Black carbon in soils and sediments:
Analysis, distribution, implications, and current challenges

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Abstract. This review highlights the ubiquity of black carbon (BC) produced by incomplete combustion of plant material and fossil fuels in peats, soils, and lacustrine and marine sediments. We examine various definitions and analytical approaches and seek to provide a common language. BC represents a continuum from partly charred material to graphite and soot particles, with no general agreement on clear-cut boundaries. Formation of BC can occur in two fundamentally different ways. Volatiles recondense to highly graphitized soot-BC, whereas the solid residues form char-BC. Both forms of BC are relatively inert and are distributed globally by water and wind via fluvial and atmospheric transport. We summarize, chronologically, the ubiquity of BC in soils and sediments since Devonian times, differentiating between BC from vegetation fires and from fossil fuel combustion. BC has important implications for various biological, geochemical and environmental processes. As examples, BC may represent a significant sink in the global carbon cycle, affect the Earth's radiative heat balance, be a useful tracer for Earth's fire history, build up a significant fraction of carbon buried in soils and sediments, and carry organic pollutants. On land, BC seems to be abundant in dark-colored soils, affected by frequent vegetation burning and fossil fuel combustion, thus probably contributing to the highly stable aromatic components of soil organic matter. We discuss challenges for future research. Despite the great importance of BC, only limited progress has been made in calibrating analytical techniques. Progress in the quantification of BC is likely to come from systematic intercomparison using BCs from different sources and in different natural matrices. BC identification could benefit from isotopic and spectroscopic techniques applied at the bulk and molecular levels. The key to estimating BC stocks in soils and sediments is an understanding of the processes involved in BC degradation on a molecular level. A promising approach would be the combination of short-term laboratory experiments and long-term field trials.

1. Introduction

Black carbon (BC) is produced by incomplete combustion of fossil fuels and vegetation [*Goldberg*, 1985]. BC can be understood as a continuum from partly charred plant material through char and charcoal to graphite and soot particles recondensed from the gas phase, with no general agreement on clear-cut boundaries [*Seiler and Crutzen*, 1980]. BC is purely terrestrial in origin and occurs ubiquitously in soils and terrestrial sediments and is coupled to a common marine fate via fluvial and atmospheric transport [*Goldberg*, 1985]. In recent years, geochemical and biological studies of different forms of BC, such as plant chars, charcoals, and soots, have received increasing attention owing to their potential importance in a wide range of biogeochemical processes. As examples, BC may represent a significant sink in the global carbon cycle [*Kuhlbusch*, 1998a], affect the Earth's ra-

diative heat balance [*Crutzen and Andreae*, 1990], be a useful tracer for Earth's fire history [*Bird and Cali*, 1998], build up a significant fraction of carbon buried in soils [*Skjemstad et al.*, 1996; *Schmidt et al.*, 1999] and sediments [*Masiello and Druffel*, 1998], and act as an important carrier of organic pollutants [*Gustafsson and Gschwend*, 1997] or heavy metals [*Hiller and Brümmer*, 1997]. The presence of BC may also have led to an overestimation of marine organic productivity [*Verado*, 1997] and soil humus content [*Skjemstad et al.*, 1996]. In soils, BC may produce highly aromatic humic acids that can interfere with extracts from soil humic substances [*Haumaier and Zech*, 1995; *Skjemstad et al.*, 1997]. In addition to burning vegetation, fossil fuel combustion presently also contributes similar amounts of aerosol BC to the global biogeochemical cycle of carbon [*Kuhlbusch*, 1998a] and up to 80% of the total soil organic carbon [*Schmidt et al.*, 1996]. Charred particles from both biomass burning and fossil fuel combustion share a relative lack of (bio) chemical reactivity and thereby strongly resist decomposition over a geological timescale. For example, BC residues are constituent of many coals dating back to the Devonian [*Taylor et al.*, 1998].

The purpose of this review is to introduce different scientific communities, including soil, sediment, and marine geochemists and biologists, to the many different aspects of the global impor-

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tance of BC. BC has been studied in a variety of widely separated scientific fields, with the result that essentially no generally accepted analytical protocols, terminologies, and conceptual approaches exist. Independent literatures on BC continue to develop depending on the medium (soil, sediment, atmosphere, or water), timescale (pre-Quaternary versus Quaternary), analytical approach (qualitative versus quantitative) and operational definitions (optical properties, chemical and thermal resistance, or indirect evidence). A combination of knowledge on BC coupled with a careful calibration of analytical techniques holds promise for a better understanding of data obtained in biogeochemical, environmental, and agricultural studies. Since the 1980s, increasing interest in fire, and thus the formation of BC in the global carbon cycle, resulted in a series of interdisciplinary conferences and monographs which attempted to integrate approaches and findings of traditionally separate scientific disciplines [Clark et al., 1997; Crutzen and Goldammer, 1993; Zepp and Sonntag, 1995].

With this review we want to bridge the gap between disciplines and enhance familiarity with information contained in literature from the fields of coal petrology, palynofacies, palynobotany, fire ecology, and marine, environmental, and soil chemistry. We point out the variability of analytical techniques and the ubiquitous presence of BC originating from vegetation burning and fossil fuel combustion in the geological record and in contemporary sediments and soils. To facilitate access to literature of the different scientific disciplines, we focus on recent and generally available publications providing access to further literature, rather than a comprehensive literature review.

2. Definitions, Fluxes, and Analytical Approaches

2.1. Definition

There is no unambiguous definition of the carbonaceous residues resulting from incomplete combustion of plants, wood, and fossil fuel [Goldberg, 1985]. In soils and sediments these residues often coexist with two other forms of carbon, i.e., thermally unaltered organic carbon (e.g., decaying plant material) and inorganic carbon. Numerous terms have been used to describe these organic particles, which vary with techniques of isolation and scientific discipline. For example, definitions in coal petrology are based mainly on optical and chemical properties. Numerous terms were introduced to describe the black, opaque constituent of coal often displaying cell morphology, e.g., fusain, fusinite, and subgroups, mineral charcoal, Faserkohle, Russkohle, and charbon fibreux [Stach et al., 1982; Taylor et al., 1998]. Astrophysical, atmospheric, and environmental science terms include elemental, polymeric, graphitic, free or black carbon, carbon black, char, charcoal, soot, and graphite. However, there is no generally accepted terminology for BC, as summarized elsewhere [Jones et al., 1997; Kuhlbusch et al., 1996]. For simplicity we will use the term BC, unless the authors of the referenced literature introduced a different term.

2.2. Formation

Formation of BC can occur in two fundamentally different ways. The volatiles recondense to highly graphitized soot-BC, whereas the solid residues form char-BC. Soot-BC forms via small molecules that are released by pyrolysis and subsequently recombine by free radical reactions. The randomness of these reactions results in a characteristic, but widely varying, spectrum of products, including polycyclic aromatic hydrocarbons (PAH) and graphitic moieties. Char-BC forms during the flaming and smol-
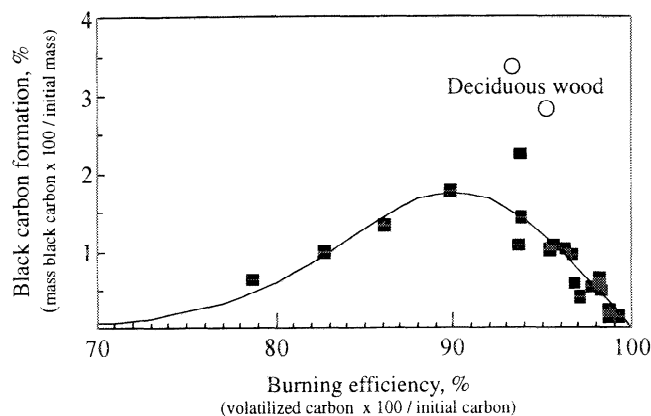
Figure 1. Black carbon formation from vegetation fires is dependent on burning efficiency, as exemplified for grasses (line) and two samples from deciduous wood (data from Kuhlbusch and Crutzen [1995]). At low burning efficiency (i.e., volatilized carbon), not all biomass is exposed to thermal degradation, yielding only a small amount of black carbon. With increasing burning efficiency, formation of BC increases up to a maximum conversion rate (1.8 ± 0.2%) of initial carbon to black carbon at 90 % burning efficiency, which is common for savanna fires [Kuhlbusch et al., 1996]. With further increasing volatilization the exposed plant material, plus the newly formed black carbon, undergo thermal alteration until all black carbon is consumed. Black carbon formation in the two deciduous wood samples is larger by a factor of 2–3, probably owing to the physically more dense structure, delaying access of oxygen.

