Fernández et al. 2004). Whereas ammonium is a direct product during biomass burning, nitrate requires nitrification. In undisturbed soils vegetation competes strongly with nitrifiers for NH_4^+. Destruction of the vegetation and combustion of allelopathic compounds, such as terpenes and phenolics, increases nitrifier abundance and thus the transformation of NH_4^+ to NO_3^- (Andersson et al. 2004). However, without any plant uptake, nitrate will be lost from the ecosystem either by denitrification or leaching. Without prompt vegetation regrowth, this N loss can affect plant succession and productivity and thus litter production. The latter will have a direct impact on size and quality of the active SOM pool.

The main P pool is in the soil mineral matter (94–98%), but organic P from litter is more readily available to plants, and cycling is primarily through the organic P pool. Burning converts the organic P pool to orthophosphate (Cade-Menun et al. 2000), the only form that is available to plants. On the other hand, removal of the vegetation by combustion depletes the above-ground P pool faster than it can be replaced by mineral weathering.

Recovery of soil nutrient levels can be very slow; even 35 years after a wildfire, N and P concentrations h ad not recovered to levels found in a control stand not subjected to burning for the last 300 years (Klopatek 1987).

Accumulation of hydrophobic compounds

After fire, a discrete layer with enhanced water repellency is typically found on the soil surface or a few centimeters below and parallel to the mineral soil surface (DeBano 2000). This layer is enriched in hydrophobic organic compounds. Although such compounds occur in fire-unaffected soils, their abundance is increased by fire (Almendros et al. 1992; Fernandez et al. 2004; Knicker et al. 2005a) due to greater stability of lipids and lignin derivatives but also due to the neoformation of aromatic polymers (Almendros et al. 2003). Additionally, burning of the litter layer on the soil surfaces vaporizes organic substances, which move downwards along steep temperature gradients. Reaching cooler areas they condense (Savage 1974). In laboratory heating experiments, the water-repellent layer moved down 10 mm after low-intensity fire and as much as 50 mm after high-intensity fire (Robichaud and Hungerford 2000). This downward movement may continue even after a fire has moved past an area, because the continuing heat transfer through the profile re-volatilizes some hydrophobic substances (DeBano 2000). Water repellency can also be intensified by heating the organic particles to an extent that they coat and become chemically bonded to mineral soil particles (Giovannini et al. 1983).

Little change in water repellency occurs when soils are heated less than 175°C (DeBano 2000) and the hydrophobic layer is destroyed at temperatures between 280°C and 400°C (Savage 1974; DeBano et al. 1977). However, depending on fire behavior and severity, and on temperature gradients in the soil, the depth and thickness of the water repellent layer produced during fire can vary widely. Also soil properties such as SOM content (Doerr et al. 1998), soil texture (Giovannini et al. 1990; Huffman et al. 2001), soil water content (Robichaud and Hungerford 2000; MacDonald and Huffman 2004) and the general soil–plant environment affect their formation. Their presence beneath a thin wettable soil layer affects infiltration of water much as would a coarse-textured layer.

Concerning the persistence of water-repellent soil layers, Huffman et al. (2001) observed a weakening 3 months after a fire. In other studies, 2 years after clear-cut and slash burning there was no evidence of fire-induced water repellency (Henderson and Golding 1983). In ponderosa pine forests, water repellency progressively weakened and was statistically undetectable 1 year after burning (MacDonald and Huffman 2004).

Impact on soil biology and enzyme activity

Size and activity of microbial biomass in soils are other parameters affecting the SOM turnover rate. Since soil microbial biomass is concentrated in the surface 2.5 cm and declines rapidly with depth, the region of highest biological activity experiences the highest temperature during fire. The immediate effect of fire on soil microorganisms is a reduction of their biomass, with fungi being more affected than bacteria (Pietikäinen and Fritze 1995; Dumontet et al. 1996). In extreme cases, the topsoil undergoes complete sterilization of metabolically active organisms, although inactive forms may survive. Thus, formation of spores and microbial adaptation in response to prior drought stress increase microbial survival after fire. Heating soil to temperatures to 600°C reduced the microbial C and N to amounts undetectable with the fumigation–extraction method regardless of the duration of the fire (Diaz-Raviña et al. 1992). Grasso et al. (1996) found no significant difference in microbial population before and immediately after heating a soil at 450°C for 3 min and related this to the relatively low temperature reached in the sample. Moisture intensified the heat-induced microbial mortality, possibly due to faster heat transfer. Also a history of repeated fire can diminish biomass C relative to soils that have been only heated once (Choromanska and DeLuca 2002).

Toxic compounds, such as polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polyaromatic hydrocarbons (PAH) are redistributed within soil after a fire (Kim et al. 2003). Such compounds can also cause mortality of soil organisms, whose survival and recolonization may then be further altered through reduction and modification of SOM as well as changed physical and chemical soil properties.

In agreement with other studies, abundance of heterotrophic bacteria, including spore formers, increased after fire (Raison 1979; Vázquez et al. 1993). The magnitude of the response appeared to be related to the amount of litter remaining after the fire. Ten days after moderate burning, Grasso et al. (1996) found that the aerobic microbial population had increased by a factor of 2.7 with respect to a control soil and explained this by the deposition of ash and the resulting nutrient flush to the soil. A nutrient flush was also noticed by Almendros et al. (1990) and Fernández et al. (1997), which can explain the increased respiration rates directly after burning. However, by 30 days after the fire, bacterial numbers had decreased considerably (Grasso et al. 1996), possibly because of leaching of the ash to lower horizons.

Soil temperatures above 120°C increase levels of soluble sugars, which has been attributed to the destruction of microbial biomass (Choromanska and DeLuca 2002). Diaz-Raviña et al. (1992)

showed that 70% of the C mineralized during heating originated from microbial tissues. However, some of the released compounds derive from destroyed non-microbial constituents (Fernández et al. 1997) such as cellulose, since heat increases SOM and litter decomposability. Four weeks after an intense fire, there was no significant difference in biomass C in a surface soil (0–5 cm) relative to a control soil. However, after 1 or 11 years of recovery, biomass C and N had decreased (Dumontet et al. 1996), possibly due to consumption of released nutrients. Similarly, soil heated at 160°C showed considerable recovery of the microbial biomass after 1 month, whereas during the following 6 months a steady decline of the microbial biomass was noted. In some soils, such alterations in the mineralization indices persisted at least 2 years after wildfire (Fernández et al. 1999). In other studies, it took microbial and fungal biomass at least 10 years after fire to recover to values reported for unburned soils in the literature (Fritze et al. 1993). To hasten reestablishment of microbial populations and soil quality after fire, organic amendments in the form of poultry manure combined with planting of a cover crop have been suggested (Villar et al. 2004).

Fire often results in effects on SOM and the microbial community that can be detected by quantifying enzyme activity. For example, acid phosphatase activity decreased after fire, a decrease still detectable 2 years later (Hernández et al. 1997; Boerner et al. 2000; 2005). It was concluded that the effect of fire on this enzyme was, to some extent, caused by a change in substrate availability. Intense fires and multiple fires also decreased *β-glucosidase* activity and enhanced *phenol oxidase* activity (Hernández et al. 1997; Boerner and Brinkman 2003). The activity of *urease* and *N-α-benzoyl-L-argininamide hydrolysing protease*, both of which are involved in the breakdown of C–N bonds in urea and polypeptides, was reduced by wildfire (Hernández et al. 1997). These changes in enzyme activity, in particular the decreases, can partly be explained by thermal enzyme denaturation or to inactivation of enzymes associated with soil colloids, but they may also result from changes in the composition of soil microflora and SOM.

Mycorrhizae play an important role in ecosystem function. Studies have shown that this symbiosis decreases with increasing levels of stress. However, fire has produced variable effects (Neary et al. 1999). Klopatek et al. (1988) found that levels of vesicular-arbuscular mycorrhizae propagules (VAM) were reduced moderately at soil temperatures <50°C, significantly at 50–60°C, and severely when temperatures reached 80–90°C. At 94°C there was a total loss of VAM. However, other studies show a temporary increase in mycorrhizal activity in a tall grass prairie ecosystem after burning (Bentivenga and Hetrick 1991). It was suggested that the response of mycorrhizal activity to fire can be attributed to changes in the host plant rather than to a direct effect of fire (Neary et al. 1999), because the fire temperatures are usually not high enough to kill all the plants, thereby leaving a large residual mycorrhizal pool in the soil and in the plant roots. Input of char after burning can stimulate the establishment and activity of ectomycorrhizae (Harvey et al. 1976), and char strongly sorbs phenols, which can inhibit mycorrhizal germination and growth. Other studies show lower microbial populations and lower activity in soils under tropical deciduous forest vegetation after fire and in unburned soils amended with ash (García-Oliva et al. 1999).

Impact of fire on SOM content

The effect of fire on SOM depends on fire intensity, vegetation type, and fuel load as well as soil texture and even slope. Intense fire can lead to complete destruction of the organic layer and SOM in the topsoil (Fernández et al. 1997; Haslam et al. 1998). After moderate and prescribed wildfire, effects are minor and organic C and N sometimes even increase due to input of partly charred material or litter from decaying trees (Almendros et al. 1988; 1990; Knicker et al. 2005a)

Burning grasslands to remove dead and dying vegetation often results in grass growth earlier in the growing season, which increases dry-matter production (Ojima et al. 1994). On the other hand, in some grassland landscapes that burn frequently, a decline of SOM content with time was reported in particular for the upper few centimeter (Bird et al. 2000; Parker et al. 2001; Fynn et al. 2003). Comparing nineteen sites across South Africa, the SOM contents in the upper cm of unburned soils were two to three times those in frequently burned plots (Mill and Fey 2004). Taking composite 0–10-cm samples, differences were less dramatic. Composite sampling can dilute the properties, of the fire-affected layer and thereby confound and obscure effects of fire on soils.

The decline in SOM as a result of frequent burning is attributable to several processes operating simultaneously. Intense fires combust the SOM in the upper few cm of the soil, but such fires also combust aboveground biomass and leaf litter reducing organic matter inputs to the soil. The removal of plant cover increases the temperature of the soil surface and the number of wetting and drying cycles, which may enhance microbial activity and thus rates of mineralization of the remaining SOM (Mill and Fey 2004). The increased alkalinity due to ash further solubilizes C, which can be removed by microbial degradation or by leaching. Plant root death, a further possible factor affecting SOM loss in burned plots, could either decrease mineralization if exudates inhibit microbial activity or increase mineralization if such compounds promote it. Lastly, loss of SOM with frequent burning was suggested to be a key factor promoting soil crusting in savannahs (Mill and Fey 2004), with important consequences for the water infiltration and erosion.

In another study fire was excluded from tropical savannahs for from 15 years to 20 years. Here, annual grasses were largely replaced by woody shrubs. Relative to shrubs and trees, grasses tend to have a shallow rooting system, which can contribute detritus to the upper soil after fire. Replacing grass by woody shrubs will reduce this input (Chen et al. 2005) and decrease SOM content, whereas the fire cycle causes vigorous grass re-growth and thus an increase in SOM (Ansley et al. 2002). However, such increases may only be observed in the upper soil horizons, because reduced tree cover tends to decrease recalcitrant soil C pools in the deeper horizons (Boutton et al. 1999). Accordingly, increased dead-root deposition in response to regular grassland burning can increase soil organic C (Ojima et al. 1994) although no increase was found at a depth of 10–20 cm (Dai et al. 2005).

The timing of burning can also greatly influence effects on SOM content. Whereas annual and biennial spring burnings seem not to affect organic C in the top 2-cm, fall and winter burning on an annual and biennial basis caused a decrease (Fynn et al. 2003). With spring burning, litter could be decomposed and incorporated into the soil in the previous winter by soil fauna. After fall and winter burning, on the other hand, the soil surface is left partly exposed over the dry winter period and some loss of surface soil and litter through wind erosion can occur.

Runoff and consequent sediment loss after fire varies considerably, both in space and time (Kutiel et al. 1995). Andreu et al. (2001) observed the highest soil losses over the first 4 months after a forest fire in Valencia, Spain. The extent of the erosion, however, depends on the time needed for recovery of the plant cover (Cerda et al. 1995) and the formation of new soil aggregates, both of which are related to microbial activity. In Mediterranean ecosystems microbial activity is greatest during winter and spring. Wild fires, on the other hand occur mostly during the dry and hot summer during which microbial activity is lowest. This leaves the post-fire soil almost unprotected during the following fall and winter during which most of the precipitation occurs (Andreu et al. 2001). Soil losses due to erosion, in particular of the topsoil, will decrease not only the remaining SOM content but also nutrient levels. Recovery of new vegetation and production of new litter will be delayed and consequently formation of new SOM will be inhibited. Both consequences have a positive feedback on soil erodability. In particular on steep slopes, such as in alpine regions, such processes can result in complete loss of mineral soil down to the bedrock.

