Review article

The effect of fire on soil organic matter—a review

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Abstract

The extent of the soil organic carbon pool doubles that present in the atmosphere and is about two to three times greater than that accumulated in living organisms in all Earth's terrestrial ecosystems. In such a scenario, one of the several ecological and environmental impacts of fires is that biomass burning is a significant source of greenhouse gases responsible for global warming. Nevertheless, the oxidation of biomass is usually incomplete and a range of pyrolysis compounds and particulate organic matter (OM) in aerosols are produced simultaneously to the thermal modification of pre-existing C forms in soil. These changes lead to the evolution of the OM to "pyromorphic humus", composed by rearranged macromolecular substances of weak colloidal properties and an enhanced resistance against chemical and biological degradation. Hence the occurrence of fires in both undisturbed and agricultural ecosystems may produce long-lasting effects on soils' OM composition and dynamics. Due to the large extent of the C pool in soils, small deviations in the different C forms may also have a significant effect in the global C balance and consequently on climate change. This paper reviews the effect of forest fires on the quantity and quality of soils' OM. It is focused mainly on the most stable pool of soil C; i.e., that having a large residence time, composed of free lipids, colloidal fractions, including humic acids (HA) and fulvic acids (FA), and other resilient forms. The main transformations exerted by fire on soil humus include the accumulation of new particulate C forms highly resistant to oxidation and biological degradation including the so-called "black carbon" (BC). Controversial environmental implications of such processes, specifically in the stabilisation of C in soil and their bearing on the global C cycle are discussed.
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1. Introduction

Soil is the largest carbon pool on the Earth's surface (2157–2293 Pg). Of this C, *ca.* 70 % is organic and the remaining consists of carbonates (Batjes, 1996). Soil organic carbon pool doubles that present in the atmosphere (760 Pg) and is about two to three times larger than that in living matter in all terrestrial ecosystems (Prentice et al., 2001; Post et al., 1990). Depending on their turnover rates in soil, three conceptual C fractions can be distinguished: active-labile and active-intermediate fractions—that may remain in soil for years or decades—and passive or refractory OM remaining in soil from centuries to millennia. In forest ecosystems, most C is stored in intermediate pools containing materials like wood fragments, litter, or partially decomposed OM that

vary in their turnover time (Balesdent and Mariotti, 1996; Schulze et al., 2000) (Table 1). Because of the large amount of C stored in soils, small deviations in the proportion of the above different forms may have a significant effect on the global C balance and therefore on climate change.

During the decomposition of the non-humified organic materials (remains of plants, animals and microorganisms) in soil, a variable proportion of organic C (60–80%) is reverted to the atmosphere as CO_2. This is a rapid mineralization process that usually takes place during the first year. The remaining, non-mineralized C undergoes slower oxidation processes and, after complex transformations, it either turns into microbial biomass or is stabilized in the form of humic substances. The latter process, referred to as humification, implies severe changes in the stoichiometry and chemical complexity of the original macromolecular materials leading to humic substances with enhanced resistance to biodegradation and mineralisation (Tate, 1987). These changes are not only a consequence of the microbial

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Table 1
Approximate decomposition time for some carbonaceous forest materials in the environment

Material	Decomposition time
Sugars (Carbohydrates)	Days
Leaves	Seasons
Living wood	Up to millennia
	(4000 years in Bristlecone pine)
Soil organic matter	Up to millennia
Black carbon (BC)	Almost unalterable
	(360 million years Famennian age)

activity but also of abiotic diagenetic transformations induced by external physical or physico-chemical factors, including fire (Hatcher and Spiker, 1988).

Vegetation fires have several ecological and environmental impacts. Biomass burning is a significant global source of atmospheric gases such as carbon dioxide (CO_2) and methane (CH_4), which are green-house gases contributing to global warming (Levine, 1994). During forest fires large amounts of CO_2 are released to the atmosphere. As the vegetation in the burned ecosystems regrows, CO_2 is again removed from the atmosphere via photosynthesis and incorporated into the new vegetative growth with a neat C balance that has been considered null (Levine, 1996a; Levine et al., 1995).

The simplest model for biomass burning assumes that the ending products are H_2O, CO_2 and minerals contained in the ash. However, the complete oxidation of biomass requires conditions for oxygen availability during the combustion process which, in general, do not concur in nature. Under environmental conditions, the combustion is often incomplete and CO, CH_4, a complex range of pyrolysis products including hydrocarbons and particulate OM fractions are also produced (Cofer et al., 1997). Therefore, vegetation fires also produce a considerable amount of newly formed C forms in addition to the thermal modification of the previously existing C forms in the ecosystem.

Only a small part of the heat generated during a forest fire is radiated to soil. The nature of the changes in soil depends on both the temperatures reached at different soil depths and the degree of heating that the different soil components can withstand before being altered. The degree of soil heating depends on factors such as the magnitude and duration of energy transferred from the fire to the soil, soil composition (including moisture), structure (porosity), etc. In general, below ground temperatures will rise very slowly due to the fact that dry soil is a very good insulator (DeBano et al., 1998), and to that in moist soils the evaporation of water will not allow a moist layer to go above the water boiling point (Campbell et al., 1995). Humphreys and Craig (1981) studied the soil temperature generated during different fire situations in Australian ecosystems finding that at 1 mm below the soil surface, the temperature only reaches 200 °C even under wildfire conditions whereas controlled burns reach only 125 °C and grasslands only 70 °C. By 2–3 cm,

under their conditions, the soil temperature never exceeds the ambient temperature. However, the real effects of temperature on soil OM is a complex issue: Firstly, it is time-dependant (i.e. the effect of 10 s at 1000 °C could or could not be comparable to that for 30 min at 300 °C, this depends on the soil parameter under study, soil moisture and mineralogy and composition of soil OM) and no in-depth studies exists on this particular; secondly, soil temperature during fires is an average value (small OM rich particles may reach more than 1000 °C when burning on the topsoil); thirdly, even in very low intensity fires, the biological activity rebuild the soil aggregates and the OM particles burnt at different temperatures are distributed very quickly within the whole organic horizons.

Distillation of volatiles and loss of organic carbon in soils start at temperatures between 100 and 200 °C (Kang and Sajjapongse, 1980; Giovannini and Lucchesi, 1997), above 200 °C the charring process starts. Between 130 and 190 °C lignins and hemicelluloses begin to degrade (Chandler et al., 1983). Higher temperatures, over 300 °C, exert structural changes, mainly decarboxylations in the soil macromolecules HAs and FAs and an increase in the proportion of aromatic structures (Almendros et al., 1990, 1992; Knicker et al., 1996). In general, changes on soil organic matter caused by fire or heat allow the definition of "pyromorphic humus". This is composed of rearranged macromolecular substances of weak colloidal properties and enhanced resistance to biological degradation, as inferred from laboratory incubation experiments with natural or laboratory-heated samples (Almendros et al., 1984b; González-Vila and Almendros, 2003).

Therefore, during a forest fire, a considerable rearrangement of C forms occurs and refractory and oxidation-resistant organic C forms of considerable residence time, including BC, are formed "de novo" (Schulze et al., 2000). Only a fraction of the total production of oxidation-resistant organic C produced from biomass burning is likely to be sequestered in the slow-cycling "geological" carbon reservoir (Bird et al., 1999). In fact, in some world's areas, like Mediterranean regions, where extreme environmental conditions alternate through the year, biological activity is not especially favorable to humification processes but to intense mineralization. Under such conditions, the relative importance of abiotic constraints such as fire and irreversible dehydration favored by intense solar radiation and drastic drying cycles, are important factors in the formation of stable OM in soil. Fire is considered the main disturbance in the Mediterranean basin (Trabaud, 1984; Naveh, 1990; Barbéro et al., 1998).