dering phases of combustion, when oxygen reacts with carbon that builds up on solid fuel surfaces. At this stage, fuel gases produced by pyrolytic reactions are insufficient to maintain the flame envelope, and oxygen must diffuse to the fuel surface to maintain combustion. Turbulence in the combustion zone enhances this transport and oxidation at the fuel surface provides heat evolution and heat feedback to accelerate pyrolytic reactions and volatilization of fuel gases [Shafizadeh, 1984; Ward, 1990]. BC is formed in an exothermic reaction occurring at temperatures between 280° and 500°C. In nature, BC is a common product of wildfires [Cope and Chaloner, 1980; Komarek, 1972]. Increased ground temperatures during wildfires are restricted to the top 30-40 mm of soil and may vary between 200° and 500°C for many fires, being lowest for grassland fires (50°-80°C) and highest for scrubland wildfires (700°-1000°C) [Raison, 1979; Scott, 1989].

The amount and type of BC produced by a fire (Figure 1) is influenced by the fuel type, fuel load, fuel condition, weather conditions, substrate heterogeneity, fire intensity, and duration of the fire [Kuhlbusch et al., 1996; MacDonald et al., 1991; Patterson et al., 1987; Shafizadeh, 1984]. Consequently, the quantity of natural BC produced and its composition can vary greatly. Production of BC has increased during the last centuries, owing to dramatically increased deforestation, shifting agriculture, plus coal and oil combustion for industrial energy supply. Global annual estimates for the formation of BC for the 1980s range from 40 to 600 Tg (=10^{12} g) from burning vegetation and 7-24 Tg by fossil fuel combustion [Crutzen and Andreae, 1990; Kuhlbusch and Crutzen, 1995; Penner et al., 1993]. The spatial and temporal

distributions of these sources vary, depending on the ecosystem, climate, living standard, and population density. Annual cycles of combustion of vegetation and fossil fuel depend on regional climate (fire season), and higher fossil fuel consumption occurs during winter for domestic heating. Combustion of fossil fuels is an important source of BC mainly in the highly industrialized countries, e.g., North America, Europe, and Japan [*Crutzen and Andreae*, 1990; *Penner et al.*, 1993].

The chemical structure of BC is highly aromatic, and carbon can form manifold forms of solid structures because of its ability to occur in different hybridization states (Figure 2). Carbon atoms in the sp^3 hybridization state form diamond structures, whereas

sp^2 hybridized carbon build up planar graphite structures. Mixed hybridization states form curved structures, which in the perfect form, are closed spheres (fullerenes). BC formed by vegetation fires often consists of randomly orientated stacks of few graphitic layers (Figure 2c). The short-, medium-, and long-term order of BC depends on combustion conditions such as temperature and the moisture content of the fuel. Structure and reactivity of BC was studied using Fourier transform infrared (FTIR) spectroscopy in combination with ozonation studies by several workers [*Akhter et al.*, 1985a; b; *Sergides et al.*, 1987; *Smith and Chughtai*, 1995]. The proposed structure for BC formed from n-hexane under laboratory conditions in the flame (Figure 2) exemplifies one of the more aromatic structures of BC.
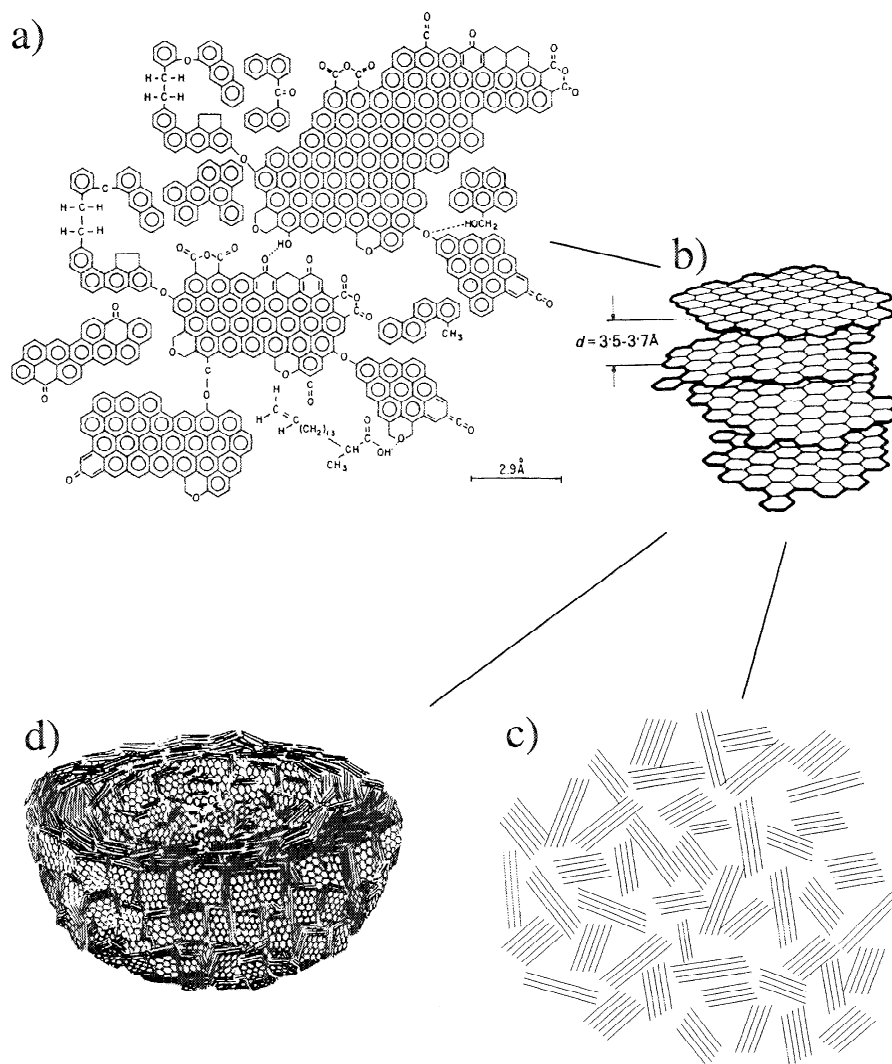
Figure 2. Basic structural units and two principal structures of black carbon. (a) Black carbon as formed in the laboratory [*Sergides et al.*, 1987], forming (b) basic structural units of three to four layers [*Heidenreich et al.*, 1968]. (c) Randomly oriented basic structural units consisting of a few graphite layers (here shown in a two-dimensional schematic diagram). (d) Onion-type particle with several condensation seeds [*Heidenreich et al.*, 1968]. *Sergides et al.* [1987] reprinted from *Appl. Spectrosc.*, *41*, Sergides, C.A., J.A. Jassim, A.R. Chughtai, and D.M. Smith, The structure of hexane soot, part III, Ozonation studies, 482-492, 1987, with permission from the Society for Applied Spectroscopy, and *Heidenreich et al.* [1968] reprinted from *J. Appl. Crystallogr.*, *1*, Heidenreich, R.D., W.M. Hess, and L.L. Ban, A test object and criteria for high resolution electron microscopy, 1-19, 1968 with permision from the International Union of Crystallography.