Impact of fire on SOM quality

To elucidate the full impact of char input on SOM structure and properties, a good knowledge of its chemistry is crucial. Although several models describing char on a molecular level are reported in the literature (Schmidt and Noack 2000), a real understanding of the chemistry of char production during vegetation fires is still missing. In the following, an overview of the modes of production of common char constituents is given.

Cellulose and pectin

Much plant char derives from cellulose, which is built up of glucose units (Fig. 1a) and comprises 20–50% of plant dry mass. No major structural changes were detected after heating microcrystalline cellulose experimentally to 200°C although a weight loss of 10% was observed (Boon et al. 1994). However, little glucose was hydrolysable from the resulting char, due probably to production of complex glucans at such temperatures. Important compositional changes were observed above 270°C. New molecular structures, detected by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, were aliphatic C, phenol and/or furan C, aromatic C, and carbonyl C. Crystalline sugars were still detected but less ordered glucans also started to appear. Fourier-transformation infrared (FTIR) spectroscopy data confirmed this general finding. Pyrolysis mass spectrometry (PYMS) revealed a change from carbohydrate dominated char at 250°C to one with mainly phenols, furans and aromatic hydrocarbons at 310°C (Fig. 1b). Furan-like compounds are major products of cellulose pyrolysis at temperatures >300°C (Ralph and Hatfield 1991; Bassilakis et al. 2001). Boon et al. (1994) found evidence that with increasing temperature nonvolatile anyhdroglucose cores with glycolaldehyde side chains act as aldol-condensation sites for volatile enolic furans, glycolaldehydes, and other small compounds released inside the char. These small dissociation products act as the molecular glue for the larger nonvolatile residues, which form a frame polymer that grows by trapping small reactive pyrolysis products. They suggested that the polyaromatic structure formed at temperatures >250°C by reactions with radicals is composed of furanoids, hydroxyaromatics, unsaturated hydrocarbon side chains, and many carbonyl and carboxyl groups. With more severe heating, a disproportionation of the furan polymer occurs by loss of CO and CO_2 leading to a purely aromatic polymer. As with cellulose, furans, pyranones, anhydrosugars and 5-hydroxymethylfurfural were also the main components of chars produced by low-temperature pyrolysis (25–300°C) of D-glucose and sucrose (McGrath et al. 2003). No polycyclic aromatic hydrocarbons (PAHs) (Fig. 2) were detected in this temperature range, but they were formed upon more severe heating (300–600°C. Various two- to four-ring PAHs were subsequently released from the char into the gas phase. Addition of oxygen reduced PAH yields. PAH formation in the 400–600°C range was thought to occur via a Diels-Alder type reactions with subsequent transformation and rearrangement reactions leading to a more condensed PAH structure (McGrath et al. 2003).

Pectin (Fig. 1c), a water-soluble galacturonoglycan, constitutes approximately 10–15% of plant dry weight. Below 350°C the char yields from both oxidative and non-oxidative pyrolysis of pectin were the same and decreased with increasing temperature. Above 350°C, the yield leveled off to approximately 20% of the initial substrate in non-oxidative runs. Supplying oxygen, pectin was oxidized totally at 550°C (Sharma et al. 2001). The analysis of the volatile products showed that their composition changed with pyrolysis temperature from mainly furans, pyranones, anhydrosugars and 5-hydroxymethyl furfural (Fig. 1a, b) at low temperatures to phenol, catechol, and substituted phenols at high temperatures.

Analyzing pectin char by solid-state NMR, Sharma et al. (2001) showed that chemically, oxidized and non-oxidized chars were virtually identical. Weak resonances of non-pectin-C, attributed to aliphatic, O-aryl, aryl and carbonyl groups were observed at 200°C. Further heating resulted in depolymerization, which occurred at a lower temperature than for pure cellulose. At 350°C signals from galacturonic ring carbons nearly disappeared, whereas the contribution of

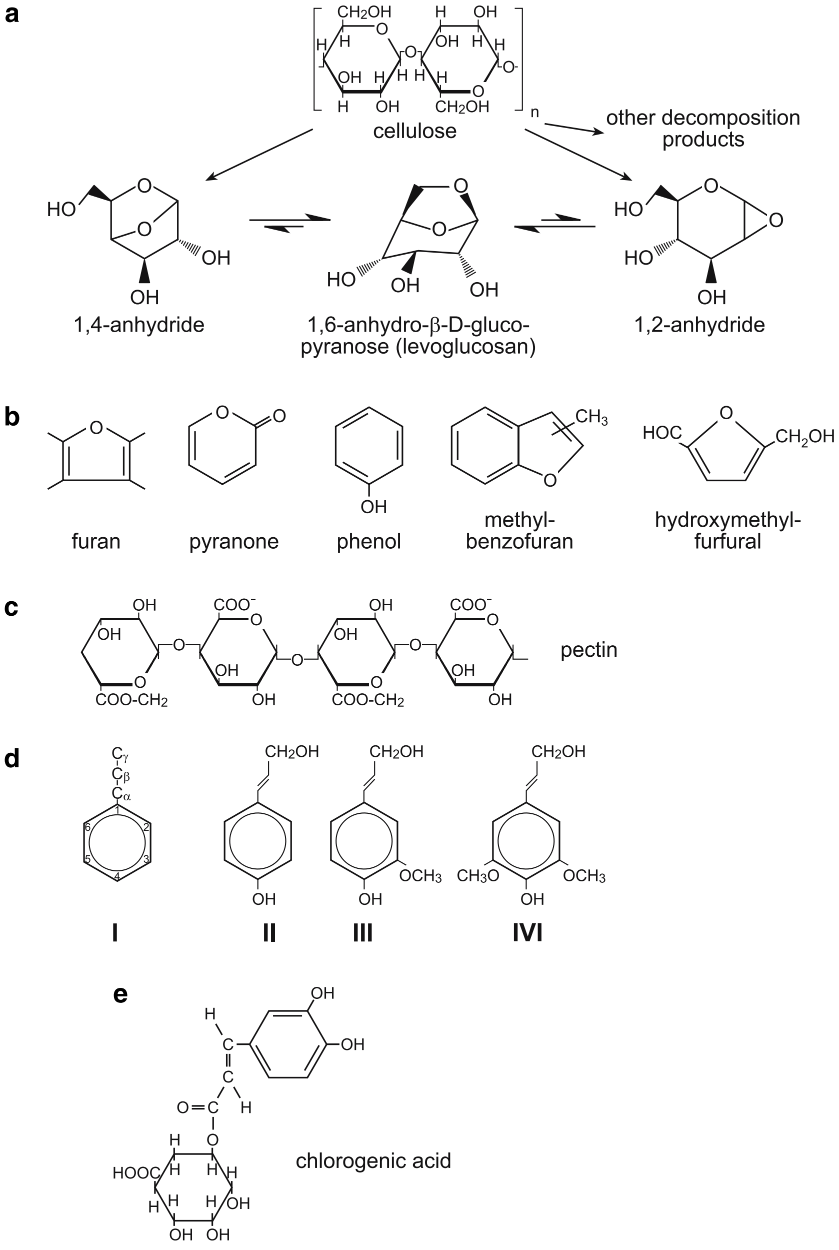

Fig. 1 (**a**) Chemical structure of cellulose and its alteration during charring (adapted from Elias et al. 2001). (**b**) Examples of products resulting from charring of cellulose. (**c**) Chemical structure of pectin. (**d**) I. Basic structure of a lignin monomer, II. p-Cumarylalcohol III. Confierylalcohol IV. Sinapylalcohol (**e**) Chlorogenic acid

aromatic C continuously increased. Concomitantly, O-aryl C showed a decrease. Only very small amounts of ketones and aliphatic moieties persisted at 550°C.

Lignin and chlorogenic acid

Lignin comprises between 20–40% of wood and 4% of grass material. The common monomeric units of this polymer are phenylpropanol (Fig. 1d), which are randomly linked together, mainly via ether bonds but also C–C bonds (Lüdemann and Nimz 1973). Heating lignin yields char and volatile products that are mainly substituted methoxyphenols. The highest yield is achieved at pyrolysis temperatures between 500°C and 600°C. Pyrolyzing pure lignin under anoxic conditions caused approximately 40% and

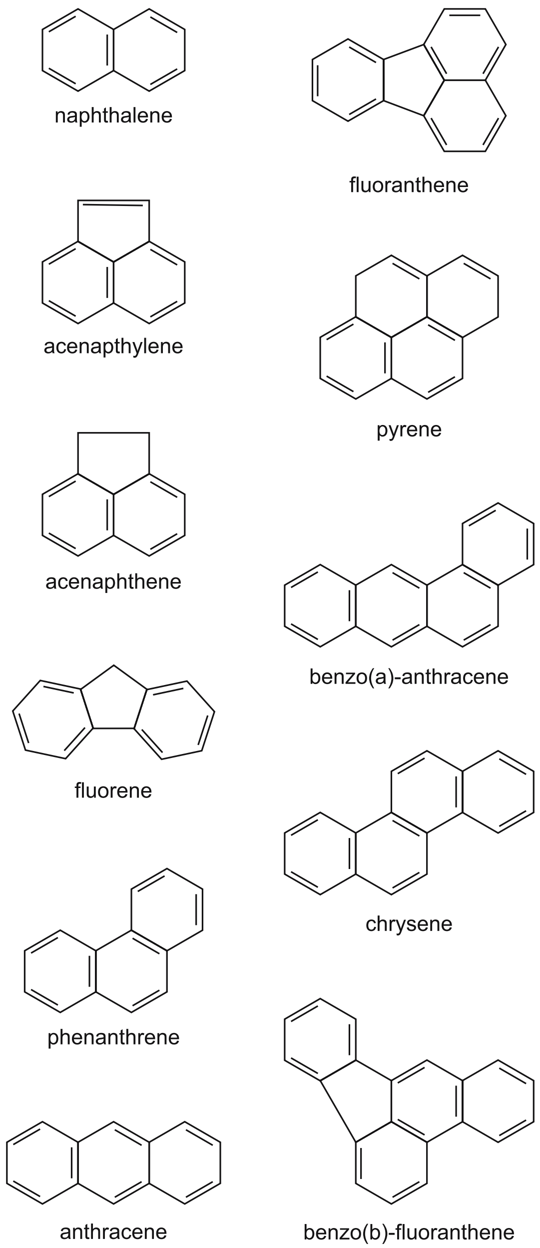

Fig. 2 Examples of polycyclic aromatic hydrocarbons (PAHs)

60% to be volatilized at 450°C and at 750°C (Sharma et al. 2004a). It was assumed that any condensation reactions among the volatile products, leading to the formation of coke were absent under such anoxic pyrolysis conditions. Repeating the experiment under oxic conditions led to similar char yields at temperatures up to 350°C, but at 550°C only 20% remained as char. Comparing the oxic and anoxic chars by infrared (IR) and solid-state ^{13}C NMR spectroscopy revealed similar qualitative alterations during pyrolysis. Elevating the temperature from 250°C to 400°C diminished phenolic C and alcoholic C yields. Concomitantly, the methoxyl C vanished upon heating the sample to 400°C. The O/C ratios declined and IR stretching, indicating aromatic hydrogen, increased. Both point towards removal of aromatic substitutions. Fused-ring systems seemed to be formed at about 400–500°C. New aromatic rings were produced neither during anoxic nor oxic degradation.

Summarizing the chemical alteration of lignin during heating, Sharma et al. (2004a) suggested that at low temperatures (<350°C) the predominant reaction is dehydration. Some decarboxylation occurs at higher temperatures but the aromatic rings still remain essentially intact. Their results indicate further that the extent of direct dehydrogenation or demethanation is small. Na and K enhanced the de-volatilization of lignin and the PAH formation but decreased char yield.

Preliminary work with chlorogenic acid (Fig. 1e) indicated that two- and three-ring PAHs were formed by secondary condensation reactions among the gas-phase pyrolysis products. Yields from such reactions exceeded those from lignin (Sharma and Hajaligol 2003), which is in agreement with a lower reactivity of lignin pyrolysis products. Also, the PAH yields were higher for chlorogenic acid than for lignin.