Occurrence of wildfires in forest ecosystems has lasting effects on both the microbial composition and the OM, and hence on the whole soil dynamics. The alteration of natural ecosystems affects OM turnover and therefore productivity and community structure may be also affected (Pastor and Post, 1986). It is well known the global effect of forest fires in the release of CO_2 and other greenhouse gases to the

atmosphere, caused by the depletion of ecosystems' above-ground biomass, including the organic topsoil horizons, composed mainly of plant litter (Crutzen and Goldammer, 1993; Levine, 1996b and references therein), this represents a severe depletion of the ecosystem's largest portion of the labile or active C pool. Fire also acts as an evolutionary force for plants and other terrestrial vegetation species that, in the course of time, co-evolved with fires (Ahlgren and Ahlgren, 1960; Pyne, 1996; Keely and Zedler, 1998). This force includes man kind (Pyne and Goldammer, 1997; Caldararo, 2002) and, from an holistic viewpoint, its effect and natural occurrence is greatest under ecophysiological formations where the availability of nutrients is suboptimum as a consequence of bioclimatic constraints or soil organo-mineral interactions. Less is known however about the effect that forest fires exerts on C stabilization in soil and on the more stable pool of C, represented mainly by the colloidal soil fractions and on the quality and quantity of soil humic materials.

2. Fires at a global scale

Unambiguous evidence for wildfires go back to the appearance of gymnosperms during the Famennian age, in the boundary between the Devonian and Carboniferous periods (Jones and Rowe, 1999). At this age (ca. 360×10^6 years b.p.) enough photosynthesis-derived atmospheric oxygen was available and, together with lightening, favored the ignition of biomass. Hence, the production of charcoal has often been considered as indicator of the occurrence of ancient fires. Most of today's fires are caused by human activities and only a minor part are produced by environmental causes (FAO, 2001).

Vegetation fires are a global phenomenon occurring in tropical, temperate and boreal regions. Biomass burning is a regular feature in tropical forests of Brazil and Indonesia, temperate forests of the United States and Europe, boreal forests of Siberia, China and Canada, tropical savannas of Africa and agricultural lands of the United Sates and Europe (Levine, 1996a). It is estimated that, at a global scale, between 530 and 555×10^6 ha are affected by fire every year. Fires annually burn $10-15 \times 10^6$ ha of boreal and temperate forest, $20-40 \times 10^6$ ha of tropical forests and up to 500×10^6 ha of tropical and subtropical savannas, woodlands and open forests (Goldammer, 1995). Fires in world's savannas and forested areas represent 60% of a total of 87 Pg biomass that burns every year (Table 2).

3. Effect of fire in soil microbes and C mineralization

After a forest fire there are several interactive factors that affect soil biota and, in turn, the evolution of OM may also be affected. These factors include direct sterilization, formation of ash, charcoal and fire-altered OM, and modifications of the soil forming factors and structure of the microflora and the whole trophic system i.e. changes in canopy and vegetation affecting soil properties.

In the short term, fire causes a drastic reduction in soil microbial biomass (Prieto-Fernández et al., 1998). In general bacteria are more tolerant to heat than fungi (Bollen, 1969), therefore, it is usually observed that burning favours bacteria over fungi (Dunn et al., 1979; Bissett and Parkinson, 1980; Sharma, 1981; Deka and Mishra, 1983). Also, after a fire there is an increase of available nutrients in soil, mainly in the form of water-soluble components of ash that became available to living organisms. The "fertilizing" effect of fire is known since the beginning of agriculture and forestry (Pyne, 2001) and also affects soil microbial populations (Bååth and Arnebrant, 1994). Part of this effect derives from an increase in soil pH frequently observed after a fire (Table 2) which is associated to an increase in exchangeable cations in soil (Viro, 1974; Raison, 1979) resembling the effect of liming the soil. Also, an increased presence of N-fixing bacteria after wildfires has been observed (Johnson, 1992).

The effect of fire on the potentially mineralizable C ("in vitro" respiratory activity measurements under laboratory conditions) of the soil OM labile C pool is variable. Increased mineralization rates have been observed after a fire event in soils under *Quercus rotundifolia* (Almendros et al., 1990), *Q. suber* (Rashid, 1987) and *Pinus sylvestris* (Fernández et al., 1997), whereas in other soils from pine forests severely affected by fire a decreased biodegradability is observed (Almendros et al., 1984a). The latter case is probably due to the high combustibility of the resinous plants and residues, almost totally destroyed by fire, that led to the accumulation of BC and other organic materials highly refractory to biodegradation (Almendros et al., 1984b). Conversely, in the former case (fresh plant biomass of low autocombustibility) the effects of fire are more effective in killing and drying than charring, i.e. resulting in soil inputs of biodegradable C-forms. Alterations in the mineralization indices of some soils lasting at least for 2 years after a wildfire have been found, accompanied by an increase in OM stabilization (Fernández et al., 1999).

Table 2
Global estimates of annual amount of biomass burning and the resulting release of carbon and CO_2 to the atmosphere (from Levine, 1994)

Source of burning	Biomass burned (Tg year^{-1})	Carbon released[a] (Tg C year^{-1})	CO_2 released[b] (Tg C year^{-1})
Savannas	3690	1660	1494
Agricultural waste	2020	910	819
Fuel wood	1430	640	576
Tropical forest	1260	570	513
Temperate and Boreal forest	280	130	117
Charcoal	21	30	27
Total wood	8700	3940	3547

[a] Based on a carbon content of 45% in the biomass material. In the case of charcoal, the rate of burning has been multiplied by 1.4.

[b] Assuming that 90% of the C released is in the form of CO_2.

The presence of variable quantities of relatively inert macroscopic charcoal fragments in soil after a fire also affects soil organisms. Charcoal stimulates the establishment and activity of ectomycorrhyzae (Harvey et al., 1976), acts as a strong sorption agent for germination- and growth-inhibiting phenolic substances (Zackrisson et al., 1996; Wardle et al., 1998) and its presence in the substrate seems to increase soil microbial respiration in sites dominated by vegetation rich in phenolics (i.e. heathers, ericaceous brushwood) (Wardle et al., 1998). Other studies show lower microbial populations and lower activity in soils with tropical deciduous forest vegetation after fire and in unburned soils amended with ash (García-Oliva et al., 1999).

Modifications caused by heat on soil humic materials include an increase in macromolecular condensation that has been proposed as one of a series of mechanisms conferring resistance to microbial attack (Almendros et al., 1990, 1992; Knicker et al., 1996). The changes exerted by heat on the chemical properties of humus have also been shown to cause changes in microbial composition (Pietikäinen et al., 2000).

Finally, forest fires exert many changes on physical and chemical soil properties that, in turn, affect the soil's water infiltration capability and hence its ability to absorb rainfall and snowmelt and to support plants and other life and resistance to erosion. Forest clearance after fire reduces the vegetation canopy and litter layers and undoubtedly affects the processes, microclimate and biodiversity of the soil. The phenomenon is comparable to that of clear-cutting (Pietikäinen, 1999) and includes mainly changes in plant activity, soil temperature and water regimes (Keenan and Kimmins, 1993), with a concomitant effect on soil microbes and humification processes.

4. Effect of fire on the quantity of soil organic carbon

4.1. Organic matter content

The effect of fire on the total soil OM content is highly variable, and depends on several factors including fire type (canopy or aboveground, underground fires), intensity, and even slope. These effects may range from the almost total destruction of the soil OM to increases that may reach 30% in the surface layers as a consequence of external inputs, mainly from dry leaves and partially burnt plant materials in fires affecting the tree canopy (Chandler et al., 1983). Soon after a fire, a sharp decrease in OM content may be observed in some soils, this could be accelerated by changes in soil physico-chemical properties (i.e., water repellency; Savage, 1974; DeBano, 2000) and the temporal removal of the herbaceous layer, with effective erosion-controlling belowground root structures. This increase in soil erodibility leads to rapid loss of topsoil layers (Díaz-Fierros et al., 1987; McNabb and Swanson, 1990; Andreu et al., 1996). However, increases in soil OM content are also reported due to an increased deposition of dry leaves and charred plant materials in fires that affect the tree canopy, as indicated above.