2.3. Loss Processes

BC is generally considered to be (bio) chemically relatively inert. Its presence in the sedimentary record back to Devonian times, in terrestrial environments over thousands to millions of years, and in glacial and lacustrine sediments of the late Quaternary are cited as evidence of its extreme resistance to degradation (Table 1). However, it would seem degradation does occur at the Earth's surface. *Goldberg* [1985] calculated, on the basis of the estimates of global biomass burning of *Seiler and Crutzen* [1980],

that without degradation it would take <100,000 years to convert the Earth's surface carbon to BC. Clearly, this is not the case. However, there is little direct evidence for photochemical and microbial oxidation, the two mechanisms proposed for the degradation of BC. Some studies have suggested microbial degradation of BC in soils. *Goldberg* [1985] described work by *Potter* [1908] leading to the proposal that microorganisms could slowly oxidize amorphous carbon. *Shneour* [1966] suggested microbial degradation to account for the release of $^{14}CO_2$ from labeled graphite that was mixed with soil and the subsequent reduction in specific

Table 1. Analytical Techniques for the Determination of Black Carbon in Sediments and Soils

Material Studied	Method			Reference
	Pretreatment	Oxidation	Determination	
Optical Techniques				
Soil	-	-	visual	*Pessenda et al.* [1996], *Saldarriaga and West* [1986], and *Sanford et al.* [1985]
Aerosol	collection plates	-	microscopy	*Schultz* [1993]
Sediment	thin section	-	microscopic counting	*Clark* [1988b] and *Clark and Hussey* [1996]
Sediment	HCl, HF, density sep.	-	microscopy	*Kruge et al.* [1994]
Sediment	HCl, HF	H_2O_2	counting	*Kershaw* [1986]
Plant/laboratory experiment	HCl, HF	-	SEM	*Jones and Chaloner* [1991]
Forest soils, N-Sweden	HCl, HF	H_2O_2	microscopy	*Wik and Renberg* [1987]
Thermal Techniques				
Aerosol	filtration	100-700°C	transmissivity	*Chylek et al.* [1995, 1987]
Plant, aerosol	HCl, filtration	340 °C for 2 h	coulometry	*Cachier et al.* [1989]
Plant, aerosol	solvent extraction	340 °C for 2 h	GC/mass balance	*Kuhlbusch* [1995]
Soot in sediments	grinding	375 °C for 24 h	HCl, elemental analysis	*Gustafsson et al.* [1997]
Plant, soil	grinding	combustion	mass balance	*Fearnside et al.* [1993]
Chemical Techniques				
Sediment, marine, K-T	HCl, HF	$Cr_2O_7^{2-}$, H_2SO_4, 50°C	mass loss, titration	*Wolbach and Anders* [1989]
Sediment	HCl, HF	KOH, H_2O_2, 55°C 48 h	counting	*Odegaard* [1993] and *Rose* [1990]
Sediment	HCl, HF	KOH, H_2O_2, room °C 24 h	combustion, MS	*Emiliani et al.* [1991]
Sediment marine	HCl	HNO_3 hot	GC	*Verado* [1997]
Plant, synthetic soil	HCl	HNO_3, 170°C	derivatization, GLC	*Glaser et al.* [1997]
Synthetic sediment	HCl, HF	H_2O_2, KOH	IR	*Smith et al.* [1975]
Soil, plant	sieving	UV photo-oxidation	^{13}C NMR, coulometry	*Skjemstad et al.* [1993, 1996]
Sediment	HCl, HF	KOH, H_2O_2, room °C 24 h	IR	*Herring* [1985]
Sediment	HCl	HNO_3 hot	combustion, MS	*Winkler* [1985, 1994]
Sediment, marine, lake, K-T	HCl, HFl	$Cr_2O_7^{2-}$, H_2SO_4, 55°C 60 h	coulometry	*Lim and Cachier*, 1996
Soil with coal/charcoal	size fractionation, HF	-	microscopy, ^{13}C NMR, ^{14}C	*Schmidt et al.* [1996]
Sediment, soil, plant	HCl, HF	$Cr_2O_7^{2-}$, H_2SO_4, 60°C 72 h + KOH, H_2O_2 60°C 8 h	combustion, MS	*Bird and Gröcke* [1997]
Indirect Evidence				
Sediment, K-T	solvent extration	-	GC-MS, PAH content	*Killops and Massoud* [1992] and *Venkatesan and Dahl*, 1989
Sediment, Boston harbour	solvent extraction	-	GC-FID, PAH partitioning	*McGroddy and Farrington* [1995], *McGroddy et al.* [1996]
Sediment, peat	-	-	magnetic susceptibility	*Thompson and Oldfield* [1986]

$Cr_2O_7^{2-}$, dichromate; HF, hydrofluoric acid; HCl, hydrochloric acid; H_2O_2, hydrogen peroxide; HNO_3, nitric acid; H_2SO_4, sulfuric acid; KOH, potassium hydroxide; K-T, Cretaceous-Tertiary boundary; GC, gas chromatography; PAH, polycyclic aromatic hydrocarbon; MS, mass spectrometry; FID, flame ionization detector; GLC, gas liquid chromatography; IR, infrared spectroscopy; SEM, scanning electron microscopy; NMR, nuclear magnetic resonance; PAH, polycyclic aromatic hydrocarbons.

activity of the residual ^{14}C in the soil. When sterilization by a number of different methods was used as a control, evolution of $^{14}CO_2$ was negligible. *Shindo* [1991] incubated charred grassland plants in volcanic ash soil at 25°C under moist conditions, and after 40 weeks, the pattern of CO_2 evolution was almost the same as that in the system containing soil only, indicating the charred materials were hardly decomposed. In comparison, there was initial evolution of CO_2 from the soil amended with noncharred plant material. At a fire trial site in well-aerated sandy savanna soils, *Bird et al.* [2000] found that BC could be significantly degraded on a decadal to centennial timescale. From stable carbon isotopic data they concluded that BC in coarse particle size classes progressively degraded, becoming part of finer particle size classes with a concomitant increase in resistance to oxidative degradation owing to progressive loss of more reactive components. *Herring* [1985] measured BC particles in Cenozoic sediments of the North Pacific Ocean. Preferential degradation of smaller particles with higher surface area to volume ratio would be expected, but no consistent trend in size distribution through the sediment column was found, implying no chemical or biological destruction of BC after deposition. *Winkler* [1985] indicated that the organic components of BC can undergo acidic breakdown in anaerobic sediments of bogs and lakes, a breakdown which was continued in the laboratory when nitric acid treatment was used in the assay technique. A marine turbidite in the Madeira Abyssal Plain provided first direct evidence for an extensive BC degradation (64%) in marine sediments [*Middelburg et al.*, 1999]. These observations indicate that the degradation rates of BC may vary in relation to particle size, chemical composition, environmental setting, and the timescale of the study. More impure, less altered BC may be more prone to alteration.