Proteins and amino acids

Proteins thermally decompose via systematic and random depolymerization reactions. One product class is cyclic dipeptides, which are known as diketopiperazines (Reeves and Francis 1998) (Fig. 3). Pyrolysis of polymerized amino acids at 285°C and subsequent analysis with matrix-assisted laser-desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS) of the char (Meetani et al. 2003) showed a mass loss of 18 Dalton (D) for polyphenylalanine and polyleucine that was not observed for polyproline. The loss of 18 D was attributed to dehydration, which can lead to the formation of cyclic

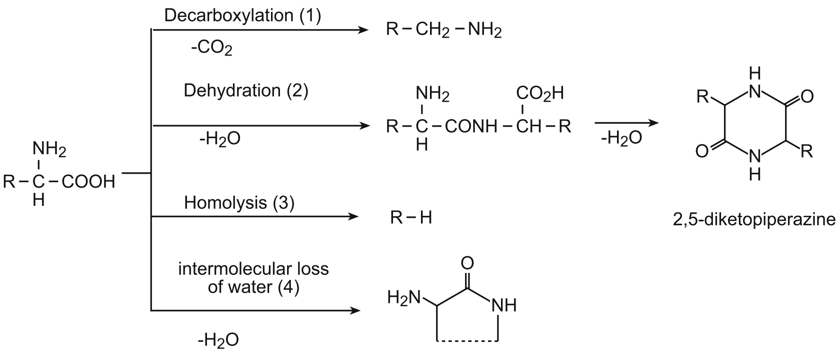

Fig. 3 Pyrolysis reactions of amino acids (Britt et al. 2004; Chiavari and Galletti 1992)

oligomers. These can be produced by nucleophilic attack by the N-terminal amino group on the C-terminal carbonyl in the chain followed by the loss of water. Alternatively, the N-terminal group can also attach to any carbonyl carbon in the chain followed by the loss of the amino acid residue to that carbonyl group. The loss of water could also occur from amino-acid side chains of otherwise straight-chain oligomers that contain serine or threonine. Using a methionine enkephaline-argenine-phenylalanine oligopeptide, Meetani et al. (2003) demonstrated that in addition to diketopiperazines other cyclic species are formed by dehydration and head-to-tail cyclization.

During pyrolysis, polypeptides (Fig. 3) can also undergo decarboxylation, deamination, and dehydration to dipeptides, followed by a second dehydration to yield a 2,5-diketopiperazine. Further reactions are homolysis of the aliphatic side chains and loss of water or ammonium to give cyclic products (Chiavari and Galletti 1992). The extent of these reactions depends on peptide structure and on conditions and duration of the pyrolysis. Low-molecular-weight heterocyclic compounds form at temperatures of 200–300°C, whereas above 500°C, polynuclear aromatic structures containing nitrogen (N-PACs) are also produced (Sharma et al. 2003) (Fig. 4). Pyrolysis of asparagine, aspartic acid, glutamine and glutamic acid at 300°C resulted in substantial char (64%, 66%, 30% and 27% of the starting mass, respectively) (Sharma et al. 2003, 2004b). Pyrolyzing char from asparagine and aspartic acid at yet higher temperatures (625°C) produced compounds related to maleimide and succinimide. Pyrolysis of glutamine at 300°C yielded glutarimide as the major product (Sharma et al. 2004b). The occurrence of these reduction products was attributed to the formation of polypeptides in the pyrolysis melt and a subsequent disportionation-type reaction leading to degradation to lower-molecular-weight products. This reaction sequence can also explain the formation of 2,6-dihydroxypyridine from poly(glutarimide).

The products from pyrolysis of proteins at 840°C consisted of aromatic hydrocarbons, their N-containing analogs (nitriles and anilines), and phenols (Higman et al. 1970). Unlike carbohydrates subjected to high temperatures, proteins yield only small amounts of benzo[a]pyrene, although higher molecular weight N-PACs, such as benzocarbazoles and acridines (Fig. 4) were observed. It is likely that N-PACs are formed in multistep reactions, involving both pyrolysis and pyrosynthesis from compounds that already contain N. Pyrolysis of poly (L) proline at 700°C yielded pyrrole (17%) and pyridine (1%) as the major products (Johnson et al. 1972). N-PACs, however, were either not found (700°C) or found in very small amounts (800°C). Indole, isoquinoline, quinoline and picoline have also been reported as pyrolysis products of proline (Higman et al. 1970). In another study, proline was completely converted into volatile products at 300°C, resulting in no char. In the tar, defined as the volatiles, which exit the oven and were trapped, the major product identified was 2,5-diketopiperazine. A similar finding was reported for pyrolysis at 600°C by Britt et al. (2004). Decarboxylation of 2,5-diketopiperazine yields pyrrolidine and a sequence of dehydrogenation steps then leads to pyrroline and pyrrole (Chiavari and Galletti

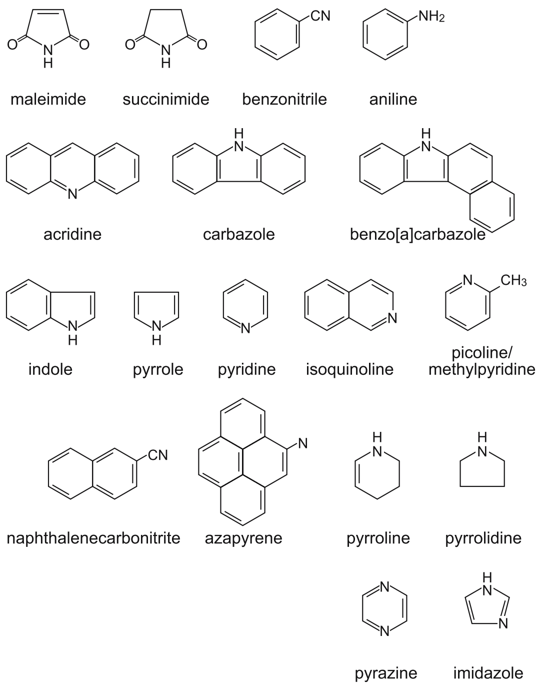

Fig. 4 Examples of heteroaromatic-N and N-containing PAHs (N-PACs)

1992). Sharma et al. (2003) heated (>870°C) the char remaining after 300°C pyrolysis of aspargine and identified significant amounts of two- to four-ring N-PACs such as naphthalenecarbonitrile, pyrrolcarbazole, benzoquinoline and azapyrene. A wide variety of PAHs were also found although yields were much lower.

The thermal stability of nine amino acids was measured in an oxygen-free atmosphere to gauge the temperatures under which amino acids can survive atmospheric entry of organic-bearing space bodies. It was found that glutamic acid and ß-alanine were the least stable, pyrolyzing completely at 400°C (Douda and Basiuk 2000). At the other extreme alanine was still detectable at 800°C (0.4% recovery). Proline was still detectable after heating to 500°C, glycine to 600°C, and valine and leucine to 700°C.

Maillard reaction

A reaction previously assumed to be responsible for the long-term stabilization of organic N in soils is the Maillard reaction (Ikan et al. 1996). During this process, ammonia or free amino groups of amino acids and amino sugars react with carbonyl groups of sugars to form Schiff bases, which subsequently undergo rearrangements via Amadori intermediates (Fig. 5) to produce dark-colored melanoidins. Doubts about the importance of this reaction in soils stem from the low reactivity of Schiff bases at room temperature. The formation of melanoidins in such environments, therefore, may be in strong competition with microbial use of released N compounds to build up new biomass. However, under fire conditions formation of such compounds can be expected.

Pyrolysis of Amadori compounds that had been formed by reacting glucose with asparagine, valine, leucine and threonine yielded ketones, aldehydes, pyridines, pyrazines, pyrroles and carboxylic acids (Coleman and Chung 2002). Pyrolysis of the Amadori product of proline with glucose produced two to eight fold more N-PACs and PAHs at 700°C and at 800°C than did pyrolysis of pure proline (Britt et al. 2004). This yield difference was attributable to the participation of glucose since pyrolysis of a 1:1 mixture of proline and glucose produced products similar to that produced by the Maillard reaction alone. It was further shown that glucose enhanced the gas-phase formation of N-PACs and PAHs during low-temperature pyrolysis of proline. Thus, glucose seems to provide a low-temperature pathway for the decomposition of proline and possibly other amino acids, which subsequently leads to formation of N-PACs and PAHs.

Charring of plant residues and SOM

Subjecting peat to controlled laboratory heating at 350°C produced a weight loss of 50% after 180 s heating time. The loss of C, H, O, N followed non-linear kinetics (Almendros et al. 2003). O and H were lost faster than C but slower than N. These results coincide with those for soil humic and fulvic fractions, and for sapwood and wood from *Eucalyptus saligna* and *E. grandis* during laboratory heating (Almendros et al. 1990; Baldock and Smernik 2002; Trompowsky et al. 2005). In fact, when the changes were plotted in a van Krevelen diagram, the progressive decrease

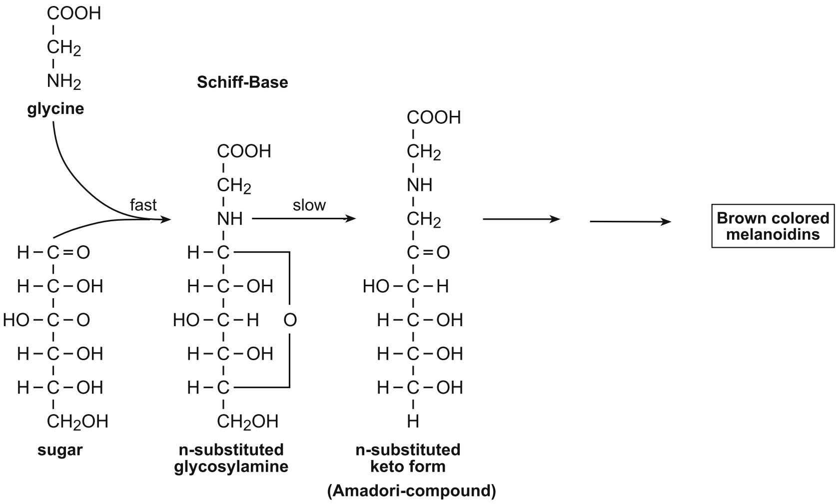

Fig. 5 Scheme of the formation of melanoidins from amino acids and carbohydrates

of the H/C and O/C atomic ratios indicate dehydration reactions in samples subjected to moderate heating, whereas decarboxylation and demethylation dominate in the more severely heated samples (Almendros et al. 2003). Solid-state ^{13}C NMR spectroscopy confirms that, under relatively mild heating, the main processes are dehydration, dehydrogenation and degradation of O-alkyl C (Freitas et al. 1999; Baldock and Smernik 2002; Almendros et al. 2003) yielding aryl C and furans. Losses were smaller for methoxyl C and N-alkyl C. For peat heated at 350°C, the carbohydrate signal vanished after only 50 s (Almendros et al. 2003). For a mineral soil, at the same temperature a heating time of 10 min was necessary to reach this stage (Fig. 6) (Dettweiler 2003). This is in agreement with efficient protection of SOM due to low heat conductivity of the mineral phase or interaction of the mineral phase with SOM. Considering that aboveground fires move quickly, SOM in the mineral horizon is unlikely to be severely affected by burning. Thus, the charred residues found in an A horizon should derive mainly from charred vegetation or from the partly combusted litter that first accumulated on the floor but later was transported into the mineral soil.

With heating of the peat at 350°C for more than 90 s, more stable alkyl C and also carboxyl C are removed and only a portion of recalcitrant, cyclic or branched paraffinic structures remain in a condensed unsaturated matrix (Almendros et al. 2003). Concomitantly the aryl-C content increases. Based on this observation the aromatic C/alkyl C ratio has been suggested as an index of the degree of charring of plant material and SOM (Knicker et al. 2005b).

Pyrolysis-GC/MS showed that even after severe heating of grass residues substantial amounts remained of some resistant plant components (González-Vila et al. 2001). Whereas the tetrapyrrole moiety of chlorophylls was rapidly destroyed, the phytol portion turned out to be more resistant, leading to phytadiens as an intermediate, and subsequently to phytenes and pristenes. The alkyl products showed characteristic yields in terms of heating time. The major decreases for the phydatdienes and fatty acids were observed after 75 s heating and for *n*-alkanes after 80 s. Paraffinics and sterols were more stable. The lignin backbone confirmed its relatively high resistance against heat as was already reported for pure lignin during pyrolysis (Sharma et al. 2004a). An increase of the relative concentration of aromatic pyrolysis products with a decreasing methoxyphenol/phenol ratio supports the idea of progressive demethoxylation and the synthesis of new aromatic structures.