There are many studies on the effects of fires on the total amount of OM (Kang and Sajjapongse, 1980; Giovannini et al., 1987; Kutiel and Kutiel, 1989). Organic carbon losses higher than 50% in the upper 10 cm of a Humic Cambisol under pine forest have been reported after a wildfire (Fernández et al., 1997) and significant C losses of ca. 100% are frequently reported in soils heated under laboratory conditions (Almendros et al., 1984b; Fernández et al., 1997).

However, after a moderate wildfire, an increase of C in soil is usually observed (Table 3) suggesting a substantial incorporation of forest necromass (Rashid, 1987). In contrast, in samples 3–3′, from a Calcaric Cambisol from a *Pinus halepensis* forest (Table 3), a sharp organic C reduction is observed after a high intensity wildfire.

Johnson and Curtis (2001) made a metadata analysis on a comprehensive database of soils from North America affected or not by different fire treatments (wildfire, prescribed fire and broadcast burning). They detected significant differences in both soil C and N after 10 years from the fire event. Lower C content was found in soils affected by prescribed fire and higher soil C content following wildfire. The latter is attributed to the accumula-

Table 3
Bulk characteristics of soils affected by natural fires, and neighbouring unaltered soil

Ref.	Soil type	Source	Vegetation	pH	C (g 100g^{-1})	C/N	Cation exchange (cmol$_c$kg^{-1})	Base saturation (cmol$_c$kg^{-1})
1	Dystric Xerochrept	Almendros et al., 1990	*Quercus rotundifolia*	4.8	1.4	16.0	10.0	2.9
1′	(burned)			6.2	1.5	12.0	18.0	5.5
2	Dystric Xerochrept	Almendros et al., 1988	*Pinus pinea*	5.7	3.0	12.0	24.6	14.3
2′	(burned)			6.7	4.0	11.0	40.2	29.2
3	Calcaric Cambisol	Tinoco, 2000	*Pinus halepensis*	6.9	21.3	14.5	70.6	49.7
3′	(burned)			8.7	3.9	12.0	13.5	13.5
4	Umbrihumic Umbrisol	Tinoco, 2000	*Pinus sylvestris*	4.6	6.9	14.5	23.5	2.14
4′	Epidystric Cambisol (burned)			5.7	6.4	8.0	41.2	4.0
5	Typic Xerochrept	González-Vila et al., 2002	*Pinus* sp.	6.1	3.9	18.6	nd	nd
5′	(burned)			6.8	8.6	15.6	nd	nd
6	Dystric Xerochrept	Almendros et al., 1984a	*Pinus pinea*	5.9	2.8	15.6	28.4	16.5
6′	(burned)			6.9	3.8	13.0	42.9	26.3

Table 4

Yield and carbon distribution in the different soil particle size fractions in a pine forest soil from Sierra de Aznalcóllar, Seville, Spain (from González-Vila et al., 2002)

Fraction	Yield (% bulk soil)		C (mg g^{-1} bulk soil)		
	FU soil[a]	FA soil[b]	FU soil	FA soil	EF[c]
Sand (2 mm–63 μm)	37	39	19	27	1.4
Coarse silt (63–20 μm)	9	12	65	181	2.8
Medium silt (20–6 μm)	16	17	44	135	3.1
Fine silt (6–2 μm)	20	14	5	11	2.1
Clay (<2 μm)	19	17	5	13	2.7

[a] Fire unaffected soil.
[b] Fire affected soil.
[c] Enrichment factor.

tion of charcoal and recalcitrant hydrophobic OM and to the encroachment of post-fire N-fixing vegetation.

The C/N ratios of soil after burning are usually lower than in the original soils (Table 3), a phenomenon frequently cited in several types of post-fire soils (Almendros et al., 1984a,b; Viro, 1974; Vega, 1986).

In general, after the passage of fire, a trend to coarser soil textures is observed. It is due to some extent to a heat-induced formation of stable aggregates from clay and silt fractions (Almendros et al., 1984a; Ulery and Graham, 1993; Ketterings et al., 2000). An increase in the C content in all size fractions of a soil mineral phase has been observed in a fire-affected Xerochrept (Table 4). The lowest enrichment corresponded to the sand-size fraction and the highest to the coarse silt-size and clay-size fractions (González-Vila et al., 2002).

Apart from the external inputs of OM from fire-affected vegetation, it is also necessary to consider that litter (which is usually removed before soil sampling) turns, after fire, into particulate, fine-earth sized (<2 mm) particles, which mix with the whole soil material in the organic horizon, thus causing a net increase in the C content, which is consistent with the protocol of soil sampling and the processes occurring, and leads to highly friable charred organic matter and particulate charcoal fractions.

4.2. Free lipids

The soil free lipids represents a diverse group of hydrophobic substances ranging from simple compounds such as fatty acids, to more complex substances as sterols, terpenes, polynuclear hydrocarbons, chlorophylls, fats, waxes, and resins. In aerobic soils lipids may consist mostly of remains of plant and microbial tissues accounting for 2 to 6% of soil humus. Some lipids are physiologically active substances such as inhibitors or plant growth promoting factors. Waxes and similar materials could be mostly responsible for the water-repellent condition of certain soils (Dinel et al., 1990; Stevenson, 1994).

After a forest fire, the lipid fraction extracted from a Dystric Xerochrept under *Pinus pinea* was more than six times greater in weight than that in the unburned one

(Almendros et al., 1988). This difference is attributed to the translocation into the soil of organic substances released from burning litter or biomass (DeBano et al., 1970, 1976). The formation of non-wettable soils after forest fires has been partially attributed to this phenomenon (Savage, 1974; Giovannini and Lucchesi, 1983). A recent review of the role of fire on soil water repellence has been recently published by DeBano (2000).

4.3. Humic acids

After natural fires and laboratory heating experiments, a relative increase in the abundance of the humin fraction is systematically observed, this occurs at the expense of the FA and HA fractions (Almendros et al., 1990; Fernández et al., 1997; González-Vila and Almendros, 2003). This effect is greater in the case of fractions with a more thermolabile character (free OM and FAs, and the non-humified (labile) and/or weakly associated to the mineral fraction mainly by physical interactions) than for the humified (stable) fractions involved in tight organo-mineral interactions. A progressive increase of the non-extractable humin fraction is very apparent and, at high temperatures, humin is the main organic component remaining in the soil, and—in the soils heavily affected by fire—would correspond to the accumulation of BC (Fig. 1).

4.4. Black carbon (BC)

Black carbon has been recently reviewed by Schmidt and Noack (2000), there is no generally accepted terminology for BC but, in recent literature this terms is preferred to alternative synonyms such as charcoal, soot, elemental carbon, pyrogenic carbon, etc.