Features which BC shares with coal are polycyclic aromatic rings as a main constituent and probably also small pores inaccessible to microorganisms. Relative to other organic substances, coals seem to offer few sites for microbial degradation [*Cohen and Gabriele*, 1982]. Effective microbial degradation of coal relies on extracellular oxidative enzymes [*Fakoussa*, 1992]. For brown coal, *Willman and Fakoussa* [1997] observed that the degradation depends on the presence of an easily available source of organic carbon, similar to cometabolic process of lignin degradation. Wood- and leaf-decaying fungi have proven their ability to degrade brown coal [*Hofrichter et al.*, 1999]. Lifetime of pyrite-free bituminous coal in air-saturated water (24°C) was estimated to be 8000 years for 10 μm particles and 80,000 years for 100 μm particles [*Chang and Berner, 1999*].

2.4. Identification and Quantification of BC

Differentiation between sources of BC has been attempted on the basis of morphology [*Griffin and Goldberg, 1975; Suman et al.*, 1997], elemental composition, and particle size [*Clark*, 1988a]. There is, however, no parameter that allows unambiguous source distinction. Particle size distribution of BC found in sedimentary environments is influenced by the combustion process and fuel type and by dispersal and depositional mechanisms. A bimodal size distribution of BC particles is produced in the burning process with submicron, framboidal particles formed in the vapor phase and larger charred particles, from tens of microns upward, which morphologically reflect the fuel structure and nature of combustion [*Goldberg*, 1985; *Ward*, 1990]. Part of the BC is transferred away from the site of the fire immediately following combustion, and some is temporarily stored in surface

soils [*Griffin and Goldberg*, 1975]. BC residues are very susceptible to erosion by wind or water [*Clark*, 1988a; *Patterson et al.*, 1987]. Large (> 50 μm) BC particles primarily originate from local fires, whereas small charcoal particles predominantly indicate nonlocal fires [*Clark*, 1988a, b, *Clark and Royall*, 1995]. Laboratory analysis procedures can also bias size distributions [*Patterson et al.*, 1987]. *Clark* [1988b] compared two methods of BC analysis: pollen slides for particles 5-80 μm in diameter and petrographic thin sections for particles 5-10,000 μm in diameter. This study indicated that aerodynamic differences between particles arise from the relationship between diameter and critical and depositional velocities. Particles >50 μm diameter, which are deposited closer to fire sites, are of greater value in detecting remnants of local fires, whereas BC on pollen slides can be used to interpret the importance of fire on broad spatial and temporal scales. The morphology of BC and associated particles originating from industrial processes, such as coking, combustion, and steel production, and found in soils (Figure 3) can provide source identification and estimation of formation temperatures [*Bailey et al.*, 1990; *Schmidt et al.*, 2000].

Analyses of BC in sediments and soils basically have to differentiate between three different forms of carbon, i.e., inorganic carbonates, thermally unaltered organic carbon, such as humic substances or plant material, and BC. Methods for BC determination can be divided into optical, thermal, chemical, and indirect categories. The first three methods rely on the assumption that the three carbon classes can be distinguished by their volatility, oxidizability, and their optical and chemical properties. Violations of these assumptions vary in degree with sample composition, characterization, and method and thus result in operational definitions. A lack of accepted standard materials and terminologies also makes interlaboratory comparisons difficult. Published methods are listed in Table 2. We summarize the principal approaches here; a more detailed analytical review is given by *Kuhlbusch* [1998b].

Microscopic methods also are a direct result of palynological studies because micron-size BC particles are isolated along with pollen. Microscopic techniques are often applied because optical properties are some of the most diagnostic for BC, and the required expertise and equipment are often available in geoscience laboratories. BC is either quantified in situ on petrographic thin or polished sections, extracted from the matrix by sieving, or concentrated by chemical methods. The preparation and examination of thin sections or polished sections with different sources of light and analytical measurements is well documented in geoscience and soil science literature, e.g., *Cady et al.* [1986], and not discussed here. The same is true for sieving, which involves sequential washing through sieves differing in mesh sizes and subsequent separation for identification and counting. Chemical digestion for the isolation of BC involves steps to deflocculate sediments (e.g., hot potassium hydroxide, KOH) and to remove carbonates (hydrochloric acid, HCl) and silicates (hydrofluoric acid, HF). Only the most recalcitrant minerals (e.g., pyrite) and organic particles (e.g., pollen or charcoal) remain and are suspended in oil and mounted on glass slides for microscopic investigation. Depending on the particle size and method, microscopy can be performed by stereoscope, light microscope, and scanning (SEM) or transmission electron microscope (TEM). Charcoal concentration is then measured on an areal basis, although this is time consuming and relies on the correct differen-

Table 2. Black Carbon in Soils and Sediments since the Devonian from Vegetation Fires and Fossil Fuel Combustion