The atomic C/O ratio for plant material and SOM heated at 350°C for various times averages about 3 (Baldock and Smernik 2002; Almendros et al. 2003; Trompowsky et al. 2005). This relatively high O concentration is inconsistent with the large and highly condensed aromatic

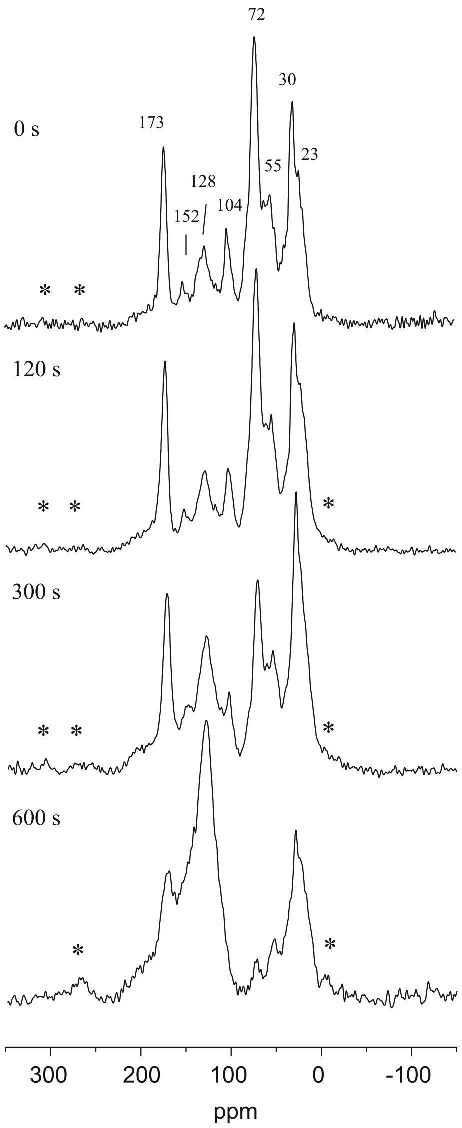

Fig. 6 Solid-state ^{13}C NMR spectra of soil material from the A horizon of a Leptosol under oak from central Spain subjected to heating at 350°C under oxic conditions. The spectra were obtained with a Bruker DSX 200 using the variable-amplitude cross-polarization magic-angle-spinning technique (Knicker et al. 2005b) after treating the sample with 10% hydrofluoric acid to remove paramagnetics and thus increase OM content. The chemical shift assignments are listed in Table 1. Asterisks indicate spinning side bands

structures commonly proposed for soot and charred organic materials (Schmidt and Noack 2000; Smernik et al. 2000), but confirms that anhydrosugars, furans or furan-like structures from cellulose and other carbohydrates are important constituents of the molecular structure of char (McGrath et al. 2003). Moderate heating leads to little change in C/N ratios, which can be as wide as 440–630 (atom/atom) for woody material (Trompowsky et al. 2005) or as narrow 7–8.1 for young grass material (Knicker et al. 1996). Charred peat and humic acids had C/N ratios between 40 and 35 and 16 to 14 (Almendros et al. 1990, 2003). For burnt straw and other plant material, C/N ratios of 29 and 47 are reported (Fernandes et al. 2003), whereas heated A-horizon SOM yielded a C/N between 13 and 32 (Dettweiler 2003). The fact that there are almost no changes of the C/N ratios during charring shows that N tends to be incorporated into compounds that are fairly resistant to heating. As demonstrated by solid-state ^{15}N NMR spectroscopy (Fig. 7) such compounds are mostly of pyrrole/indole type with minor contributions of pyridine. Using Curie-point pyrolysis-GC/MS, increasing yields of imidazoles (Fig. 4) were observed with progressive isothermal heating of grass residues (González-Vila et al. 2001).

Charred sapwood showed an atomic H/C ratio of 0.54 (Baldock and Smernik 2002). Using solid-state ^{13}C NMR spectroscopy to measure this ratio for the aromatic moiety of peat samples charred under anoxic condition at 400°C (Freitas et al. 1999) and under oxic conditions at 350°C (Knicker et al. 2005b), ratios of 0.71 and 0.52 were reported. A plant derived char particle found in a fire affected Cambisol A horizon (Knicker et al. 2005a) had a H/C ratio of 0.63 (unpublished result) and char from wood from *Eucalyptus saligna* and *E. grandis* produced at 550°C revealed atomic H/C ratios of 0.36 and 0.37 (Trompowsky et al. 2005). Using those ratios, one can calculate that in such chars on average almost every second aromatic C is connected to a proton. Even commercially obtained barbeque charcoal yielded an atomic H/C of 0.48, indicating that on average every second C is protonated (Knicker et al. 2005b). This relatively high protonation degree is supported by using dipolar dephasing solid-state ^{13}C NMR experiments and demonstrates that most of the aromatic C in char must occur in relatively small clusters of at most six aromatic rings, possibly connected by approximately two bridging Cs or Os. Alternatively, benzanthracene-like structures with two to five bridging C are possible. Fourier-transform ion-cyclotron resonance mass spectrometry has confirmed the occurrence of such relatively small clusters in humic acid fractions derived from volcanic-ash soils (Kramer et al. 2004) with linear chains of four to seven fused aromatics. Condensed aromatic structures linked by bridgehead carbons were detected only in minor amounts. By comparison, char lacking a high proportion of bridgehead carbon or graphitic structures was also reported for forest-floor samples collected after surface fires in Siberian Scots pine forests (Czimczik et al. 2003).

Table 1 Tentative chemical shift assignments of various peaks in a ^{13}C NMR spectrum

ppm	Assignment
0–45	Alkyl C
45–110	O and N alkyl C
45–60	Aliphatic C–N, methoxyl C
60–95	O alkyl (carbohydrates, alcohols)
95–110	Acetal and ketal C (carbohydrates)
110–160	sp^2-hybridized C
110–140	H aryl and C aryl C, olefinic C
140–160	O aryl C and N aryl C
160–220	Carbonylic C/carboxylic C/amide C
160–185	Carboxyl and amide C
185–220	Aldehyde and ketone C

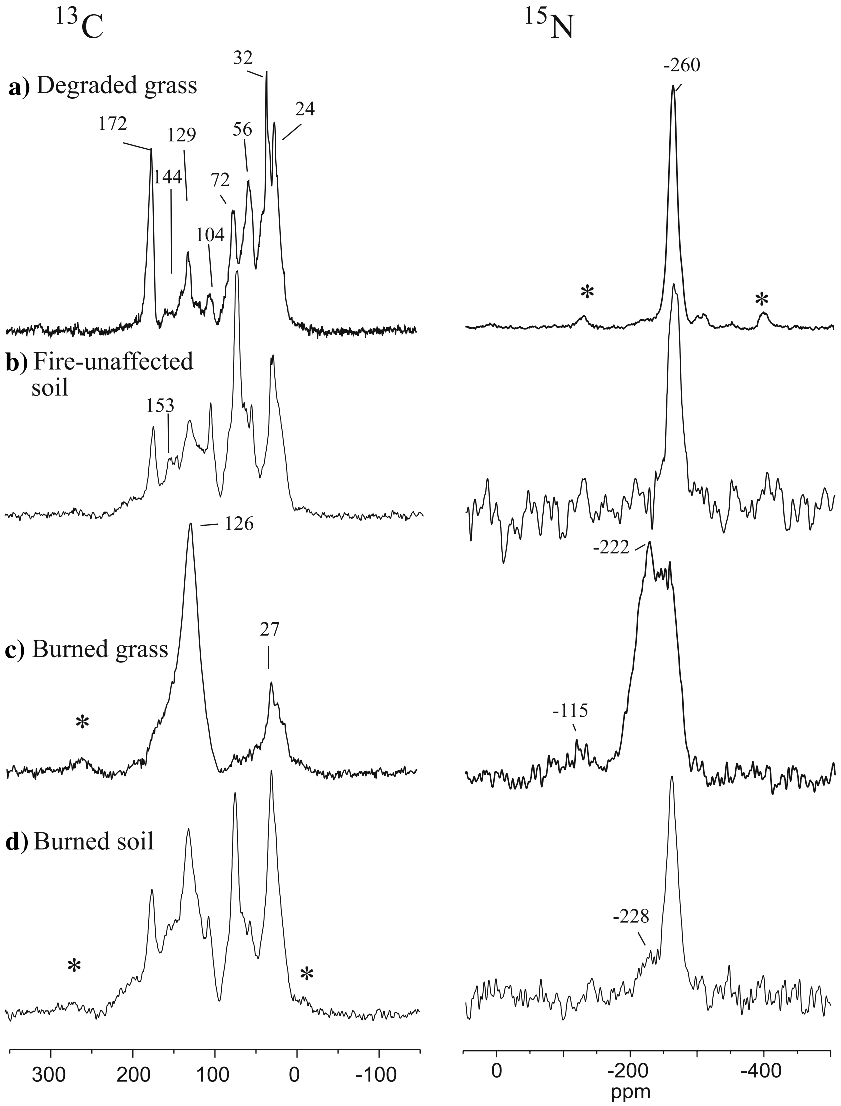

Fig. 7 Solid-state ^{13}C and ^{15}N NMR spectra of (**a**) Residues of *Lolium perenne* degraded for 6 years under oxic conditions (60 % WHC) (**b**) Unburned soil material from the A horizon of a Cambisol from southern Spain after HF treatment (10% HF) (Knicker et al. 2005a) (**c**) Residues of *Lolium perenne* charred for 2 min under oxic conditions at 350°C (**d**) Burned soil from the A horizon of a Cambisol from southern Spain 5 years after fire. Prior to NMR spectroscopy it was treated with 10% HF (Knicker et al. 2005a). Asterisks indicate spinning side bands. Chemical shift assignments are listed in Tables 1 and 2

Table 2 Tentative assignments for the various chemical shifts in a ^{15}N NMR spectrum

ppm	Assignment compounds in biomass	Other assignments
25 to –25		Nitrates, nitrites, nitro groups
–25 to –90		Imines, phenazines, pyridines, Schiff-bases
–90 to –145	Purine (N-7)	Nitrile groups
–145 to –220	Chlorophyll, purines/pyrimidines, indoles, imidazoles, pyrroles	Maillard products
–220 to –285	Amides/peptides, N-acetyl derivatives of aminosugars, tryptophanes, prolines	Lactame (pyrroles, carbazoles, indoles)
–285 to –325	NH in guanidines	Aniline derivatives
–325 to –375	NH_4^+, $–NH_3^+$, $–NH_2$, –NHR and $–NR_2$ groups, free amino groups in amino acids and amino sugars	Anilinium salts

Char content in soils

Measurements of char in soils often produce conflicting results. For example, determination of char concentrations in a reference material (National Institute of Standards and Technology SRM 1649a) by various methods gave values ranging from 7% to 50% (Currie et al. 2002). In an earlier intercomparison, the range of values was even more striking, varying by a factor of 500 (Schmidt et al. 2001). These discrepancies maybe due in part to lack of a common definition of char, also often termed "black carbon" (BC) (Masiello 2004) and to the fact that different methods were used that only cover a certain range of combustion products included in the term BC. In general BC is a continuum, ranging from slightly charred biomass, which may be still microbially degradable, to soot. The latter is a refractory secondary combustion product formed by condensation of volatiles, most probably via a radical mechanism. It differs significantly from charcoal, which retains enough features to identify its biological origin. Methods for quantification and characterization of BC include microscopy, optical techniques to determine the blackness of a sample, thermal and chemical degradation techniques, and spectroscopic methods focusing on the identification of typical pyrogenic chemical structures (Schmidt and Noack 2000; Massiello 2004). However, one has to bear in mind that each technique is appropriate only for a specific region within the combustion continuum.

Estimates of char content in soils range from 2% to 8% of the SOM in tropical savannah burn sequences (Bird et al. 1999) to 30% in some US agricultural soils (Skjemstad et al. 2002). Char constituted up to 24% of SOM in a Fimic Anthrosol from the Amazon region (Glaser et al. 1998) and 4–17% in native North American prairies soils (Glaser and Amelung 2003). In sloping land under tropical slash-and-burn agriculture in Northern Laos, char contributed 3–5% to the total organic C content in the B horizon and between 6% and 7% in the A horizon (Rumpel et al. 2006). In a number of German Chernozems, up to 45% of SOM was char, most of which occurred in the light fraction (Schmidt et al. 1999). In Japanese Andosols the percentage contribution of charred plant fragments in the light fractions ranged from 3.4% to 33% of the dry weight (Shindo et al. 2004).

In three studies based on fractionation by size fractionation rather than density, most of the char comprising 30% of the SOM in some Australian topsoils was recovered in the <53-µm fraction (Skjemstad et al. 1996, 1999). Similarly, the clay- and silt-size fractions also constituted the main char pool in native grassland soils from North America (Glaser and Amelung 2003). In terra preta soils, char concentrations were generally higher in the light fraction than in the heavier fraction, indicating that a major part of it was not stabilized by interaction with the mineral phase (Glaser et al. 2000). The char in the heavier fractions, on the other hand, was partly embedded within plaques of Fe and Al oxides on mineral surfaces. Enhanced complexation of SOM with metals after burning was also observed by Fernández et al. (1997). The association with Al was favored compared to that with Fe. Interactions with metal oxides were suggested to be an important stabilization mechanism for char in an acid Haplic Chernozem in Germany (Brodowski et al. 2005).

Char enrichment at 30- to 40-cm soil depth has been reported for several soils, such as terra preta soils in Brazil, but also Oxisols and Ultisols of the Upper Rio Negro region of Colombia and Venezuela, (Saldarriaga and West 1986; Glaser et al. 2000). The Rio Negro pattern was attributed to washing out of light char particles from the surface by erosion, whereas the char transport in terra preta soils was explained by bioturbation by earthworms and termites. Char enrichment in the silt fraction at a depth of 38–48 cm was also reported for a Brazilian agricultural Acrisol (Dieckow et al. 2005) and may have been due to grassland fires that occurred before the area was converted to agriculture. In Spanish soils sampled 1 year after a severe fire, char-derived compounds were identified in the B horizon, which may indicate that at least some pyrogenic compounds can be quickly transported into deeper soil horizons (Knicker et al. 2006). On steep sites, however, horizontal transport may be more important than vertical transport (Rumpel et al. 2006).