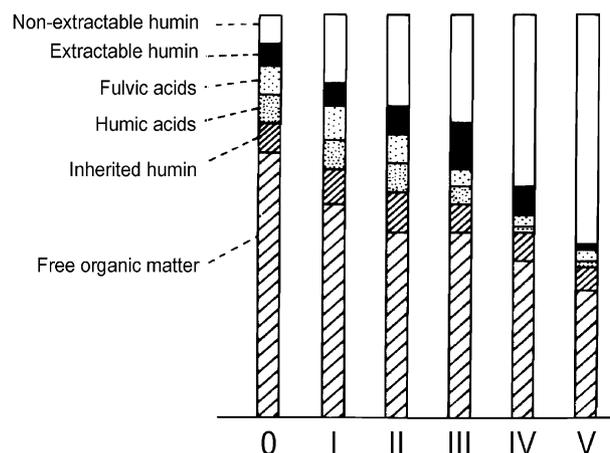Novakov (1984) defined BC as "combustion-produced black particulate carbon having a graphitic microstruc-

Fig. 1. Effect of progressive heating (laboratory experiment) on the soil humus fractions from a Dystric Xerochrept. The soil samples were heated in an oven set at 1000 °C for a variable period of time. 0: Control (no heating); I: 20 s; II: 40 s; III: 80 s; IV: 160 s; V: 320 s (from Almendros et al., 1984b).

ture'', however, better than this narrow sense, BC can be understood as a continuum from partly charred plant material through char and charcoal to graphite and shoot particles condensed from the gas phase. It is an ubiquitous material product of the incomplete combustion of vegetation and fossil fuels, with a level of organization that goes from that of a low rank coal like material to that resembling coal and anthracite (Goldberg, 1985; Kuhlbusch, 1998a). The micromorphological and chemical features of this refractory material are described in Schmidt and Noack (2000), Poirier et al. (2000, 2002). It behaves as a highly aromatic material and, in the case of that formed by vegetation fires, it often consists of randomly oriented stacks of few graphitic layers. In any case, the final BC produced is not necessarily graphitic, and this black material, even when completely amorphous, contains a substantial alkyl domain and a considerable oxygen content (endocyclic or lactone-like) (Poirier et al., 2002; Almendros et al., 2003).

There are serious methodological problems in isolating and quantifying BC in nature mainly due to the heterogeneous nature of this material and the wide range of analytical approaches available (Kuhlbusch, 1998b), and there is an urgent need for standard reference materials and the development of adequate protocols for analysis (Schmidt and Noack, 2000).

Global BC production by vegetation burning is estimated to account for as much as 0.2 Pg year^{-1}, i.e., 2.7 times the average total fossil fuel emissions of Spain and Portugal (0.0602 and 0.0137 Pg C year^{-1}) for the period 1988–1998. Black carbon formation affects the net C balance and may constitute a substantial fraction of the ''missing carbon'' in the global C budget i.e. it is estimated that BC is reducing net CO_2 release caused by permanent deforestation by up to 18% (Kuhlbusch, 1998a) and C emissions by biomass burning by up to 5.1%. The intensity of fire and the amount and nature of fuel determine the charcoal produced. Forest fires produce more charcoal than savanna or grassland fires (Stocks and Kauffman, 1997).

As a whole, BC represents between 1 and 6% of the total soil organic carbon. It can reach 35% like in Terra Preta Oxisols (Brazilian Amazonia) (Glaser et al., 1998, 2000) up to 45 % in some chernozemic soils from Germany (Schmidt et al., 1999) and up to 60% in a black Chernozen from Canada (Saskatchewan) (Ponomarenko and Anderson, 1999).

At a regional scale, an estimation of BC production in the form of particulate residues or aerosols emitted (soot) by forest fires have been made for Andalusia, a Mediterranean region with very high forest fire incidence. It was estimated that up to 31,222 Mg of refractory materials can be formed by forest fires every year, at a rate of 1.8 Mg burnt ha^{-1}. Part of this BC, between 767 and 920 Mg year^{-1}, would be emitted in the form of aerosols (soot) to the atmosphere and after some time (40 h to 1 month) deposited and incorporated into sediments worldwide. However, most BC, a maximum of 30,300 Mg year^{-1}, will remain as fire residues

and eventually incorporated into the soil, in or nearby, the place of the fire (González et al., 2002).

5. Effect of fire in the quality of soil organic carbon

As indicated above, wildfires are accompanied by the release of large amounts of CO_2, CH_4 and NO_x to the atmosphere and a considerable production of severely and/ or partly charred necromass, which is deposited on the site as fire remains or transported in the form of soot (Kuhlbusch, 1998a). Previous studies on natural ecosystems, as well as laboratory experiments simulating the effect of fire on natural or synthetic soils, demonstrated that this pyromorphic material consists of rearranged, relatively inert macromolecular substances mostly derived from plant biomass and highly aromatic in nature (Almendros et al., 1988, 1992; Baldock and Smernik, 2002; Freitas et al., 1999; Knicker et al., 1996).

The effect of fire on soil OM has been compared to that of natural maturing, at least from the viewpoint of the increase in extent of most surrogate indicators of the degree of polymerization and humification of the OM (Almendros et al., 1984b; Shindo et al., 1986a,b; González-Vila and Almendros, 2003).

Aside from the remains of more or less altered lignin (González-Vila et al., 2001) and from the condensation of lignin-degradation products, new aromatic structures are formed derived from the alteration of carbohydrates (Almendros et al., 1997; Baldock and Smernik, 2002; Dennis et al., 1982; González-Vila et al., 2001), lipids and peptides (Almendros et al., 2003; Knicker et al., 1996).

Compared to the humic substances formed during predominantly microbial or enzymatic humification processes, there are some important qualitative differences in the molecular structure of humic substances affected by abiotic factors such as intense solar irradiation or fire. Whereas biochemical processes lead to carboxyl-containing macromolecular constituents, thermal treatment removes preferentially external oxygen groups yielding materials with comparatively reduced solubility and colloidal properties (Almendros et al., 1990, 1992). The decline in functional groups is expected to change sorptive interactions with other soil constituents and therefore retention of cations and/or xenobiotics.

The main detected changes that fire may exert on the different soil C pools are described below.

5.1. Free lipids

A general observation after a wildfire is the tendency towards a selective decrease in chain length for free lipids (Almendros et al., 1988). High temperatures seem to cause a reduction of the chain length of alkyl compounds (alkanes, fatty acids and alcohols). In a recent comparative study of the homologous series of alkyl compounds in control and

fire-affected pine forest and agricultural soils in Continental Mediterranean region (Madrid, Spain), the higher relative abundance of the alkanes $<C_{25}$ and fatty acids $<C_{20}$ in fire-affected soils was recognized, this indicating a possible thermal fragmentation of long-chain molecules (Tinoco, 2000; Dettweiler et al., 2003).

Differences in the abundance of terpenoids (resin acids) have also been observed: a decrease in the proportions of pimaric acid, that shows the lowest thermal resistance, and an increase in dehydroabietic acid, probably at the expenses of other comparatively labile terpenes (Takeda et al., 1968, 1969). This process also occurs through natural diagenesis (Simoneit and Mazurek, 1982) indicating that fire mimics the effect of diagenesis in fire-unaffected soils (Almendros et al., 1988). In a high intensity fire, the effect on soil terpenes consisted basically of a reduction in the amounts of monoterpene, sesquiterpene and diterpenoid compounds, together with an increase in the proportion of aromatic diterpenoid hydrocarbons. This is probably a consequence of decarboxylation, aromatization and ring opening (as in the case of secodehydroabietic acids) reactions exerted by fire in the soil lipid fraction (Tinoco, 2000).

An increase in the presence of benzenecarboxylic acids as peripheral functional groups in heated HAs and FAs, was attributed to peripheral incorporation of lipid compounds probably derived from thermal distillation of soil necromass during burning (Almendros et al., 1990). The presence of benzenecarboxylic acids have been suggested as a valid descriptor of the impact of fire on soil OM (Glaser et al., 1998).

5.2. Maillard's reactions

A direct contribution from the water-soluble OM fraction to the humic soil fraction mediated by fire is also possible through Maillard's reactions (Maillard, 1916; Hodge, 1953; Ellis, 1959). This reaction occurs through the condensation of reducing sugars and the amine groups from aminoacids and peptides to form macromolecular substances known as melanoidins (Rubinsztain et al., 1984; Hayes and Swift, 1990). The possible occurrence of such processes in soils is not widely accepted mainly because Maillard's products are formed through a number of successive reactions occurring at relatively high temperatures (e.g. >100 °C) and some authors consider that such reactions will be very slow at the common temperature of most soils.