Strata	Black Carbon Identified	Reference(s)
Proterozoic		
Low-grade metamorphized shungite	fullerenes	*Ebbesen et al.* [1995] and *Parthasarathy et al.* [1998]
Devonian		
Gedinian	fusinized tissue of fossil wood	*Burgess and Edwards* [1988]
Carboniferous		
Mississippian	charred fossil wood	*Beck et al.* [1982]
Illinois coals	inertinite 9-16%	*Harvey and Dillon* [1985]
Pennsylvanian coals	fusain 8-14 vol.%	Robinson [1997] compilation
Marine sediments	fusain	*Nichols and Jones* [1992]
Permian		
Gondwana coals	fusain 20-85%	*Cook* [1975], *Taylor and Cook* [1962] and *Taylor et al.* [1989]
Jurassic		
Fluviatile, coastal, deep marine sediments	charcoal	*Cope and Chaloner* [1980], *Harris* [1958] and *Jones and Chaloner* [1991]
Gondwana coal, India, Australia	fusinite	*Beeston* [1987] and *Taylor et al.* [1989]
Coal, Russia	fusinite up to 25%	*Lapo* [1976]
Cretaceous		
Coal, USA	high proportions of inertinite	*Kalkreuth and Leckie* [1989]
Coal bed in Colorado, USA	fusinite	*Tschudy et al.* [1984]
Cretaceous/Tertiary (K/T) boundary		
Marine sediment (boundary clay) New Zealand, Spain, Turkey	elemental C (soot, charcoal)	*Wolbach et al.* [1985; 1988, 1990] and *Wolbach and Anders* [1989]
Sediment, Mexico	fossil charcoal, fusinite	*Kruge et al.* [1994]
Sediment, USA	evidence for fire	*Venkatesan and Dahl* [1989]
Tertiary		
Miocene Niger Delta sediments	charred grass cuticle	*Morley and Richards* [1993]
Miocene brown coal	charcoal	*Kershaw et al.* [1993]
Brown coal	fusain up to 1% fusain	*Robinson* [1989], *Robinson et al.* [1997] compilation of Pennsylvania State University database
Quaternary		
BC from vegetation fires		
Marine sediments, Atlantic, Pacific, Mediterranean	BC particles	*Griffin and Goldberg* [1975], *Herring* [1985], *Lim and Cachier* [1996], *Middelburg et al.* [1999], *Smith et al.*, [1975], *Suman* [1986] and *Verado and Ruddiman* [1996]
Lake sediments	BC in sediments	*Clark* [1988a, 1988b], *Clark and Royall* [1995], *Cwynar* [1978], *Swain* [1973, 1978] and ; *Waddington* [1969]
Sediments, biomass burning in Australasia, Central and South America, Africa		compilation by *Kershaw et al.* [1997] with ~40 references describing charcoal and fire history
Soils, South America	charcoal in soils	*Pessenda et al.* [1996], *Saldarriaga and West* [1986] and *Sanford et al.* [1985]
Soils, Australia	charcoal up to 30% of soil organic matter	*Skjemstad et al.* [1996]
Soils, Germany	charcoal up to 45% of organic C	*Schmidt et al.* [1999]
Fluvial sediment or soil		*Anderson and Smith* [1994]
Soils, savanna, South Africa	black carbon from savanna fires	*Kuhlbusch et al.* [1996]
BC from fossil fuel combustion		
River sediment	charcoal from Roman ore smelters	*Foellmer et al.* [1997]
Marine sediment	fly ash	*Dueser et al.* [1983]
Harbor sediments, United States	indirect evidence for a soot-like phase	*Gustafsson and Gschwend* [1998], *McGroddy and Farrington* [1995], *McGroddy et al.* [1996]
Lake sediments	fly ash	compilation by *Wik and Renberg* [1996]
Forest soil, Sweden	carbonaceous spherules	*Wik and Renberg* [1987]
Forest soil, Germany	combustion residues, bituminous coal	*Schmidt et al.* [2000]
Agricultural soil, Germany	brown coal, combustion residues	*Schmidt et al.* [1996]
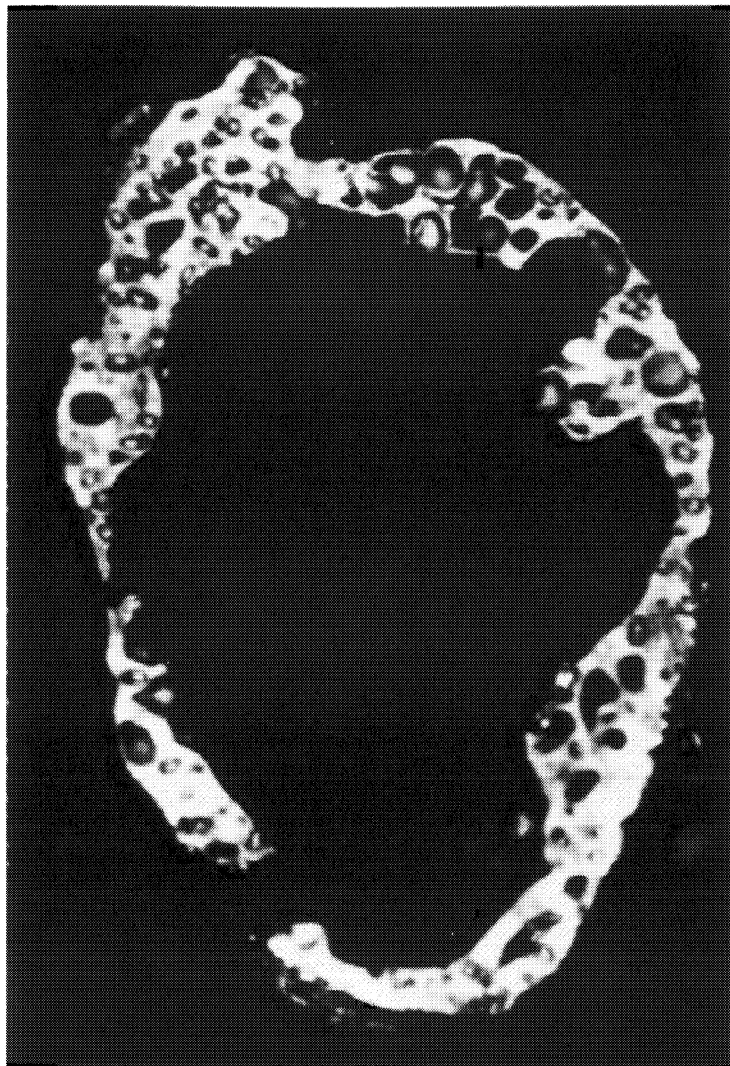
Figure 3. Airborne carbonaceous particle in a German forest soil originating from industrial coal processing. This char sphere has a maximum diameter of 200 μm and probably was formed in steel smelters at temperatures of 1500°C. Included in these spheres are coal particles, mainly inertinite particles, which probably already were formed in Carboniferous swamps. The particle was found in the mineral horizon of a Podzol. [*Schmidt et al.*, 2000].

tiation among charcoal, pyrite, and other opaque or dark-colored debris. Advantages of optical methods include the potential for particle size analysis and morphological description which can give information on sources and transport distances. Charcoal identification by light microscopy, however, is limited by size to approximately >10 μm. Coupling electron microscopy and chemical analyses by energy dispersive X-ray spectrometry (EDX) provides additional information on the elemental composition of the particles. Quantification of aerosol BC particles collected on filter papers can be conducted by measuring light absorption.

Thermal techniques often are applied for analysis of atmospheric BC particles (Table 2). These methods typically rely on the combustion of a sample in oxygen, thereby converting all carbon to CO_2, which can then be measured. Carbonate content is calculated by comparing results between HCl-treated and untreated samples. Separation of BC relies on the assumption that

temperature conditions can be chosen to thermally oxidize other organic carbon while BC remains nonvolatile. Such methods, developed for atmospheric BC particles, are not directly applicable to a complex matrix as found in soils and sediments. Soils and sediments may have lower BC concentrations and may also have closely associated macromolecular organic matter, which is not easy to thermally degrade or volatilize. Because BC comprises a continuum of compounds, a single "true" thermal limit does not exist for this heterogenous component, and an operationally defined cutoff temperatures need to be set empirically.

Chemical techniques often involve removal of carbonates and silicates as a pretreatment step. To remove kerogen, humic substances, and other organic material, chemical oxidants, such as acid dichromate, nitric acid, hydrogen peroxide or UV light, are used, often in combination and at different temperatures. The resistant carbon fraction can then be characterized by counting, elemental or isotopic composition, molecular tracer techniques

[Glaser et al., 1997], and spectroscopic methods, such as infrared [Herring, 1985], raman, nuclear magnetic resonance [Skjemstad et al., 1993, 1996], and mass spectroscopy [Bird and Gröcke, 1997; Winkler, 1985, 1994].

Indirect evidence for the presence of BC can be obtained by magnetically enhanced secondary ferrimagnetic oxides, which may be formed in the burning of soils. Changes in magnetic susceptibility and saturated isothermal remnant magnetization can aid in the interpretation of fire history because the magnetic values of burnt soils can be several orders of magnitude greater than those of unburned soils [Rummery, 1983]. Another form of indirect evidence for the presence of BC is its ability to act as a strong partition medium for PAH in aquatic systems [Gustafsson and Gschwend, 1997].

Summarizing, an enormous range of analytical approaches have been applied to determine the content of BC in soils and sediments. The problem with the large variation in BC methods is that BC is a continuum of thermally altered material, whereas many methods rely on operational definitions with clear-cut boundaries leading to incomparable results. Sizes and positions of analytical windows strongly depend on objectives of the study (e.g., quantification of BC, assessing fire history etc.), and vary with the associated matrix (aerosol, soil, or sediment). Very little is known about the comparability of the chemical and physical properties of the BC components measured by the individual methods. Systematic intercomparison exercises on well-defined standard materials could help immensely to circumvent these problems and allow more accurate determinations of BC types and fluxes in sediments and soils.

3. BC Distribution in Sediments and Soils

BC is distributed via wind and water to many natural environments including soils, peat bogs, lake sediments, and marine sediments. The distribution of BC in the environment is dependent both on the amount of BC produced and its subsequent dispersal, deposition, and preservation throughout the geological record. Major sources of BC have included burning vegetation, now augmented by increasing contributions by fossil fuel combustion.