Chemical alteration of SOM in fire-affected soils

Direct effects on bulk soil organic carbon

Based on the differing chemical composition of biologically altered and heavily charred plant residues (Fig. 7), char inputs to soil could be expected to lead to a considerable increase in aromatic C in SOM (Golchin et al. 1997). This increase would contribute to a decrease in polarity and enhancement of water repellency as is often observed in post-fire soils. However, SOM at depths below the upper few centimeters mostly remains unaffected by the fire. Thus the extent to which the chemical composition and properties of native SOM persist post-fire depend on the quality and quantity of the char input (Knicker et al. 2006).

Attributable to a more complete volatilization during severe heating, the SOM of top horizons of some Spanish soils showed a lower char accumulation after intense and very intense fires compared to medium intense burnings. The stronger fire intensities resulted in a wider aromatic C to alkyl C ratio of the incorporated char, demonstrating that depending on the heat intensity the produced chars can vary considerably with respect to their chemical structure. Irrespective of the fire type, indications were found that oxidation of char can occur very early after the fire. Multiple burning does not necessarily increase the aromaticity of SOM as was seen for a double-burn forest site in Central Spain (Knicker et al. 2006). This may be because the first fire destroyed the ground vegetation together with the litter layer and killed most of the trees. During the second fire 2 years later, the new shrub and herb cover together with the decaying char provided a more accessible fuel, which burned completely leaving little char. Using C content and solid-state NMR spectroscopy, it was shown that at this site during the 2 years after the second fire, fresh litter, rather then char, was the main source of new SOM.

In some soils, char addition seems to cause increases in proportions of aromatic C and darkening of the SOM. For example, relationships between the L-value (lightness) and char content were observed for a color sequence of German Chernozems (Schmidt et al. 1999). Char input has been assumed to be important in the formation of some deep black soils in Russia, Eurasia, Canada, and California (Schmidt and Noack 2000) and of Australian grassland soils that had been under aboriginal use presumably for 1,000s of years (Skjemstad et al. 1990).

Solubility of SOM

Humic extracts from soil and soot, from charred grass, and from barley straw treated with HNO_3 and H_2O_2 all revealed high aromaticity with considerable contributions of carboxyl C (Hatcher et al. 1981; Schnitzer and Calderoni 1985; Arshad and Schnitzer 1988; Haumaier and Zech 1995). Commercial charcoal and cinder prepared by quenching a wood fire yielded a humic-acid fraction only after pre-treatment with $KClO_3$-HNO_3, indicating that depolymerization and carboxylation of the char was required before it became base-extractable. Similarly, the humic-acid fraction was only a minor constituent of char from bulk soil collected 5 years after a fire in southern Spain (Knicker et al. 2005a), indicating that under natural conditions some time for degradation is needed to form humic and fulvic fractions.

Soil organic matter and humic fractions from volcanic ash soils in Japan that had been burned annually contained more aromatic and carbonyl C than unburned soils and soils where burning ceased up to 100 years ago (Golchin et al. 1997). Based on the observed similarities between the humic acid fractions from volcanic ash soils and from charred plant residues, it was suggested that charring processes may be one of the mechanisms responsible for humic-fraction formation in these soils (Shindo et al. 2004).

Highly carboxylated humic-acid fractions with hydrogen-deficient condensed aromatic structures were also extracted from volcanic-ash soils by Kramer et al. (2004) and from 100-year-old char particles in a forest soil (Hockaday et al. 2006). Kramer et al. (2004) concluded that, if many of these highly carboxylated char-like molecules are water soluble, a mechanism would exist for char mobilization and transport from soils to aquatic systems. This idea is consistent with the detection of significant concentrations of heterocyclic N in type-A humic-acid extracts from both the subsoil of paddy fields and the surface layer of Andosols (Maie et al. 2006). The heterocyclic N was assumed to derive from charring processes, but since burning is highly unlikely in paddy subsoils, they were assumed to have been transported by leaching.

Heating of soils is also connected to drastic changes in solubility properties of SOM (Fernández et al. 2004). Temperatures above 250°C have been shown to lower yields of humic-acid fractions from volcanic ash soils (Shindo and Urabe 1993). In an early stage of progressive heating of a humic-acid fraction at 350°C, half of the sample was rapidly transformed into alkali-insoluble macromolecular compounds (Almendros et al. 1990). The atomic O/C was observed revealing important losses of O-containing groups, which was discussed as the main process responsible for the progressive transformation into structures that are increasingly colloidal in nature. A similar transformation was observed for a fulvic acid that was first transformed into an acid-insoluble material and then into an alkali-insoluble substance.

Similar observations have been reported for HNO_3-reflux hydrolysate of wood from *E. grandis* and *E. saligna* at various temperatures (Trompowsky et al. 2005). A humic-acid-like fraction was obtained by extraction of the residue with NaOH and precipitation after acidification of the supernatant. This procedure resulted in a decrease of fulvic extract with increasing pyrolysis temperature. Humic extract yields, on the other hand, increased, peaking around 450°C, after which condensation into polycyclic compounds was so intense that yields of the humic-acid fraction began to decrease.

Alteration of the organic N fraction

Fire results in an enrichment of pyrrole-type N (Fig. 7), which was not detected in most solid-state ^{15}N NMR spectra of the SOM obtained from fire-unaffected areas (Knicker et al. 1993; Knicker 2004). Five years after a fire in Spain, most of the soil heteroaromatic N was identified in the humin fraction, although minor amounts were detected in the humic and fulvic fractions (Knicker et al. 2005a). However, amide N still dominated the solid-state ^{15}N NMR spectra. Possibly these amides derived from peptides of fire-unaffected SOM or survived as especially persistant peptide structures in the char. Alternatively, the amides may have been protected within Maillard products formed during charring. Interestingly, HCl hydrolysis of UV-photo-oxidized fine particle-size fractions of some Australian soils containing char (Knicker and Skjemstad 2000) revealed that some amide N was associated with peptides that were not destroyed by the photo-oxidation. They may have been stabilized by being isolated within the core of aggregates or char particles.

Impact of recovery time

For some soils from central Spain, 1–2 years of recovery time after fire were insufficient for development of a substantial amount of new non-char SOM (Knicker et al. 2006). In contrast, 5 years recovery time allowed the accumulation of considerable amounts of unburned fresh organic matter in a Cambisol from southern Spain (Knicker et al. 2005a). Such material can originate from fire-unaffected or only partly affected litter and roots from the decaying trees. In addition, the liming effect of ash and increased nutrient availability (Fernández et al. 1997; Prieto-Fernández et al. 2004) may have promoted the observed quick development of a new herbaceous layer. Enhanced litter production together with an often observed decrease in microbial activity after fire (Choromanska and DeLuca, 2002) could thus have increased the amount of non-char SOM.

Stability of char

As one of the most resistant forms of SOM, char is widely viewed as composing a major proportion of the slow-cycling C in ocean sediments and soils. This view is supported by the observation that char is still detectable in recent and fossil sediments as well as in buried fossil soils and at archeological sites (Schmid et al. 2002; Canti 2003; Dickens et al. 2004; Cao et al. 2006). Solid-state NMR analysis of some Neolithic soils in Germany and paddy soils from China has revealed high aromatic C contents typical for SOM with significant char (Schmid et al. 2001; Cao et al. 2006). In some of the buried ancient paddy soils, almost all the organic C and N is attributable to char (Fig. 8). On the other hand, soils under grassland that had been invaded by forest after annual burning had stopped demonstrated a fast change in the nature of the soil C (Golchin et al. 1997). The greatest changes occurred during the first 20–30 years and were manifested in a decrease in the ratio of aromatic to alkyl C. It seems that with long recovery times the char becomes masked by the input of fresh litter. However, considering the high degradability of most fresh litter, this requires either a high biomass-production rate or implies that some char is lost. Possible loss mechanisms would be in situ degradation, losses due to surface erosion, and translocation of char into deeper horizon.

Those observations confirm suggestions by Masiello (2004) that char production and loss do not balance. She speculates further that, if char has been produced since the last glacial maximum via biomass burning at the same rate as it is now produced, char should account for 25–125% of the total soil organic carbon pool. Although a few measurements indicate char contents as large as 25%, even that lower bound is rarely realized char loss due to physical transport processes such as surface erosion and leaching may be facilitated if the char occurs as colloids or DOM. Evidence for the presence of char-derived compounds in DOM and the possible formation of DOM during oxidation of soot have recently been reported (Decesari et al. 2003; Kim et al. 2004; Shindo et al. 2004; Maie et al. 2006). Chemical characterization of char-derived soluble compounds indi-

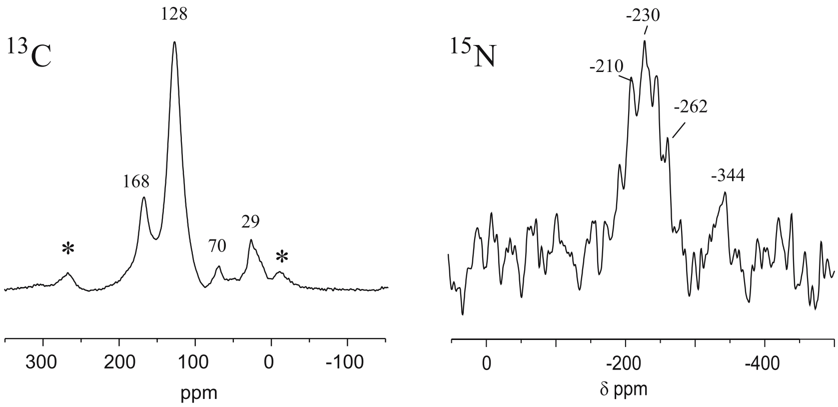

Fig. 8 Solid-state ^{13}C and ^{15}N NMR spectra of a HF-treated fossil paddy soil (4276 BC) from the Yangtze River Delta, found at a depth of 130 to 150 cm

cates a relatively high content of carboxyl C. This polar group decreases hydrophobicity and thus contributes to the solubility of such compounds. Their transport into deeper horizons may thus explain the increase of aromatic C in the B horizon of a Spanish Cambisol 2 years after a severe fire (Knicker et al. 2006). In this context, note the clear signal at 168 ppm attributable to carboxyl C in aromatic structures in the solid-state ^{13}C NMR spectrum of the buried Neolithic paddy soil in Fig. 8. High carboxyl-C contributions were also found in fire-affected soils in Spain only 1 year after fire and for char in Australian soils (Skjemstad et al. 1993), although in the latter case it was speculated that the high carboxyl-C content was due to the UV-photo-oxidation pre-treatment. Near-edge X-ray-absorption fine-structure spectroscopy showed highly oxidized regions at the surface of char from soils near Manaus, Brazil (Lehmann et al. 2005).

The presence of carboxyl C may also explain the observation that char is less recalcitrant than commonly assumed (Bird et al. 1999). In line with this are studies showing unexpectedly high lability of char in sediments: char persisted on timescales of 1,000s of years, with more rapid turnover under oxic conditions (Middelburg et al. 1999; Massiello and Druffel 2003). More direct evidence for char degradability comes from measurements of CO_2 production as a result of microbial degradation of char (Hamer et al. 2004). Addition of glucose caused a priming effect and increased rates of char mineralization. A positive response to adding microbial inoculum to artificially produced char confirmed microbial degradation (Baldock and Smernik 2002).

Conclusions

Molecular structure of char and its impact on char quantification in SOM

Char has been shown to consist of rearranged, recalcitrant macromolecular substances, which are highly aromatic (Almendros et al. 1988, 1992; Freitas et al. 1999; Baldock and Smernik 2002). Considering the results of charring experiments and reports from the pyrolysis literature reviewed in this paper, the aromatic skeleton of char remaining after fire must contain remnants of the lignin backbone as well as pyrolysis products such as furans and anhydrosugars from cellulose and heteroaromatic N from peptides. Thus plant char models assuming a graphite-like structure as described by Sergides et al. (1987) (Schmidt and Noack 2000; Smernik et al. 2000) may be oversimplified. Further, it has to be borne in mind that features such as chemical composition and charring temperature vary widely but strongly affect amounts of O-, N- and even S-containing functional groups as well as size and conformation of the polycyclic aromatic ring. Although aromatization and condensation occur even at temperatures below 350°C, formation of significant amounts of graphite-like structures requires higher temperatures (Freitas et al. 1999; Sharma and Hajaligol 2003; Sharma et al. 2004a). Under oxic conditions, most of the organic matter volatilizes at temperatures above 350°C (Sharma et al. 2001, 2004a; Sharma and Hajaligol 2003). Open air space, such as in surface organic horizons, promotes fast removal of the released volatiles, minimizing formation of condensation products (soot). Within the mineral soil pores, however, condensation can occur, especially as volatiles move downward into deeper and cooler regions.