Maillard's reactions have been invoked to justify the formation of aquatic substances in specific ecosystems with lignin-lacking species typically aquatic sediments, hydromorphic soils or dissolved OM not receiving terrestrial inputs (Benzing-Purdie and Ripmeester, 1983). The presence of levoglucosan (a dehydrated glucose containing an intramolecular glycoside bond formed during pyrolysis of cellulose) in lacustrine sediments has been used as an indicator of episodic forest fire in the past (Elias et al., 2001).

There are several features common to Maillard's products and macromolecules formed abiotically from carbohydrate dehydration in nitrogen lacking media (pseudomelanoidins) (Hodge, 1953; Feather and Harris, 1973; Almendros et al., 1989; Almendros and Leal, 1990). Despite the fact that N-compounds increase the reaction rates and lower the temperature required for this condensation, it is also possible that simple sugars can be condensed into a variety of reactive anhydrosugar-like reactive compounds ranging from levoglucosenone to furans and even to benzenic compounds (Popoff and Theander, 1976). Such reactions resemble typical caramelization or charring of carbohydrates (Ikan et al., 1986; Almendros et al., 1989) and other high oxygen-content molecules (Hodge, 1953) and can occur in either solution or solid state (Feather and Harris, 1973; Hedges, 1978; Almendros et al., 1997). It has been indicated that peatlands with *Sphagnum* and other lignin-lacking mosses (where acid-catalyzed carbohydrate dehydration processes would prevail) or soils affected by high temperatures generated during wildfires or controlled burnings (Kumada, 1983; Shindo et al., 1986a) are the most probable environmental scenarios in which these specific humification pathways (exclusively based on carbohydrate, but favoured by mineral catalysts and by the presence of additional reactive compounds in soil) could occur to a significant extent. In extreme situations, such as in soils affected by fires, these processes lead to the formation of a series of charred organic particles from aliphatic precursors (including carbohydrates) which originally contain appreciable amounts of *O*-alkyl and alkyl structures (Almendros et al., 1997) and, when heavily heated, display characteristics of BC (Haumaier and Zech, 1995).

The high recalcitrance of this melanoidin-like material was demonstrated by Poirier et al. (2002). The refractory organic fraction isolated from an ancient (^{14}C age of ca. 8300 years) tropical soil from Congo, and accounting for ca.
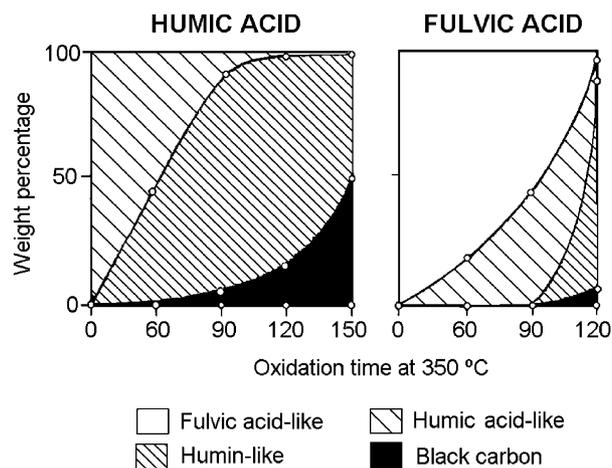

Fig. 2. Progressive transformation of humic acid fulvic acids into mixtures of humic-like macromolecular fractions in laboratory-controlled conditions. The data are expressed as percentages of the final weight (from Almendros et al., 1990).
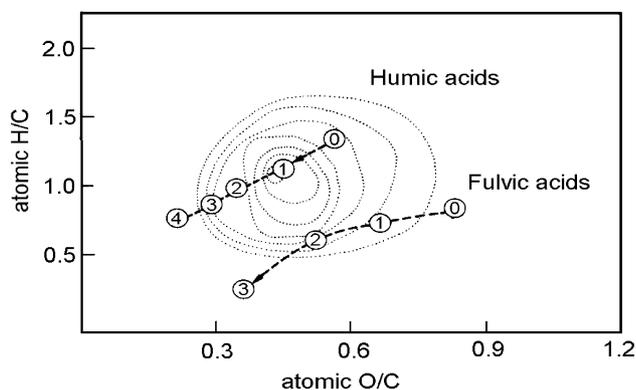
Fig. 3. Changes in the elementary composition of humic and fulvic acids heated at 350 °C for 0–150 s in a laboratory-controlled experiment (encircled numbers 0–4). For comparison purpose, the kinetics are superimposed on a contour diagram showing the natural variability in the atomic H/C and O/C ratios of another 273 HAs from different types of soil (from Almendros et al., 1990).

5% of total OM, was found to be composed mainly of melanoidins with a high degree of condensation and cross-linking. Diagenetic alteration in this ancient soil resulted in a still higher condensation of melanoidins and in the selective elimination of the less ordered BC forms.

5.3. Humic substances

The transformations exerted by fire on the soil humus fractions (HAs and FAs) have been modelled and studied in detail by Almendros et al. (1990) for wildfire-affected soils and simulation laboratory experiments using a mineral soil phase mixed with isolated humic fractions that

were submitted to isothermal heating (350 °C) at variable time periods.

Severe transformation of the original humic materials was observed with a drastic change in solubility properties. In an early stage, half the HA was rapidly transformed into an alkali-insoluble macromolecular material. This insolubility drastically increased during subsequent thermal stages. A similar transformation was also observed for the FA that was first transformed into an acid-insoluble macromolecule (HA-like) and then into an alkali-insoluble substance (humin-like) (Fig. 2). In addition, after alkaline permanganate oxidation of both humic fractions, a variable amount of black unoxidized residue remained. It displayed, after IR spectroscopy and elementary analysis, those characteristics that would be expected for a BC-like material.

The changes observed in solubility are related to changes in the elementary composition of the HAs and FAs. The corresponding atomic H/C and O/C ratios are presented in a Van Krevelen (1950) diagram (Fig. 3). This plot was firstly developed for the study of diagenetic transformation in coals but later on widely used to monitor the evolution of humic substances (Visser, 1983). Heating leads to a simultaneous decrease in the atomic H/C ratio, suggesting an increase in aromaticity, and to a decrease in the atomic O/C ratio, indicating a substantial loss of oxygen-containing functional groups. In particular, simultaneous dehydration and decarboxylation were found after both natural and laboratory burnings which might explain the progressive alteration in the colloidal properties of soils affected by wildfires.

The transformation paths of the atomic ratios shown in Fig. 3 lie within the variability limits of the elementary composition of soil HAs until stage 2 for FAs and 3 for
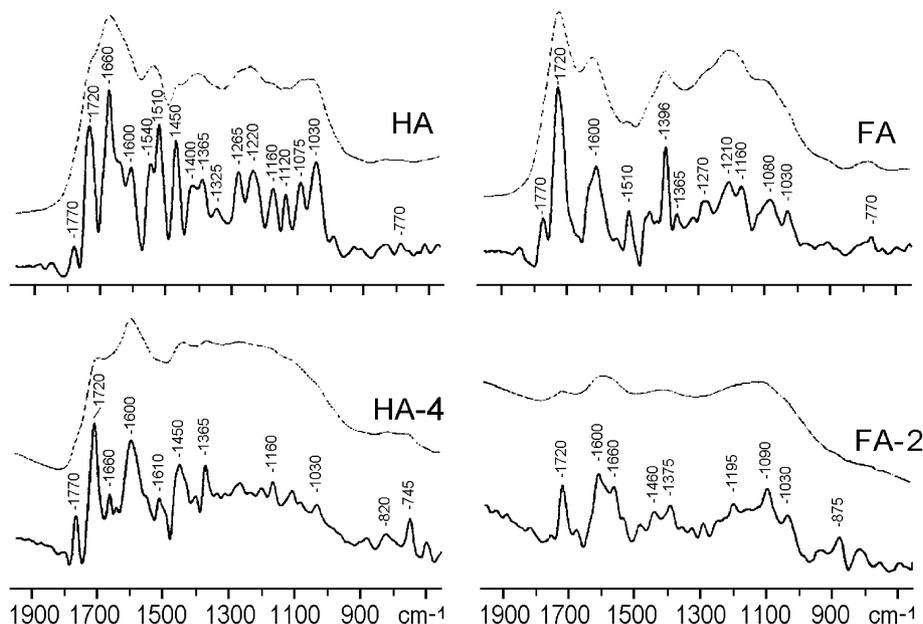