3.1. Devonian to Tertiary

BC in the form of fullerenes has been detected in low-grade metamorphosed Proterozoic rocks [Ebbesen et al., 1995; Parthasarathy et al., 1998]. Burning vegetation has produced BC since the Late Devonian (~350 Ma), as evidenced by the local abundance of charcoalified plant fragments, called inertinite, in many post-Devonian sedimentary sequences [Cope and Chaloner, 1980; Goldberg, 1985; Jones and Chaloner, 1991]. Overall, inertinite seems to be ubiquitous, though not abundant, in most Carboniferous coals (Table 1). There are exceptions, such as fusinite-rich coal seams in the German coal fields in Zwickau and Ibbenbüren and vast quantities of charcoal in Lower Carboniferous carbonates and clastics of Ireland. The latter were interpreted as the product of a single catastrophic wildfire in a former coastal environment [Falcon-Lang, 1998]. Debate on the recognition and origin of fossil charcoal (fusain) in the geological record was reviewed by Scott [1989], who produced experimental criteria for a wildfire origin by comparing chars produced in the laboratory with fossil material. Random reflectance of charcoal has been shown to increase linearly with temperature of formation [Jones and Chaloner, 1991; Kruge et al., 1994]. When the correlation

was applied to Carboniferous fossil charcoal from Yorkshire coal measurements, a paleowildfire temperature of 370°-480°C ±100°C was indicated, which is consistent with temperatures recorded for modern wildfires. Winston [1993] presented further evidence against the existence of fusinite formed without undergoing charring or oxidation (primary fusinite) and fusinite formed owing to decay or degradation (degradofusinite). The acceptance of a fire origin for at least some fusain has enabled its use as an indicator of wildfire since at least the Late Devonian, with broad implications for paleoatmospheric oxygen content.

Paleoatmospheric oxygen concentrations have been estimated using the occurrence of BC in the geological record as an indicator [Cope and Chaloner, 1980]. During pyrolysis, gases are generated which support the combustion of wood. As the availability of oxygen decreases, the temperature range for combustion of these gases is restricted, eventually to a level below which there is no combustion. The minimum atmospheric oxygen content required to initiate and maintain this combustion process has been determined by several workers [Chaloner, 1989; Cope and Chaloner, 1980]. On the basis of these data it is generally agreed that if the oxygen content fell below a factor of 0.6-0.7 of the present atmospheric level (13-15 mol % oxygen), combustion of plant material by wildfire could not occur. The fairly continuous record of plant material with charcoal characteristics since the Late Devonian suggests that the oxygen level has been sufficient to support wildfires. A maximum oxygen level of 35 mol % has been suggested by Chaloner [1989] on the basis of the flammability of vegetation. In the absence of anthropogenic influence most wildfires are ignited by lightning strike [Cope and Chaloner, 1980; Watson et al., 1978]. At the present atmospheric level of oxygen, only dry lightning would initiate fire. At a raised oxygen content of 25 mol %, vegetation at the fiber saturation point has a significant chance of ignition even in a rainstorm, and the probability of fire ignition becomes extremely high. Owing to this increased likelihood of ignition and combustion, Watson et al. [1978] concluded that the existence of land-based vegetation is incompatible with atmospheric oxygen levels of 25-35 mol %. Thus the presence of charcoal in the environment indicates a minimum limit for the oxygen content of the atmosphere near 15 mol %, and the absence of total combustion of vegetation provides an upper limit of ~35 mol %.

The Cretaceous/Tertiary (K/T) boundary ~66 million years ago is marked by massive extinctions on a global scale. The cause of this global catastrophe has been variously attributed to impact by a meteorite and massive terrestrial volcanism. Debate continues on the actual cause of these extinctions, including the impact of a global winter [McLean, 1991] and the possibility of wildfires on a global scale as evidenced by BC in the geological record (Figure 4). Graphitic carbon was found in clay samples from the K/T boundary at much higher concentration than in adjacent strata [Wolbach et al., 1985]. The mean carbon abundance of 0.021 g cm^1 represents a worldwide flux 10^4 times the present flux [Goldberg, 1985] and 10^3 times that of the Late Cretaceous-early Tertiary, as determined from samples immediately above and below the K/T boundary. Scanning electron microscopy indicated a bimodal size distribution, with submicrometer particles having morphologies characteristic of BC derived from flaming combustion as soot, and large micrometer particles were similar to those obtained from forest fires. Wildfires were postulated as the source of the charcoal layer. Subsequent work by Wolbach et al. [1988] was improved with better techniques, which allowed the resolution of kerogen and elemental carbon and for the esti-
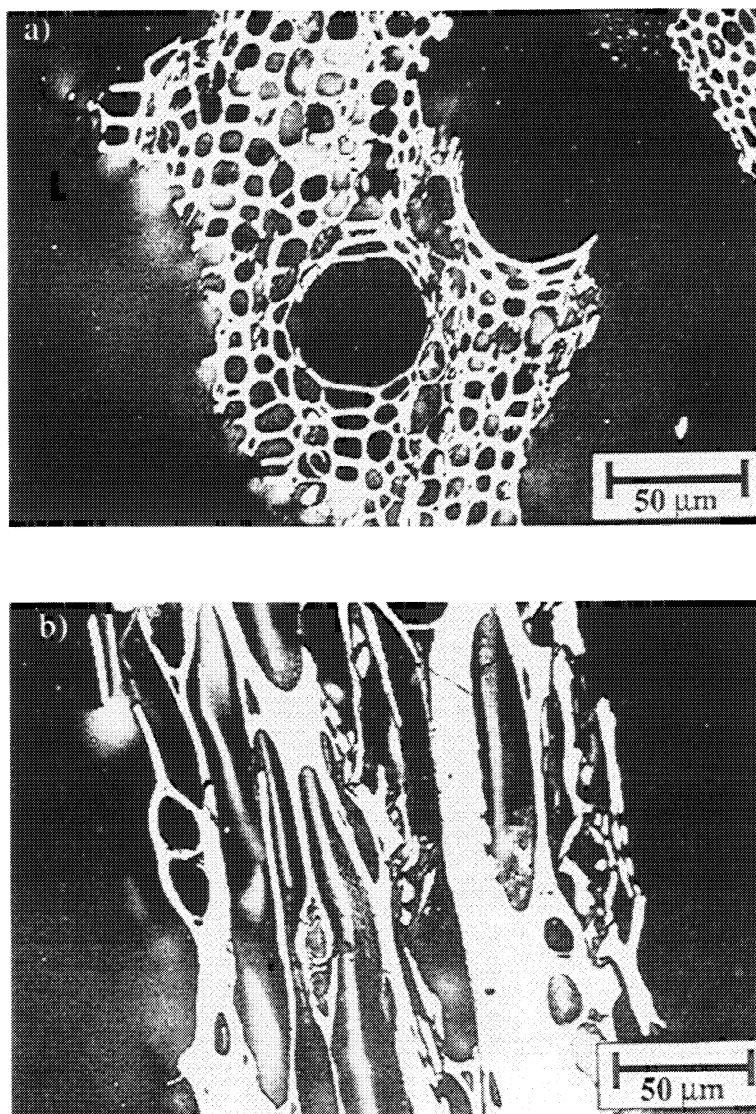
Figure 4. Charred organic particles from the Creataceous-Tertiary (KT) boundary layer, as seen by reflected light microscopy [*Kruge et al.*, 1994]. The morphology is typical for xylem cell structures from plants, both in (a) cross and (b) longitudinal section. The chemical structure, however, was typical for products of partial combustion. Analytical pyrolysis–gas chrromatography–mass spectrometry revealed a highly (poly) aromatic character. Reprinted from *Geochim. Cosmochim. Acta, 58*, Kruge, M.A., A.B. Stankiewicz, J.C. Crelling, A. Montanari, and D.F. Bensley, Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave, 1393-1397, 1994, with permission from Elsevier Science.

mation of the proportion of the fine soot and coarse carbon fractions of the elemental carbon. Their refinements showed that soot enrichment coincides with the iridium layer and suggested that the fire was triggered by meteorite impact.