Based on these results and expectations, I propose that char is a heterogeneous mixture of thermally altered biomolecules, whose degree of alteration depends on the severity of the fire and the chemistry of the original plant tissues. N, O and likely also S substitutions are common features of the char products. In contrast to soot, the aromatic skeleton of char has few graphitic domains.

The highly heterogeneous structure proposed here has implications for the stability of char in soils and for its behavior during analytical procedures. Being less graphite-like and thus less recalcitrant than assumed, portions of the charcoal may not survive some of the harsh chemical and thermal degradation procedures used commonly for char identification in soils. This can lead to underestimation of its contribution. Others approaches, in particular biomarker approaches, rely on the identification of degradation products from polyaromatic clusters (Glaser et al. 1998). However, in chars produced at lower temperatures, such clusters may be only a minor constituent.

A heterogeneous structure is further supported by the observation that structure and chemical composition of char vary with fire severity. Only intensively charred material is entirely aromatic, whereas alkyl-C contributes in chars produced at moderate temperature (Knicker et al. 2005b). Such compositional differences are likely to cause variability in char recalcitrance and degradability. Consequently, the long-term impact of char on the chemical composition and stability of post-fire SOM may also vary with type and intensity of the fire. This implies that measures of amounts of char in soils alone may not allow adequate consideration of the role of char in ecosystem C budgets.

Importance of ‘‘black nitrogen’’

Immediately after fire, increases in inorganic N are reported. Due to low microbial activity and the destruction of the vegetation, leaching is likely during the first rainfalls leading to substantial inorganic N loss from the system. The remaining organic N, on the other hand, is mainly immobilized in recalcitrant heteroaromatic N structures, formed by heat-induced transformation of more or less easily degradable plant proteins. Since such heteroaromatic compounds were not observed in SOM modified solely by microorganisms (Knicker et al. 1993, 1997; Knicker 2000) they have been proposed as indicators of recent fire (Knicker et al. 2005a). However, these char-derived heterocyclic N compounds are most likely to be more refractory than organic N compounds entering the soil in the absence of fire. Thus, burning may increase the N content of SOM while altering its chemical structure with likely long-term consequences for N availability and thus primary production (Knicker and Skjemstad 2000).

C/N ratios are similar for samples subjected to moderate heating and for untreated material and can reach values as narrow as 7 (atom/atom) for heated young grass material (Knicker et al. 1996). For SOM from char-rich soils under burnt pine stands, C/N ratios of 12 and 16 have been reported (Knicker et al. 2006). Those narrow C/N ratios indicate that char input did not markedly widen the C/N ratio and that this char derived mainly from non-woody sources that are N-rich. Based on this observation, one can conclude that ‘‘black N’’ plays a more important role than commonly assumed. This fraction certainly needs to be more carefully considered if a complete understanding of the role of char as a C sink in soils is sought. This is particularly true for savannahs, where N-rich litter is the major fuel.

Charcoal structure and its short-term impact on SOM properties

Pyrogenic SOM differs qualitatively in its molecular structure from SOM formed via biodegradation and humification. Whereas biological processes lead to carboxyl-rich macromolecules that are relatively soluble (Knicker and Lüdemann 1995), thermal treatment removes external O groups, yielding materials with reduced solubility (Almendros et al. 1990, 1992). Thus burning can increase soil hydrophobicity with important effects on soil water flow. For example, over the long term, char-rich soils may contain hydrophobic spots that prevent water movement and thus cause patchy distribution of nutrients. Additionally, decreases in polar groups may change soil sorption properties and thus increase leaching of nutrients and pollutants. It can also affect interactions between SOM, silicate clays, and metal oxides and thus the formation and stability of aggregates.

Impact of char input on quality and quantity of SOM

With respect to changes in SOM stores due to fire, patterns are inconsistent. Effects range from complete loss to substantial increases. In addition to char input to the soil, increases in SOM can be attributed to the incorporation of unburned surface litter and roots originating from trees and shrubs that were killed or weakened but not combusted by the fire (Fig. 9). Moreover, release of nutrients (including N) from ash and an increase in pH after fire promotes quick

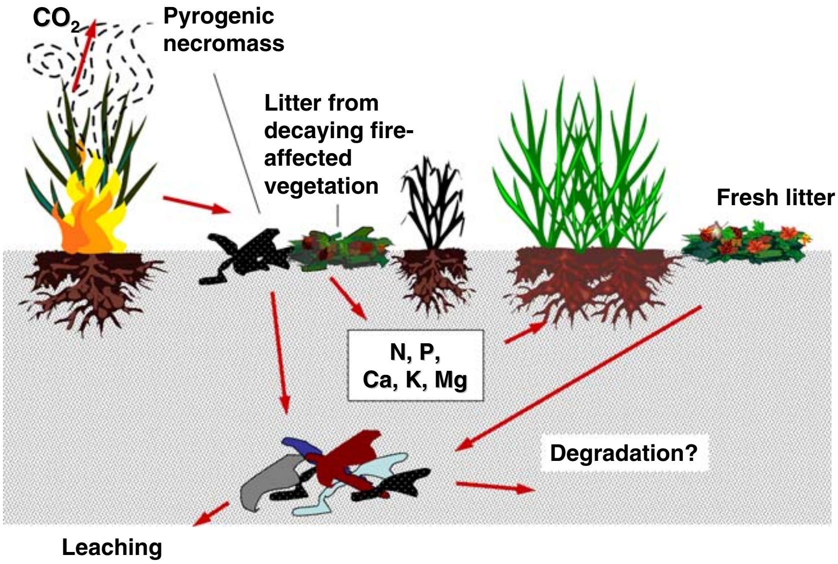

Fig. 9 Conceptual model of the impact of vegetation fires on SOM quality and quantity

development of a new herbaceous layer and thus enhances litter production. SOM accumulation rates can be even increased by the sterilization effect of fire, which reduces microbial activity and thus slows down the degradation of the newly produced litter. Even if amounts of SOM increase after fire due to char inputs, this increase may have little effect on the size of the refractory SOM pool because much of the char may not have been altered enough to increase its recalcitrance.

With respect to SOM quality a common pattern is recognizable. It includes both a relative and an absolute increase post-fire in aromatic C and the conversion of peptide N into heteroaromatic structures (Knicker et al. 2005a). Low-intensity fire seems to produce more char than intense fires but the degree of charring, expressed as its aromaticity, is lower (Knicker et al. 2006), which may affect recalcitrance and degradability of the char. Consequently, after its incorporation into the soil, the long-term impact of the char on the chemical composition and stability of SOM is also expected to vary with respect to type and intensity of the fire. However, with increasing recovery time after fire, amounts of char appear to decrease, perhaps due to inputs of fresh litter input that mask the presence of char, but perhaps due also to loss of char through time by degradation, leaching or erosion.

Degradability and solubility of char residues

In the model suggested here, char is a heterogeneous mixture of aromatic structures with domains of relatively small polyaromatic clusters but considerable substitution by N, O and S functional groups. This model seems more realistic than a more graphitic one because it provides for sites that can be attacked both by biotic and abiotic processes. Biotic oxidation could be performed by lignin-degrading fungi, which have been shown to also degrade coal (Fakoussa and Hofrichter 1999). *Phanerochaete chrysosporium*, for example was found to partially depolymerize coal polymers prepared by treating sub-bituminous German coals with nitric acid (Wondrack et al. 1989). Using ^{14}C dating with reclaimed coal mine soils, lignite C was traced into microbial biomass (Rumpel and Kögel-Knabner 2004). However, with both abiotic and biotic oxidation, the resulting chemical alterations of the char are likely to increase its susceptibility to further microbial attack. It should be noted, however, that because lignin degraders are participating, oxygen is essential for an efficient decomposition of char. Thus, supported by fresh litter input as a co-metabolic substrate, char on and within the upper soil horizons suffers degradation (Hamer et al. 2004). In buried soils and sediments or at archeological sites, oxygen depletion prevents further char destruction, whereas remaining easily usable compounds such as carbohydrates, acids and peptides are preferentially fermented. Such a scenario could at least partly explain why typical char levels decrease in some fire-affected soils over time (Golchin et al. 1997), whereas in sediments char can survive for millenia.

Amounts of topsoil char may also be decreased by carboxylation, which increases water solubility and thus leaching into deeper horizons (Fig. 9). The resulting increase in polarity can also, however, promote adsorption to the mineral phase, in particular to metal oxides, which would be a stabilizing influence. Such a mechanism may help to explain the occurrence of char in deep horizons of Brazilian Acrisols and terra preta soils (Dieckow et al. 2005). At the same time, sorption to mineral phases could increase char loss via erosion.

References

Almendros G, González-Vila FJ, Martín F (1990) Fire-induced transformation of soil organic matter from an oak forest. An experimental approach to the effects of fire on humic substances. Soil Sci 149:158–168

Almendros G, González-Vila FJ, Martín F, Fründ R, Lüdemann H-D (1992) Solid state NMR studies of fire-induced changes in the structure of humic substances. Sci Tot Environ 117/118:63–74

Almendros G, Knicker H, González-Vila JF (2003) Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. Org Geochem 34:1559–1568

Almendros G, Martín F, González-Vila FJ (1988) Effects of fire on humic and lipid fractions in a Dystric Xerochrept in Spain. Geoderma 42:115–127

Andersson M, Michelsen A, Jensen M, Kjoller A (2004) Tropical savannah woodland: effects of experimental fire on soil microorganisms and soil emissions of carbon dioxide. Soil Biol Biochem 36:849–858

Andreu V, Imeson AC, Rubio JL (2001) Temporal changes in soil aggregates and water erosion after a wildfire in a Mediterranean pine forest. Catena 44:69–84

Ansley RJ, Dugas WA, Heuer ML, Kramp BA (2002) Bowen ratio/energy balance and scaled leaf measurements of CO_2 flux over burned *Prosopis* savanna. Ecol Appl 12:948–961

Arshad MA, Schnitzer M (1988) Characterization of humic acids from termite mounds and surrounding soils, Kenya. Geoderma 42:213–225

Baath E, Arnebrant K (1994) Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. Soil Biol Biochem 26:995–1001

Badìa D, Martí C (2003) Plant ash and heat intensity effects on chemical and physical properties of two contrasting soils. Arid Land Res Manag 17:23–41

Baldock JA, Smernik RJ (2002) Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Org Geochem 33:1093–1109

Bassilakis R, Carangelo RM, Wójtowicz MA (2001) TG-FTIR analysis of biomass pyroysis. Fuel 80:1765–1786

Bentivenga SP, Hetrick BAD (1991) Relationship between mycorrhizal activity, burning, and plant productivity in tallgrass prairie. Can J Bot 69:2597–2602

Bird MI (1995) Fire, prehistoric humanity, and the environment. Interdisc Sci Rev 20:141–154

Bird MI, Veenendaal EM, Moyo C, Lloyd J, Frost P (1999) Stability of elemental carbon in a savanna soil. Glob Biogeochem Cycles 13:923–932

Bird MI, Veenedaal EM, Moyo C, Llyod J, Frost P (2000) Effect of fire and soil texture on soil carbon in a sub-humid savanna (Matopos Zimbabwe). Geoderma 94:71–90

Björkman L, Bradshaw RHW (1996) The immigration of *Fagus sylvatica* L. and *Picea abies* (L.) Karst. into a natural forest stand in southern Sweden during the last 2000 years. J Biogeograph 23:235–244

Boerner REJ, Brinkman JA (2003) Fire frequency and soil enzyme activity in southern Ohio oak-hickory forests. Appl Soil Ecol 23:137–146

Boerner REJ, Brinkman JA, Smith A (2005) Seasonal variations in enzyme activity and organic carbon in soil of a burned and an unburned hardwood forest. Soil Biol Biochem 37:1419–1426

Boerner REJ, Decker KLM, Sutherland EK (2000) Prescribed burning effects on soil enzyme activity in a southern Ohio hardwood forest: a landscape-scale analysis. Soil Biol Biochem 32:899–908

Boon JJ, Pastorova I, Botto RE, Arisz PW (1994) Structural studies on cellulose pyrolysis and cellulose chars by PYMS, PYGCMS, FTIR, NMR and by wet chemical techniques. Biomass Bioenergy 7:25–32

Boutton TW, Archer SR, Midwood AJ (1999) Stable isotopes in ecosystem science: structure, function and dynamics of a subtropical Savanna. Rapid Commun Mass Spectrom 13:1263–1277

Britt PF, Buchanan AC, Owens CV Jr, Skeen J (2004) Does glucose enhance the formation of nitrogen containing polycyclic aromatic compounds and polycyclic aromatic hydrocarbons in the pyrolysis of proline? Fuel 83:1417–1432

Brodowski S, Amelung W, Haumaier L, Abetz C, Zech W (2005) Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Geoderma 128:116–129