Fig. 4. Resolution-enhanced infrared spectra (continuous line: obtained by subtracting, from the original spectrum, a positive multiple of its second derivative) and original spectrum (dashed line) of unheated humic (HA) and fulvic (FA) acids and the same samples subjected to laboratory isothermal heating at 350 °C for 150 s (HA-4) or 90 s (FA-2).
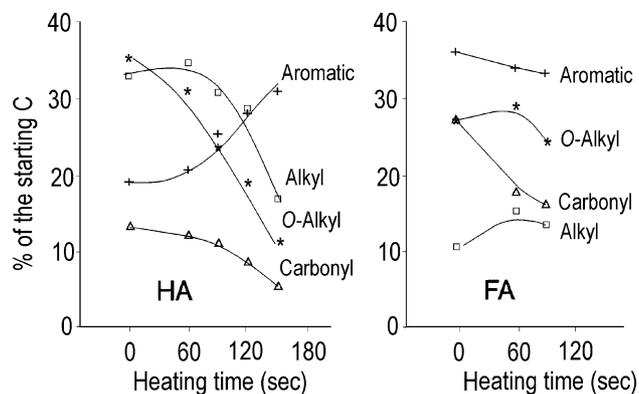
Fig. 5. Changes in the different C-types as detected in the ^{13}C-NMR spectra of humic (HA) and fulvic (FA) acids as a result of heating. The percentages of the d ifferent C types are calculated in terms of the C-losses under laboratory conditions.

HAs, whereas at higher temperatures both acids reach a stoichiometry outside the variability limits usual for HAs and could be in extreme cases ascribed to that of BC.

Resolution-enhanced infrared (IR) spectroscopy (Fig. 4) (Almendros et al., 1992) displayed a pattern that resembled that of lignin: aromatic ring vibrations at 1600 and 1510 cm^{-1} and a series of diagnostic peaks at 1450, 1400, 1365, 1325, 1265, 1220 and 1030 cm^{-1} (Fengel and Wegener, 1984); peaks at 1660 and 1540 cm^{-1} corresponded to amide bands. Bands at around 2920 and 1460 cm^{-1} are ascribed to alkyl stretching and bending vibrations, respectively. The spectra show the typical 1720 cm^{-1} C–O

vibration for carboxyl groups and a 1770 cm^{-1} peak that may be due to O-containing heterocyclic rings as cyclic anhydrides, which can be formed by heat treatment (Wright and Schnitzer, 1961). After laboratory heating (HA-4), the lignin pattern disappears, as well as the amide bands and the IR pattern resembles that of BC (Van der Marel and Beutelspacher, 1976; Durand, 1980): relatively intense peaks at 1620 and 1510 cm^{-1} may correspond to resistant (or newly formed) aromatic groups as results of thermal treatment (Wang and Griffiths, 1985), and a new maximum at between 900 and 700 cm^{-1} may be due to substitutions in polycyclic structures characteristic of carbonized materials. A similar evolution was observed for the FA: the intensity of bands of oxygen-containing functional groups (mainly 1720, 1395 and 1210 cm^{-1}) decreased greatly, the major peaks now corresponding to aromatic and alkyl bending bands (between 1550 and 1350 cm^{-1}), but some residual alcoholic OH groups in carbohydrate-derived structures were suggested from the 1100–100 cm^{-1} region.

The results from the integration of selected regions in the ^{13}C-NMR spectra of the progressively heated samples are shown in Fig. 5. In the case of the HA, there was a substantial depletion of alkyl and O-alkyl materials and the amount of carboxyl C also decreased progressively, whereas that of aromatic C increased with heating time. This observation is compatible with the newly formed unsaturated and/or aromatic material during heating O-alkyl constituents such as sugars, a phenomenon reported during carbohydrate dehydration that leads to the formation of melanoidins (Feather and Harris, 1973; Hedges, 1978).
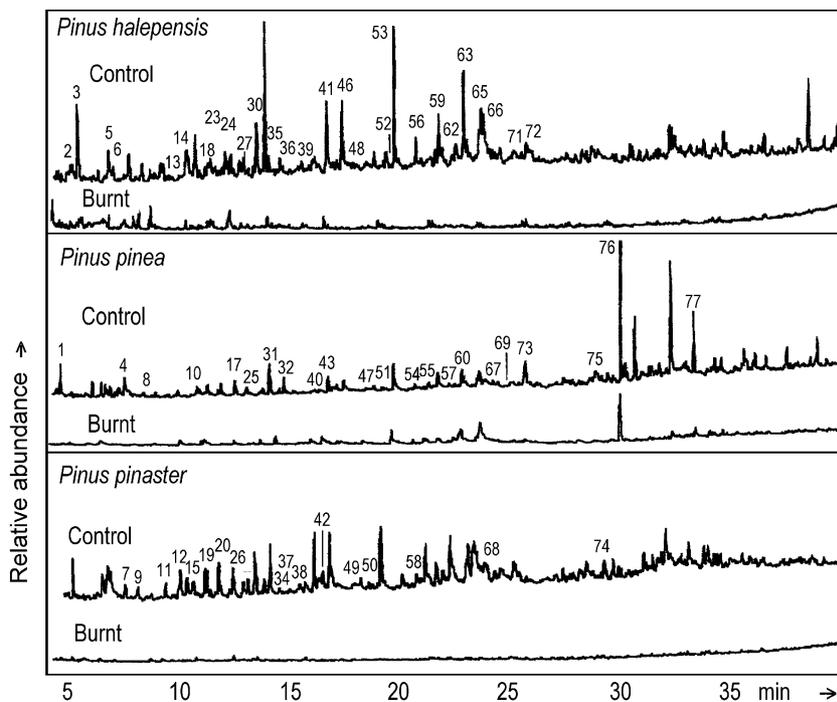

Fig. 6. Pyrograms (Py-GC/MS) of soil samples from different pine forests formations unaffected (control) and affected (burnt) by wildfires. Numbers on the peaks corresponds to the pyrolysis compounds listed in Table 5 (from González et al., 2002).

Table 5

Pyrolysis compounds identified by GC/MS in the control soils (from González et al., 2002)