Herring [1985] calculated BC fluxes from charcoal concentration and sediment accumulation rates in Cenozoic sediments from deep-sea cores of the North Pacific Ocean. Charcoal concentrations were consistently greater in Holocene than older sediments. Charcoal fluxes were small through the Paleogene and began to increase in the Neogene to ~2 orders of magnitude greater in the late Neogene. Chemical or biological destruction of the charcoal in older sediments was ruled out on the basis of con-

sistent size distributions of charcoal particles throughout the sediment column. Increased charcoal flux was related to increasing plant burning on land, which is consistent with paleobotanical and paleoclimatical evidence, indicating an increasingly cool climate throughout the Cenozoic and increased relative abundance of temperate, more combustible plants. Charcoal fluxes for the last 5 million years indicated the annual removal of $\sim 10^{14}$ g of carbon in this form from the atmosphere.

3.2. Quaternary

3.2.1. BC from vegetation fires. In lacustrine sediments, there is considerable evidence of the presence and persistence of

BC. For example, *Singh et al.* [1981] found that charcoal has remained plentiful since ~120,000 years before present in the clay sediments of Lake George, New South Wales, Australia. In the 200,000 year sedimentary record of Lynch's Crater, Queensland, Australia, charcoal peaks corresponded with major vegetational change and the abundance of charcoal increased by an order of magnitude 35,000 years BP, coinciding with the arrival of aboriginals, who through their use of fire, changed the vegetation. Pollen and charcoal analysis of sediment from Rutz Lake, Minnesota, both indicated that fire was more frequent and severe during the mid-postglacial warm period [*Waddington*, 1969]. Annual laminations, called varves, provided excellent time control in sediments from the Lake of Clouds, Minnesota, and allowed the calculation of charcoal and pollen influxes for comparison through the postglacial period [*Swain*, 1973]. Peaks in the concentration of charcoal were correlated with post 1690 AD fires inferred by analysis of tree rings, and indices were devised to identify peaks in charcoal attributable to fire. Further studies [*Swain*, 1978] demonstrated a direct correlation between charcoal in lake sediments and patterns of fire occurrence on a broad, regional scale. Pollen, charcoal, aluminum, and vanadium analyses were made on decadal segments of a 500 year section, spanning 750-1270 AD, of laminated sediment from Greenleaf Lake, Algonquin Park, Ontario, Canada [*Cwynar*, 1978]. Peaks in charcoal to pollen ratios were considered to indicate major fires, of which six were identified.

In marine sediments, *Smith et al.* [1973] investigated charcoal contents in samples taken from the top 150 mm of sediment of Pacific Ocean deposits, representing an estimated 150,000 year sedimentation history. Charcoal in pelagic sediments increased from the southern equatorial regions northward, the latitudinal zonation corresponding to distributions of nontropical forest. Debris from burning biomass was transported through the lower atmosphere by zonal wind systems. These were the easterly trade winds of the equatorial zone, blowing east to west, the mid-latitudinal westerlies which were more intense at higher elevations, and the polar easterlies of relatively low intensity and high variability. Reanalyzing this data, *Suman et al.* [1997] concluded that BC in marine sediments varied not zonally but with distance from continents.

BC is commonly found in soils as microscopic and macroscopic particles of charcoal. Although BC in soil is generally an indicator of past fire, without the time constraints offered by laminated sediments its use in the interpretation of fire history is limited. BC is introduced to agricultural soils as a result of land clearing practices, and subsequent straw burning would add finely divided BC. In soils the formation of BC by savanna fires is reported from southern Africa [*Kuhlbusch et al.*, 1996], with >90% of the charcoal remaining on the ground after fires. Charcoal seems to be common in soils of rain forests in the northern central Amazon Basin, and ^{14}C dating indicated the occurrence of numerous fires since the mid-Holocene, with the earliest evidence of fire predating evidence of human presence [*Saldarriaga and West*, 1986; *Sanford et al.*, 1985]. Isotopic data from charcoals collected from soils suggested widespread occurrence of forest fires in central Brazil during the Holocene [*Pessenda et al.*, 1996] and in east Borneo in the late Pleistocene [*Goldammer and Seibert*, 1989]. Thus fire disturbance appears to be a natural part of rain forest ecosystems. Wildfires in tropical rain forest have been observed in dry seasons, for example during the drought years of 1982-1983, wildfires burned in rain forest of east Borneo [*Goldammer and Seibert*, 1989] and near San Carlos, Venezuela [*Sanford et al.*, 1985].

Charcoal deposited at the soil surface is very susceptible to erosion by wind and water. *Griffin and Goldberg* [1975] measured charcoal in soils from San Diego County and suggested charcoal was not persistent in soil owing to resuspension and removal. Nevertheless, analysis of soil profiles has indicated the presence of charcoal throughout the soil profile; its persistence being attributed to its inert nature. Charcoal fragments of millimeter dimension are incorporated into the soil either at the time of deposition with aeolian silt, during mass movement, or by biological or frost churning [*Fedoroff et al.*, 1990]. Smaller fragments of micrometric dimension are translocated to lower horizons with clay particles [*Fedoroff et al.*, 1990; *Ohta et al.*, 1986]. The possibility of breakage and damage of charcoal pieces due to abrasion during movement down the profile in the coarse fabric environment of mineral soil was proposed for discussion by *Patterson et al.* [1987]. It seems likely that charcoal would be physically broken down; however, this search of the literature did not find any research testing this hypothesis.

Charcoal is commonly found in the light fraction of soils and contributed up to 45% of the whole soil organic carbon in a number of Chernozemic soils in Germany [*Schmidt et al.*, 1999]. *Spycher et al.* [1983] identified charcoal in the light fraction (<1.65 Mg m^{-3}) of a forest soil by scanning electron microscopy. The charcoal, which was encrusted with colloidal soil materials that had not been removed by the ultrasonic treatment, was irregularly distributed down the soil profile, which was sampled to 83 cm depth. This distribution biased the carbon to nitrogen (C:N) ratios of the light fractions, which were very high (30.8-70.7), with large standard deviations. This was particularly important at very low concentrations of nitrogen where analytical errors also contribute significantly to variance in the C:N ratio. Charcoal particles were found in the black humus of sandy grassland soils with C:N ratios >16, whereas the two sandy soils used with C:N ratio <16 containing brown humus and the loams and clays containing gray-colored humus did not contain charcoal [*Hassink*, 1994]. When the effect of soil texture on soil organic carbon and nitrogen contents and rates of mineralization were assessed, differences in C:N confused the relationships between these properties. The presence of inert carbon as charcoal in the sandy soils with high C:N ratio could explain the negative correlation between the C:N ratio and carbon mineralization. .

Charcoal was found in the particulate organic matter (POM) fraction (>53 μm) of grassland soils by *Cambardella and Elliot* [1992]. It was contained in the heavy fraction (>1.85 Mg m^{-3}) of the POM and accounted for most of the carbon in this fraction, representing 5-10% of the POM by weight. The charcoal component would have increasing importance to the turnover rate of POM with increasing decomposition of the other components. *Skjemstad et al.* [1990] found charcoal in light fractions (<1.6 Mg m^{-3}) obtained from grassland and rainforest soils. The presence of charcoal imposed uncertainties on the interpretation of $\delta^{13}C$ results, and consequently, charcoal was removed prior to analysis.

The presence of charcoal in soil can cause misleading interpretations of soil organic matter parameters, such as content and chemical structure of organic matter, mineralization rates, and age as measured by ^{14}C dating. As examples, concentrations of "soil organic carbon" might be overestimated by dry combustion owing to the presence of charcoal. Charcoal may produce humic acids and thus may interfere with chemical extracts of humic substances [*Haumaier and Zech*, 1995; *Skjemstad et al.*, 1996].