Cade-Menun BJ, Berch SM, Lavkulich LM (2000) Phosphorus forms and related soil chemistry of Podzolic soils on northern Vancouver Island. II. The effect of clear-cutting and burning. Can J For Res 30:1726–1741

Caldararo N (2002) Human ecological intervention and the role of forest fires in human ecology. Sci Total Environ 292:141–165

Campbell GS, Jungbauer JD, Bristow KL, Hungerford RD (1995) Soil temperature and water content beneath a surface fire. Soil Sci 159:363–374

Canti MG (2003) Aspects of the chemical and microscopic characteristics of plant ashes found in archaeological soils. Catena 54:339–361

Cao Z, Ding J, Hu Z, Knicker H, Kögel-Knabner I, Yang L, Yin R, Lin X, Dong Y (2006) Ancient paddy soils from the Neolithic age in China's Yangtze River Delta. Naturwissenschaften 93:232–236

Carcaillet C, Almquist H, Asong H, Bradshaw RHW, Carrión JS, Gaillard M-J, Gajewski K, Haas JN, Haberle SG, Hadorn P, Müller SD, Richard PJH, Richoz I, Rösch M, Sánchez-Goni MF, von Stedingk H, Stevenson AC, Talon B, Tardy C, Tinner W, Tryterud E, Wick L, Willis KJ (2002) Holocene biomass burning and global dynamics of the carbon cycle. Chemosphere 49:845–863

Cerda A, Imeson AC, Calvo A (1995) Fire and aspect induced differences on the erodibility and hydrology of soils at La Costera, Valencia, southeast Spain. Catena 24:289–304

Certini G (2005) Effects of fire on properties of forest soils: a review. Oecologia 143:1–10

Chambers DP, Attiwill PM (1994) The ash-bed effect in *Eucalyptus regnans* forest: chemical, physical and microbiological changes in soil after heating or partial sterilization. Aust J Bot 42:739–749

Chandler C, Cheney P, Thomas P, Trabaud L, Williams D (1983) Forest fire behavior and effects. Fire in forestry. Wiley, New York

Chen X, Hutley LB, Eamus D (2005) Soil organic carbon content at a range of north Australian tropical savannas with contrasting site histories. Plant Soil 268:161–171

Chiavari G, Galletti GC (1992) Pyrolysis-gas chromatography/mass spectrometry of amino aicds. J Anal Appl Pyrolysis 123:123–137

Choromanska U, DeLuca TH (2002) Microbial activity and nitrogen mineralization in forest mineral soils following heating: evaluation of post-fire effects. Soil Biol Biochem 34:263–271

Coleman WM, Chung HL (2002) Pyrolysis GC-MS analysis of Amadori compounds derived from selected amino acids and glucose. J Anal Appl Pyrolysis 62:215–223

Crutzen PJ, Andreae MO (1990) Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science 250:1669–1678

Currie LA, Benner BA et al (2002) A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. J Res NIST 107:279–298

Czimczik CI, Preston CM, Schmidt WI, Schulze E-D (2003) 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). Global Biogeochem Cycles 17:1020–1033

Dai X, Boutton TW, Glaser B, Ansley RJ, Zech W (2005) Black carbon in a temperate mixed-grass savanna. Soil Biol Biochem 37:1879–1881

DeBano LF (2000) The role of fire and soil heating on water repellency in wildland environments: a review. J Hydrol 231–232:195–206

DeBano LF, Mann LD, Hamilton DA (1977) Fire's effects on physical and aggregate stability in hydrophobic soil. In: Forest (ed) Proc Symp Envir Cons Fire and Fuel Manag Medit Ecosys, (pp 65–74) Forest Serv U.S.D.A

DeBano LF, Neary DG, Ffolliott PF (1998) Fire's effect on ecosystems. Wiley, New York

Decesari W, Facchini MC, Matta E, Mircea M, Fuzzi S, Chughtai AR, Smith DM (2003) Water soluble organic compounds formed by oxidation of soot. Atmos Environ 36:1827–1832

Dettweiler C (2003) Auswirkungen von Vegetationsfeuer auf Bodeneigenschaften und auf die Zusammensetzung des organischen Bodenmaterials Diploma Thesis. Lehrstuhl für Bodenkunde. TU-München, Freising-Weihenstephan, Germany

Diaz-Raviña M, Prieto A, Acea MJ, Carballas T (1992) Fumigation–extraction method to estimate microbial biomass in heated soils. Soil Biol Biochem 24:259–264

Dickens AF, Gelinas Y, Hedges JI (2004) Physical separation of combustion and rock sources of graphitic black carbon in sediments. Mar Chem 92:215–223

Dieckow J, Mielniczuk J, Knicker H, Bayer C, Dick PD, Kögel-Knabner I (2005) Composition of organic matter in a subtropical Acrisol. Eur J Soil Sci 56:705–715

Doerr SH, Shakesby RA, Walsh RPD (1998) Spatial variability of soil hydrophobicity in fire-prone eucalyptus and pine forests, Portugal. Soil Sci 163:313–324

Douda J, Basiuk VA (2000) Pyrolysis of amino acids: recovery of starting materials and yields of condensation products. J Anal Appl Pyrolysis 56:113–121

Dumontet S, Dinel H, Scopa A, Mazzatura A, Saracino A (1996) Post-fire soil microbial biomass and nutrient content of a pine forest soil from a dunal Mediterranean environment. Soil Biol Biochem 28:1467–1475

Elias VO, Simoneit BRT, Cordeiro RC, Turcq B (2001) Evaluating levoglucosan as an indicator of biomass burning in Carajás, Amazonia: a comparison to the charcoal record. Geochim Cosmochim Acta 65:267–272

Fakoussa RM, Hofrichter M (1999) Biotechnology and microbiology of coal degradation. Appl Microbiol Biotechnol 52:25–40

Fernandes MB, Skjemstad JO, Johnson BB, Wells JD, Brooks P (2003) Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features. Chemosphere 51:785–795

Fernández I, Cabaneiro A, Carballas T (1997) Organic matter changes immediately after a wildfire in an Atlantic forest soil and comparison with laboratory soil heating. Soil Biol Biochem 29:1–11

Fernández I, Cabaneiro A, Carballas T (1999) Carbon mineralization dynamics in soils after wildfires in two Galician forests. Soil Biol Biochem 31:1853–1865

Fernández I, Cabaneiro A, González-Prieto SJ (2004) Use of ^{13}C to monitor soil organic matter transformations caused by a simulated forest fire. Rapid Commun Mass Spectrom 18:435–442

Freitas JCC, Bonagamba TJ, Emmerich FG (1999) ^{13}C high-resolution solid-state NMR study of peat carbonization. Energy Fuels 13:53–59

Fritze H, Pennanen T, Pietikäinen J (1993) Recovery of soil microbial biomass and activity from prescribed burning. Can For Res 23:1286–1290

Fynn RWS, Haynes RJ, O'Connor TG (2003) Burning causes long-term changes in soil organic matter content of a South African grassland. Soil Biol Biochem 35:677–687

García-Oliva F, Sanford RL, Kelly E (1999) Effect of tropical deciduous forest soil in Mexico on the microbial degradation of organic matter. Plant Soil 206:29–36

Giovannini G, Luchessi S, Cerevelli S (1983) Water-repellent substances and aggregate stability in hydrophobic soil. Soil Sci 135:110–113

Giovannini G, Lucchesi S, Giachetti M (1990) Effects of heating on some chemical parameters related to soil fertility and plant growth. Soil Sci 149:344–350

Glaser B, Amelung W (2003) Pyrogenic carbon in native grassland soils along a climosequence in North America. Global Biogeochem Cylces 17:1064

Glaser B, Balashov E, Haumaier L, Guggenberger G, Zech W (2000) Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. Org Geochem 31:669–678

Glaser B, Haumaier L, Guggenberger G, Zech W (1998) Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Org Geochem 29:811–819

Golchin A, Clarke P, Baldock JA, Higashi T, Skjemstad JO, Oades JM (1997) The effects of vegetation and burning on the chemical composition of soil organic matter in a volcanic ash soil shown by ^{13}C NMR spectroscopy. I. Whole soil and humic acid fraction. Geoderma 76:155–174

Goldammer JG (1993) Historical biogeography of fire: tropical and subtropical. In: Crutzen PJ, Goldammer JG (eds) Fire in the environment, the ecological, atmospheric and climatic importance of vegetation fires. John Wiley and Sons, Chichester, pp 297–314

González-Pérez JA, González-Vila FJ, Almendros G, Knicker H (2004) The effect of fire on soil organic matter—a review. Environ Intern 30:855–870

González-Vila FJ, Tinoco P, Almendros G, Martin F (2001) Pyrolysis-GC-MS analysis of the formation and degradation stages of charred residues from lignocellulosic biomass. J Agric Food Chem 49:1128–1131

Grasso GM, Ripabelli G, Sammarco ML, Mazzoleni S (1996) Effects of heating on the microbial populations of a grassland soil. Int J Wildland Fire 6:67–70

Hamer U, Marschner B, Brodowski S, Amelung W (2004) Interactive priming of black carbon and glucose mineralisation. Org Geochem 35:823–830

Harvey AE, Larsen MJ, Jurgensen MF (1976) Distribution of ectomycorrhizae in mature Douglas-fir/larch forest soil in western Montana. For Sci 22:393–398

Haslam SFI, Chudek JA, Goldspink CR, Hopkins DW (1998) Organic matter accumulation following fires in a moorland soil chronosequence. Global Change Biol 4:305–313

Hatcher PG, Schnitzer M, Dennis LW, Maciel GE (1981) Aromaticity of humic substances in soils. Soil Sci Soc Am J 45:1089–1094

Haumaier L, Zech W (1995) Black carbon—possible source of highly aromatic components of soil humic acids. Org Geochem 23:191–196

Henderson GS, Golding DL (1983) The effect of slash burning on the water repellence of forest soils at Vancouver, British Columbia. Can J For Res 13:353–355

Hernández T, García C, Reinhardt I (1997) Short-term effect of wildfire on the chemical, biochemical and microbiological properties of Mediterranean pine forest soils. Biol Fertil Soil 25:109–116

Higman EB, Schmeltz I, Schlotzhauer WS (1970) Products from the thermal degradation of some naturally occurring materials. J Agr Food Chem 18:636–639

Hockaday WC, Grannas AM, Kim S, Hatcher PG (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Org Geochem 37:501–510

Hopkins MS, Graham AW, Hewett R, Ash J, Head J (1990) Evidence of late Pleistocene fires and eucalypt forest from a north Queensland humid tropical rainforest site. Aust J Ecol 15:345–357

Huffman EL, MacDonald L, Stednick JD (2001) Strength and persistence of fire-induced soil hydrophobicity under ponderosa and lodgepole pine, Colorado Front Range. Hydrol Process 15:2877–2892

Ikan R, Rubinsztain Y, Nissenbaum A, Kaplan IR (1996) Geochemical aspects of the Maillard reaction. In: Ikan R (ed) The Maillard reaction; consequences for the chemical and life sciences. John Wiley & Sons, Chichester, pp 1–25

Ivany LC, Salawitch RJ (1993) Carbon isotopic evidence for biomass burning at the K-T boundary. Geology 21:487–490

Johnson DW, Curtis PS (2001) Effect of forest management on soil C and N storage: meta analysis. Forest Ecol Manag 140:227–238

Johnson WR, Nedlock JW, Hale RW (1972) Mechanisms of pyrolysis of poly (amino acids). Tob Sci 17:89–93

Jones TP, Chaloner WG (1991) Fossil charcoal, its recognition and palaeoatmospheric significance. Palaeogeogr Palaeoclimatol Palaeoecol 97:39–50

Kim S, Kaplan LA, Benner R, Hatcher PG (2004) Hydrogen-deficient molecules in natural riverine water samples-evidence for the existence of black carbon in DOM. Mar Chem 92:225–234

Kim EJ, Oh JE, Chang YS (2003) Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil. Sci Total Environ 311:177–189

Klopatek JM (1987) Nitrogen mineralization and nitrification in mineral soils of pinyon-juniper ecosystems. Soil Sci Soc Am J 51:453–457

Klopatek CC, DeBano LF, Klopatek JM (1988) Effets of simulated fire on vesicular-arbuscular mycorrhizae in pinon-juniper woodland soil. Plant Soil 109:245–249

Knicker H (2000) Biogenic nitrogen in soils as revealed by solid-state carbon-13 and nitrogen-15 nuclear magnetic resonance spectroscopy. J Environ Qual 29:715–723

Knicker H (2004) Stabilization of N-compounds in soil and organic matter rich sediments—What is the difference? Mar Chem 92:167–195

Knicker H, Almendros G, González-Vila FJ, González-Pérez JA, Polvillo O (2006) Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Mediterranean ecosystems: a solid-state ^{13}C NMR study. Eur J Soil Sci 57:558–569

Knicker H, Almendros G, González-Vila FJ, Martín F, Lüdemann H-D (1996) ^{13}C- and ^{15}N-NMR spectroscopic examination of the transformation of organic nitrogen in plant biomass during thermal treatment. Soil Biol Biochem 28:1053–1060