1. Benzene
2. 2-Methyl-2-cyclopentene-1-one
3. Toluene
4. Furfural
5. 1*H*-pyrrole, 3-methyl
6. 2-Hydroxymethylfuran
7. Styrene
8. Cyclopente-1-ene-3,4-dione
9. 2-Methyl-2-cyclopente-1-one
10. 2-Acetylfuran
11. 2,3-Dihydro-5-methylfuran-2-one
12. 5-Methyl-2-furfuraldehyde
13. Benzylalcohol
14. Benzaldehyde
15. Phenol
16. 5-Methyl-2-furfuraldehyde
17. 4-Hydroxy-5,6-dihydro-(2*H*)-pyran-2-one
18. 5,6-Dihydropyran-2,5-dione
19. 3-Hydroxy-2-methyl-2-cyclopenten-1-one
20. 2,4-Dihydropyran-3-one
21. 2-Methoxytoluene
22. 2-Hydroxy-3-methyl-2-cyclopenten-1-one
23. 4-Isopropyltoluene
24. 2,3-Dimethylcyclopenten-1-one
25. Hydroxymethyldihydropyranone
26. 5-Ethyl-2-furfural
27. *o*-Cresol
28. 2-Furoic acid methyl ester
29. *p*-cresol
30. 2,6-Dimethylphenol
31. Guaiacol
32. Levoglucosenone
33. 3-Hydroxy-2-methyl-(4*H*)-pyran-4-one
34. Dimethyldihydropyranone
35. Phenylacetonitrile
36. 3-Hydroxy-2methyl-(4*H*)-pyran-4-one
37. 2,4-Dimethylphenol
38. Benzoic acid
39. 4-Ethylphenol
40. Catechol
41. 2-Acetoxy-5-ethylfuran
42. 3,5-Dihydroxy-2-methyl-(4*H*)-pyran-4-one
43. Methylguaiacol
44. 5-Hydroxy-2-furfuraldehyde
45. Methoxymethylbenzene
46. 4-Vinylphenol
47. 4-Methylcatechol
48. 4-Ethyl-2-methylphenol
49. 4-Ethylguaiacol
50. 4-Hydroxybenzyl alcohol
51. Indole
52. 1,4-Dideoxy-*D*-glycerohex-1-enopyranos-3-ulose
53. Vinylguaiacol
54. *trans*-Propenylphenol
55. 2,6-Dimethoxyphenol
56. Eugenol
57. 4-Propylguaiacol
58. 3-Methylindole
59. Vanillin
60. *cis*-Isoeugenol
61. 4-Hydroxyacetophenone
62. Homovanillin
63. *trans*-Isoeugenol

Table 5 (*continued*)

64. 1-(4-Hydroxy-3-methoxyphenyl) propyne
65. Acetovanillone
66. Vanillic acid methyl ester
67. 4-Ethyl-2,6-dimethoxyphenol
68. Guaiacylacetone
69. 2,6-Dimethoxy-4-vinphenol
70. 1,6-Anhydro-*b*-glucofuranose
71. Guaiacylpropan-2-one
72. Propiovanillone
73. Guaiacyl vinyl-2-one
74. *trans*-Coniferaldehyde
75. Retene
76. Myristic acid
77. Palmitic acid

Almendros et al. (1990) used oxidative degradation with potassium permanganate and analyzed the resulting fragments by GC/MS to provide some insight into the effect of fire on the assemblages of degradation products from HAs and FAs. After a wildfire, they observed an increase in the lowest boiling point of α,ω-alkanoic diacids together with an increase in the relative abundance of bezenecarboxylic acids, pointing to a breakdown in aliphatic or alicyclic structures. In this work, the same trends were observed in laboratory controlled burning, suggesting a preferential destruction of aliphatic and OH-containing structures. In contrast with the low thermal stability of the peripheral structures, the most stable domain of the humic substances, assumed to be formed by aromatics and cross-linked alkyl bridges, was found resistant to the effects of fire, even under the most severe conditions used during laboratory controlled heating.

Heat-induced dehydration and cyclization reactions lead to the accumulation of large amount of condensed structures including heterocyclic nitrogen forms (Baldock and Smernik, 2002; Almendros et al., 2003; Knicker et al., 2003). The formation of the latter was not observed in soil OM solely formed by microbial reworking (Knicker et al., 1993, 1997; Knicker, 2000). Pyrrole-type N was identified using ^{15}N NMR in certain Australian soils containing charcoal (Knicker and Skjemstad, 2000) but were not present in soil OM from fire unaffected sites nor from other humic materials with no fire history (Knicker et al., 1993). It has also been suggested that the heterocyclic N present in HA fractions from some sub-fossil materials could be formed by fires in the past, or by self-burning processes frequent in Mediterranean peatlands (Almendros et al., 2000b). This supports the pyrogenic origin of those heterocyclic N compounds and also that the occurrence of such N-forms in soil OM may be taken as a first indication for the presence of pyromorphic humic material.

5.4. Charring processes, BC and possible contributions of the carbonized materials to the soil colloidal phase

During charring of organic material an increase in aromaticity is a common fact. It has been observed in

experiments involving woody residues (Baldock and Smernik, 2002; Czimczik et al., 2002), peat (Freitas et al., 1999; Almendros et al., 2003), humic fractions (Almendros et al., 1988, 1992; Golchin et al., 1997) and progressively heated grass material (Knicker et al., 1996). Those studies also indicate that this phenomenon is caused not only by a selective enrichment of residual heat-resistant aromatic components, but mainly by endothermic neoformation reactions involving previous dehydration of carbohydrates, amino acids and unsaturated alkyl chains.

Evidence for the formation of refractory organic C forms in natural soils affected by wildfires has been recently reported by González-Vila et al. (2002) using analytical flash pyrolysis and solid-state ^{13}C-NMR. Fig. 6 and Table 5 show the changes in the pyrolytic patterns of raw forest soil samples affected (burned) and non-affected (control) by wildfires. Pyrolysis products released by control soils include a wide variety of molecules arising from carbohydrates, lignin, lipids and protein. On the contrary, in soils affected by wildfire, most of the pyrolysis products present in control soils are absent and the dominance of charred "non-pyrolysable" refractory carbonaceous material is evident. The formation of condensed, presumably refractory materials is again evident in the solid-state ^{13}C-NMR spectra from a representative case (*P. halepensis* forest) affected by severe fire (Fig. 7) where an increase in the intensity of the aromatic C region (160–110 ppm) is observed, which occurs at the expenses of the *O*- and *N*-alkyl C region (110–60 ppm). This indicates that the increase in C amounts observed in the affected soil, two years after the fire event, is mainly due to the soil enrichment in charred material rather than to inputs of fresh litter after rapid growing of post-fire vegetation. This is further corroborated when analyzing the NMR ratio (160/110 ppm)/(110/45 ppm), that is <1 in all particle fractions of unaffected and >1 in all particle fractions of fire-affected soil.

By means of ^{13}C NMR spectroscopy, Golchin et al. (1997) studied the HA fraction of a chronosequence of Andosols subjected to grassland annual burning (never burned, recently burnt and subjected to annual burning 20–30, 40–50, >100 years ago). They found that the burning practices contributed to soil formation and allowed the probable evolution of this soil to be traced. From the soil subjected to annual burning practices, with a very C-rich (18.4 %) epipedon and a highly aromatic HA, towards soils being not burned for up to 100 year with less C content (12.8 %) and an aliphatic HA.

It is assumed that carbonized materials and especially BC are recalcitrant against chemical and microbial degradation (Jones et al., 1996; Kuhlbusch, 1998a). Based on chemical characteristics, the possible significance of carbonized materials in the formation of humic substances has been addressed by Kumada (1983) and Haumaier and Zech (1995). Shindo et al. (1986a,b) compared optical properties, IR spectra and X-ray diffraction patterns of HAs from volcanic ash soils with those from charred plant residues and concluded that charring process could be one out of the possible mechanisms for the formation of HAs in some volcanic soils (Andosols).

Lignin is the main source of phenolic compounds in soil HAs, however there are certain soils with a remarkably low phenolic content in their humic material (Hatcher et al., 1989; Tate et al., 1990). It has been postulated that carbonized materials produced during vegetation fires (BC) may be a major precursor of the aromatic substances present in these soils. Haumaier and Zech (1995) compared the ^{13}C NMR spectra of HAs extracted from laboratory-oxidized BC obtained from different plant materials and found the typical low abundance or absence of resonance other than those of carboxyl and non-oxygenated aromatic carbon. This fire-mediated process probably occurs in areas with a high incidence of fires and subsequent high rates of oxidation.
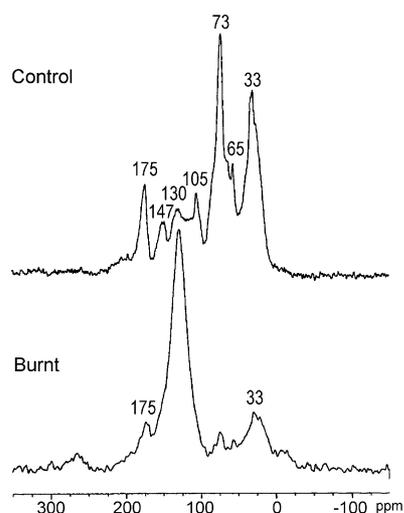
Integrated region (ppm)	Assignment	Control	Burnt
245 – 185	Carbonyl (amide, ketone, ester) 160–200 ppm=	3.4	2.9
185 – 160	carbonyl (172= carboxyl, 198= ketone/aldehyde)	8.6	8.0
160 – 110	110–160 ppm= aromatic/unsaturated (126= unsubstituted, 147= heterosubstituted)	18.5	60.9
110 - 60	45–110 ppm= *O*-alkyl (56= methoxyl, 73= glucopyranosyde-derived)	34.0	11.5
60 – 45	60–45 ppm= methoxyl and N-Alkyl C	8.2	3.0
45 – 0	0–45 ppm= alkyl (13= methyl, 21= acetate, 33= polymethylene)	27.4	13.8

Fig. 7. Solid-state ^{13}C-NMR spectrum of a forest soil sample affected (Burnt) and not affected (Control) by fire with the distribution of different C types.

Although from a different geochemical origin, lignite structure resembles that of BC (Poirier et al., 2000). Many laboratory studies show evidence that lignite can be degraded by microorganisms (Cohen and Gabriele, 1982; Hölker et al., 2002; Rumpel and Kögel-Knabner, 2002). The peroxidase enzymes involved in lignite degradation were found to be produced by soil-inhabiting basidiomycetes (Bonnen et al., 1994). Carbon from the degradation of lignite was found as part of the humic fraction in lignite-rich mine soils, which may indicate that lignite is oxidized during biodegradation and incorporated to the humic fraction (Rumpel and Kögel-Knabner, 2002).

6. Conclusions

The effect of fire on soil OM is highly dependent on, among other factors, the type and intensity of the fire, soil moisture, soil type, and nature of the burned materials. Therefore, the effect on soil processes and their intensity influenced by fire are highly variable and no generalized tendencies can be suggested for most of the fire-induced changes in humus composition. Nevertheless, systematic

changes in the combustion of humus after intense burning has been summarized by Almendros et al. (1990) showing a generic model for the OM dynamics leading to pyromorphic humus (Fig. 8).

Oxygen-containing functional groups of humic macromolecules are especially labile to heat. In natural fires, part of the HA fraction can be transformed into humin. Simultaneously, part of the soil FAs may turn into HA-like macromolecules, and the additional inputs of alkali-soluble lignin materials inherited from the incompletely burned necromass in addition to newly formed Maillard's products will also contribute to the acid-insoluble HA-like substances. In the early transformation stages the selective destruction of the less condensed structural domains of HAs, with a predominant aliphatic nature, may be compensated by lipid compounds derived from the thermal distillation of soil necromass, partly responsible for the water repellence observed in burned soils to which the comparatively hydrophobic surfaces in the HA fractions probably contributes, as a consequence of the above-referred dehydration associated to the removal of oxygen-containing groups.

Laboratory incubation experiments indicated that humic substances formed in fire affected soils (pyromorphic hu-
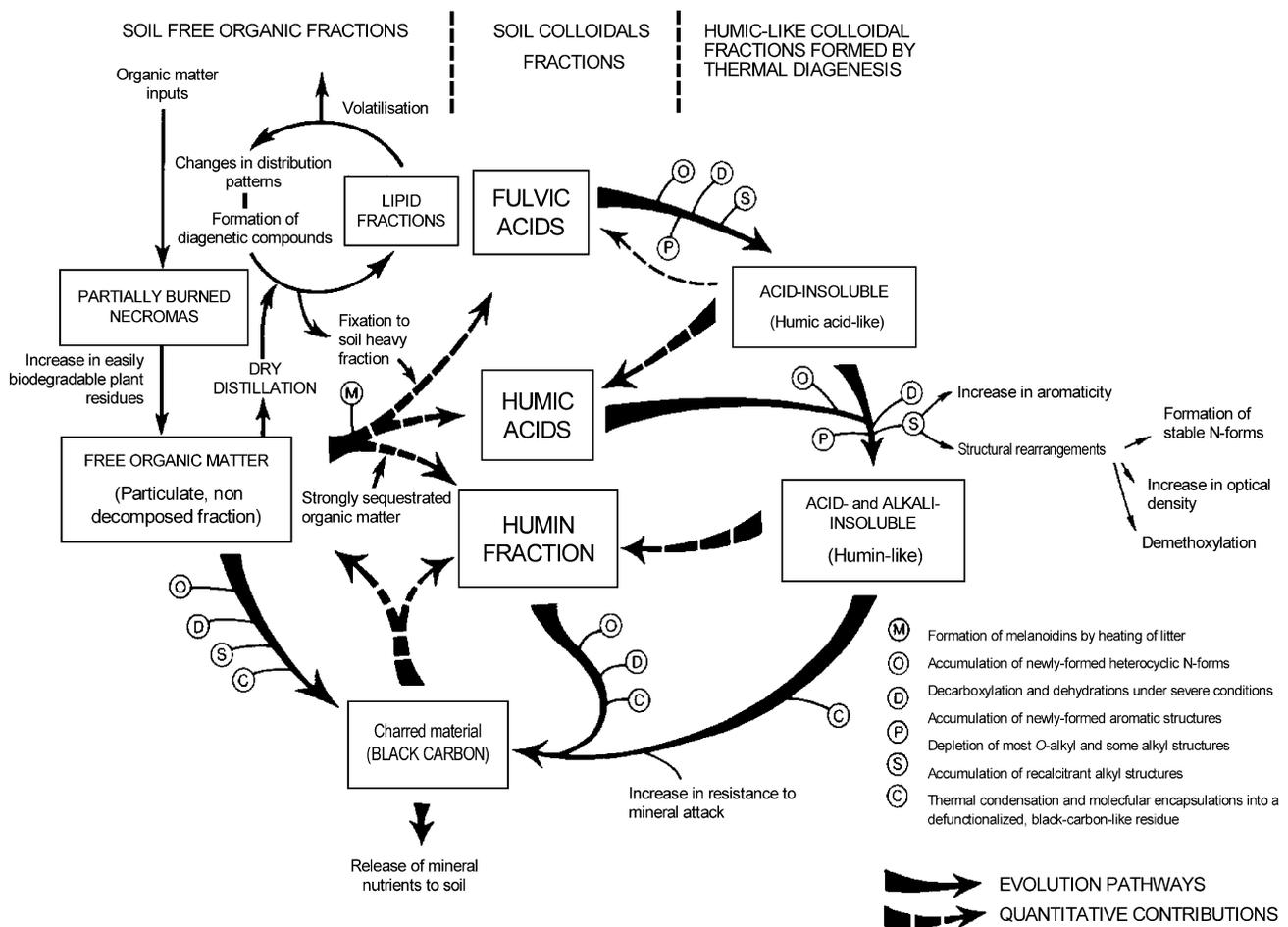

Fig. 8. Hypothetical processes occurring in the organic matter of a Mediterranean oak soil affected by a severe fire (from Almendros et al., 1990).

mus) show an increased stability to chemical and biological degradation, hence fire could be considered as a C stabilization factor with implications for the global geochemical cycles. The introduction of fire-generated, highly condensed and resilient materials into soils is assumed to increase the passive soil OM pool (Schmidt et al., 1999; Knicker and Skjemstad, 2000; Skjemstad et al., 1999). Although this is advantageous for the long term removal of climate affecting gases from the atmosphere, the impact on the long-term availability of N, P and other bioelements that may be sequestered together in the stable soil humus formations should not be neglected (Almendros et al., 2000a).

Acknowledgements

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