Knicker H, Fründ R, Lüdemann H-D (1993) The chemical nature of nitrogen in soil organic matter. Naturwissenschaften 80:219–221

Knicker H, Lüdemann H-D (1995) N-15 and C-13 CPMAS and solution NMR studies of N-15 enriched plant material during 600 days of microbial degradation. Org Geochem 23:329–341

Knicker H, Lüdemann H-D, Haider K (1997) Incorporation studies of NH_4^+ during incubation of organic residues by ^{15}N-CPMAS-NMR-spectroscopy. Eur J Soil Sci 48:431–441

Knicker H, Skjemstad JO (2000) Nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils as revealed by solid-state ^{13}C and ^{15}N NMR spectroscopy. Aust J Soil Res 38:113–127

Knicker H, González-Vila FJ, Polvillo O, González JA, Almendros G (2005a) Fire-induced transformation of C- and N-forms in different organic soil fractions from a Dystric Cambisol under a Mediterranean pine forest (*Pinus pinaster*). Soil Biol Biochem 37:701–718

Knicker H, Totsche K-U, Almendros G, González-Vila FJ (2005b) Condensation degree of burnt peat and plant residues and the reliability of solid-state VACP MAS ^{13}C NMR spectra obtained from pyrogenic humic material. Org Geochem 36:1359–1377

Kramer RW, Kujawinski EB, Hatcher PG (2004) Identification of black carbon derived structures in a volcanic ash soil humic acid by Fourier transform ion cyclotron resonance mass spectrometry. Environ Sci Technol 38:3387–3395

Kuhlbusch TAJ (1995) Method for determining black carbon in residues of vegetation fires. Environ Sci Technol 29:2695–2702

Kuhlbusch TAJ (1998) Black carbon and the carbon cycle. Science 280:1903–1904

Kuhlbusch TAJ, Crutzen PJ (1995) Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and a source of O_2. Glob Biogeochem Cycles 9:491–501

Kutiel P, Inbar M (1993) Fire impacts on soil nutrients and soil erosion in a Mediterranean pine forest plantation. Catena 20:129–139

Kutiel P, Lavee H, Segev M, Benyamini Y (1995) The effect of fire-induced surface heterogeneity on rainfall-runoff-erosion relationships in an eastern Mediterranean ecosystem, Israel. Catena 25:77–87

Lehmann J, Liang B, Solomon D, Lerotic M, Luizao F, Kinyangi J, Schäfer T, Wirick S, Jacobsen C (2005) Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping non-scale distribution of organic carbon forms in soil: application to black carbon particles. Global Biochem Cylces 19:doi: 10.1029/2004GB002435

Lide DR (2004) CRC handbook of chemistry and physics. CRC Press, Boca Raton, FL

Lüdemann H-D, Nimz H (1973) Carbon-13 nuclear magnetic resonance spectra of lignins. Biochem Biophys Com 52:1162–1169

MacDonald L, Huffman EL (2004) Post-fire soil repellency: persistence and soil moisture thresholds. Soil Sci Soc Am J 68:1729–1734

Maie N, Knicker H, Watanbe A, Kimura M (2006) Heterocyclic N in the highly humified humic acids extracted from subsoil of paddy fields and surface ando soils. Org Geochem 37:12–19

Masiello CA (2004) New directions in black carbon organic geochemistry. Mar Chem 92:201–213

Masiello CA, Druffel ERM (1998) Black carbon in deep-sea sediments. Science 280:1911–1913

Masiello CA, Druffel ERM (2003) Organic and black carbon ^{13}C and ^{14}C through the Santa Monica Basin oxic-anoxic transition. Geophys Res Lett 30:doi:10.1029/2002GL015050

McGrath TE, Chan WG, Hajaligol R (2003) Low temperature mechanism for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of cellulose. J Anal Appl Pyrolysis 66:51–70

Meetani MA, Basile F, Voorhees KJ (2003) Investigation of pyrolysis residues of poly(amino acids) using matrix assisted laser desorption ionization-time of flight-mass spectrometry. J Anal Appl Pyrolysis 68/69:101–113

Middelburg JJ, Nieuwenhuize J, van Breugel P (1999) Black carbon in marine sediments. Mar Chem 65:245–252

Mill AJ, Fey MV (2004) Frequent fires intensify soil crusting: physicochemical feedback in the pedoderm of long-term burn experiments in South Africa. Geoderma 121:45–64

Neary DG, Klopatek CC, DeBano LF, Fgolliott PF (1999) Fire effects on belowground sustainability: a review and synthesis. For Ecol Manage 122:51–71

Ojima D, Schimel DS, Parton WJ, Owensby CE (1994) Long and short-term effects of fire on nitrogen cycling in tallgrass prairie. Biogeochem 24:67–84

Parker JL, Fernandez IJ, Rustad LE, Norton SA (2001) Effects of nitrogen enrichment, wildfire, and harvesting on forest-soil carbon and nitrogen. Soil Sci Soc Am J 65:1248–1255

Pietikäinen J, Fritze H (1995) Clear-cutting and prescribed burning in coniferous forest: comparison of effects on soil fungal and total microbial biomass respiration activity and nitrification. Soil Biol Biochem 27:101–109

Prieto-Fernández A, Carballas M, Carballas T (2004) Inorganic and organic N pools in soils burned or heated: immediate alteration and evolution after forest wildfires. Geoderma 121:291–306

Pyne SJ (2001) Fire, a brief history. University of Washington Press, Seattle, WA

Raison RJ (1979) Modifications of the soil environment by vegetation fires: a review. Plant Soil 51:73–108

Ralph J, Hatfield RD (1991) Pyrolysis-GC-MS characterization of forage materials. J Agric Food Chem 39:1426–1437

Reeves JB, Francis BA (1998) Pyrolysis-gas chromatography for the analysis of proteins: with emphasis and forages. In: van Bergen PF (ed) Nitrogen-containing macromolecules in the bio- and geoshpere. American Chemical Society, Washington, DC, pp 47–62

Robichaud PR, Hungerford RD (2000) Water repellency by laboratory burning of four northern Rocky Mountain forest soils. J Hydrol 231–232:207–219

Rollins MS, Cohen AD, Durig JR (1993) Effects of fires on the chemical and petrographic composition of peat in the Snuggedy Swamp, South Carolina. Int J Coal Geol 22:101–117

Rumpel C, Alexis M, Chabbi A, Chaplot V, Rasse DP, Valentin C, Mariotti A (2006) Black carbon contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture. Geoderma 130:34–45

Rumpel C, Kögel-Knabner I (2004) Microbial use of lignite compared to recent plant litter as substrates in reclaimend coal mine soils. Soil Biol Biochem 36:67–75

Rundel PW (1983) Impact of fire on nutrient cycles in Mediterranean-type ecosystems with reference to chaparral. In: Kruger FJ, Mitchell DT, Jarvis JUM (eds) Mediterranean-type ecosystems: the role of nutrients. Springer-Verlag, New York, pp 192–207

Saldarriaga JG, West DC (1986) Holocene fires in the northern Amazon basin. Quaternary Res 26:358–366

Savage SM (1974) Mechanism of fire-induced water repellency in soil. Soil Sci Amer Proc 38:652–657

Schmid E-M, Knicker H, Bäumler R, Knabner-Kögel I (2001) Chemical composition of the organic matter in neolithic soil material as revealed by CPMAS ^{13}C NMR spectroscopy, polysaccharide analysis and CuO oxidation. Soil Sci 166:569–584

Schmid E-M, Skjemstad JO, Glaser B, Knicker H, Kögel-Knabner I (2002) Detection of charred organic matter in soils from a Neolithic settlement in Southern Bavaria, Germany. Geoderma 107:71–91

Schmidt MWI, Noack AG (2000) Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Glob Biogeochem Cycles 14:777–793

Schmidt MWI, Skjemstad JO, Czimczik CI, Glaser B, Prentice KM, Gélinas Y, Kuhlbusch TAJ (2001) Comparative analysis of black carbon in soils. Glob Biogeochem Cycles 15:163–167

Schmidt MWI, Skjemstad JO, Gehrt E, Kögel-Knabner I (1999) Charred organic carbon in German chernozemic soils. Eur J Soil Sci 50:351–365

Schnitzer M, Calderoni G (1985) Some chemical characteristics of paleosol humic acids. Chem Geol 53:175–184

Scotter DR (1970) Soil temperatures under grass fires. Aust J Soil Res 8:273–279

Sergides CA, Jassim JA, Chughtai AR, Smith DM (1987) The structure of hexane soot, part II, ozonation studies. Appl Spectrosc 41:482–492

Sharma RK, Chan WG, Seeman JI, Hajaligol MR (2003) Formation of low molecular weight heterocycles and polycyclic aromatic compounds (PACs) in the pyrolysis of α-amino acids. J Anal Appl Pyrolysis 66:97–121

Sharma RK, Hajaligol MR (2003) Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. J Anal Appl Pyrolysis 66:123–144

Sharma RK, Wooten JB, Baliga VL, Hajaligol MR (2001) Characterization of chars from biomass-derived materials: pectin chars. Fuel 2001:1825–1836

Sharma RK, Wooten JB, Baliga VL, Lin X, Chan WG, Hajaligol MR (2004a) Characterization of chars from pyrolysis of lignin. Fuel 83:1469–1482

Sharma RK, Chan WG, Wang J, Waymack BE, Wooten JB, Seeman JI, Hajaligol MR (2004b) On the role of peptides in the pyrolysis of amino acids. J Anal Appl Pyrolysis 72:153–163

Shindo H, Honna T, Yamamoto S, Honma H (2004) Contribution of charred plant fragments to soil organic carbon in Japanese volcanic ash soils containing black humic acids. Org Geochem 35:235–241

Shindo H, Urabe M (1993) Changes in the humus composition of volcanic ash soils by heating at various temperatures. Soil Sci Plant Nutr 39:189–192

Skjemstad JO, Clarke P, Taylor JA, Oades JM, McClure SG (1996) The chemistry and nature of protected carbon in soil. Aust J Soil Res 34:251–271

Skjemstad JO, Janik LJ, Head MJ, McClure SG (1993) High energy ultraviolet photo-oxidation: a novel technique for studying physically protected organic matter in clay- and silt-sized aggregates. J Soil Sci 44:485–499

Skjemstad JO, Le Feuvre RP, Prebble RE (1990) Turnover of soil organic matter under pasture as determined by ^{13}C natural abundance. Aust J Soil Sci Res 28:267–276

Skjemstad JO, Reicosky DC, Wilts AR, McGowan JA (2002) Charcoal carbon in US agricultural soils. Soil Sci Soc Am J 66:1249–1255

Skjemstad JO, Taylor JA, Smernik RJ (1999) Estimation of charcoal (char) in soils. Commun Soil Sci Plant Anal 30:2283–2298

Smernik RJ, Skjemstad JO, Oades JM (2000) Virtual fractionation of charcoal from soil organic matter using solid state ^{13}C NMR spectral editing. Aust J Soil Res 38:665–683

Smith P, Smith JU, Powlson DS, McGill WB, Arah JRM, Chertov OG, Coleman K, Franko U, Frolking S, Jenkinson DS (1997) A comparison of the performance of nine soil organic matter models using datasets from seven long-term experiments. Geoderma 81:153–225

Trompowsky PM, Benites VM, Madari BE, Pimenta SA, Hockaday WC, Hatcher PG (2005) Characterization of humic like substances obtained by chemical oxidation of eucalyptus charcoal. Org Geochem 36:1480–1489

Ulery AL (1993) Wood-ash composition and soil pH following intense burning. Soil Sci 156:358–364

Vázquez FJ, Acea MJ, Carballas T (1993) Soil microbial populations after wildfire. FEMS Microbiol Ecol 13:93–103

Venkatesan MI, Dahl J (1989) Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary. Nature 338:57–60

Villar MC, Petrikova V, Díaz-Ravina M, Carballas T (2004) Changes in soil microbial biomass and aggregate stability following burning and soil rehabilitation. Geoderma 122:73–82

Willcox G (1999) Charcoal analysis and Holocene vegetation history in southern Syria. Quat Sci Rev 18:711–716

Wittenberg U, Heimann M, Esser G, McGuire AD, Sauf W (1998) On the influence of biomass burning on the seasonal CO_2 signal as observed at monitoring stations. Glob Biogeochem Cycles 12:531–544

Wolbach WS, Gimour I, Anders E, Orth CJ, Brooks RR (1988) Global fire at the Cretaceous-Tertiary boundary. Nature 334:665–669

Wondrack L, Szanto M, Wood WA (1989) Depolymerization of water soluble coal polymer from subbituminous coal and lignite by lignin peroxidase. Appl Biochem Biotechnol 20/21:765–780

Zhukov AB (1976) The impact of anthropogenic factors on forest biogeocenosis in Siberia. Ecol Bull 21:41–45