3.2.2. C from fossil fuel combustion. With increasing human activities the fraction of BC from fossil fuel combustion has continuously increased. In lake sediments, particles from coal com-

bustion have been identified by microscopy [*Lim and Renberg*, 1997; *Renberg and Wik*, 1985; *Wik and Renberg*, 1987, 1991]. BC from Lake Michigan was analyzed by *Griffin and Goldberg* [1979; 1983] to determine the impact of fossil fuel consumption. Sediments deposited after 1900 contained coal-, oil- and wood-derived BC, whereas older sediments contained only wood charcoal based on the morphology of the particles. The size distribution also reflected the onset of the industrial revolution and increased intensity of fossil fuel combustion during the twentieth century. The <1 μm fraction, primarily from burning of wood, dominated prior to 1900, whereas after 1900, larger particles, particularly >32 μm, derived from burning of coal and oil made a larger contribution to charcoal concentrations. The input of larger particles is indicative of a shorter distance from their major sources, the power plants along the shore of the lower Lake Michigan Basin. A decrease in BC concentration in deposits after 1960 to the time of the study was attributed to improved emission controls on power plants and industrial facilities. In a microscopic study of Lake Michigan sediments, *Karls and Christensen* [1998] differentiated between coal-, wood-, and oil-derived carbon particles and correlated this pattern to the local combustion history between 1900 and 1990.

In soils the potential influence of emissions from coal industries on the properties of soil organic matter has only recently been recognized. Increased magnetic susceptibility in British soils and peats gave indirect evidence for the presence of carbon-rich particles, most likely originating from industrial combustion [*Thompson and Oldfield*, 1986]. Coal, char and coke resulting from recent industrial processes were found to be preserved in urban soils [*Hiller and Brümmer*, 1997]. In soils of highly industrialized areas of Germany the atmospheric deposition of combusted particles and coal dust from coal processing industries contributed up to 80% of the total soil organic carbon, which was equivalent to 35 kg m^{-2} for the top 25 cm layer [*Rumpel et al.*, 1998; *Schmidt et al.*, 1996; 2000].

4. BC in Recent Soils and Sediments: Implications

4.1. BC and Soil Organic Matter Composition

The presence of BC has been proposed as a source of highly aromatic components of soil humic acids extractable from soils [*Haumaier and Zech*, 1995; *Skjemstad et al.*, 1996]. *Shindo et al.* [1986] found the physico-chemical and spectroscopic properties of humic acids of charred residues from *Miscanthus sinensis* (pampas grass) were similar to those from the A horizons of volcanic ash soils, indicating charred products of grassland vegetation as a possible source of the A type humic acids found in Japanese volcanic ash soils. *Kumada* [1983, 1987] compared humic acids prepared from charred materials with soil humic acids. Charcoal collected from soil horizons yielded the largest amounts of humic acids, followed by samples picked up from bonfires. However, commercial charcoal and cinder prepared by quenching a wood fire contained no alkali-extractable materials until after treatment with $KClO_3$-HNO_3, which seemed to indicate some depolymerization and carboxylation of the carbonaceous material was required to make it extractable. Thus *Kumada* [1983] proposed that carbonaceous products of plant combustion are "weathered" under natural conditions to form parts of the humic and fulvic acid fraction. Experimental burning increased proportions of aromatic humic acids [*Kumada et al.*, 1967; Kumada 1987], whereas in other humic acids, aliphatic and aromatic car-

bon dominate [*Tate et al.*, 1990]. Heating of some volcanic ash soils above 250°C lowered yields of humic acids [*Shindo and Urabe*, 1993].

The higher aromatic carbon content of humic acids could be due in part to a history of burning [*Almendros et al.*, 1988]. Higher yields of aromatic products were obtained from humic acids after heating, either in the laboratory at 160° and 210°C, or from a forest soil burnt 2 years prior to sampling. Although high yields of aromatic products and high benzene carboxylic-to-phenolic ratios of degradation products has long been considered an indication of a high degree of biological transformation, it has now been shown that these properties can also be induced by thermal alteration. Heating humic acids at 350°C increased the proportion of aromatic structures observed by CPMAS ^{13}C nuclear magnetic resonance (NMR), whereas alkyl, O-alkyl, and carboxyl forms of organic matter were depleted [*Almendros et al.*, 1992]. In later work on Japanese volcanic ash soils, *Golchin et al.* [1997b] found by ^{13}C NMR that soils managed as *Miscanthus sinesis* grassland by regular burning contained a greater proportion of aromatic and carbonyl carbons compared to sites left to return to forest with cessation of burning. Using proton spin relaxation editing (PSRE), an NMR experiment which exploits differences in relaxation properties between spatially distinct domains, subspectra were generated. The faster-relaxing subspectrum from the currently burnt site was very similar to those obtained for charred residues and charcoal. When density fractions of soils were studied where vegetation burning was practiced [*Golchin et al.*, 1997a], ^{13}C NMR and PSRE indicated the presence of considerable amounts of charred plant residues and charcoal in free and mineral occluded forms. *Takahashi et al.* [1994] concluded that burning vegetation has been an important factor in the formation of deep black soils in the xeric moisture regime of northern California.

Several studies reveal an apparent relation between deep black soil color and the presence of BC or high proportions of extractable highly aromatic humic acids. Studies of volcanic ash soils in Japan and New Zealand revealed a relationship between grassland and melanic (deep black) soil color (*Sase and Hosono* [1996] and references to Japanese literature therein). Using light microscopy, several workers have found blackish, coal-like particles often occur with a cellular structure and diameters between 2 and 10 μm. Such particles occur in numerous typical Chernozems from the central Russian highland forest steppe on loess-loam [*Kubiena*, 1938; *Pawluk*, 1985; *Yarilova*, 1972], Canadian Chernozems (Pawluk, 1985) and other soil types with dark A horizons [*Altemüller*, 1992]. There is also indirect evidence that BC in soils produces highly aromatic humic acids such as volcanic ash soils [*Hatcher et al.*, 1989], Chernozems [*Kononova*, 1966; *Schnitzer*, 1992], Vertisol in Mali [*Gehring et al.*, 1997], and an Argentinean Hapludoll [*Zech et al.*, 1997]. Australian grassland soils, which were under aboriginal fire management presumably for thousands of years, are characterized by black A horizons with up to 30% of the soil carbon present in charred form, whereas adjacent forested soils that were not subjected to regularly burning are gray and contain little char [*Skjemstad et al.*, 1997]. In a systematic study of northern Eurasian soils, humic acid contents increased in the order gray forest soils < dark gray forest soils < Chernozems [*Kononova*, 1966]. A 10 km color sequence of four German chernozemic soils, which were very similar in chemical and physical properties, showed a strong relation between color and BC content [*Schmidt et al.*, 1999].

Overall, these observations give further support to the concept that charred organic materials are the source of the chemically

stable aromatic components of soil organic matter. It seems that soils subjected to continued burning comprise considerable amounts of BC and often have a dark color.

4.2. BC and Soil Ecology

Studies of wildfire in boreal forests suggest that charcoal particles can act as foci for microbial activity and have adsorbing capacity for allelopathic compounds, such as phenolica [*Wardle et al.*, 1998; *Zackrisson et al.*, 1996]. Charcoal particles therefore have a comparable ecological role for biodegradation of phytotoxic compounds to that of clay in mineral soil. From bioassays the authors concluded that charcoal has sorptive abilities for only the first 100 years following its formation but can be reactivated by subsequent fires.

In laboratory heating experiments in the absence of oxygen, *Miltner and Zech* [1997] found that the presence of inorganic matter increased organic carbon loss as CO_2. The presence of birnesite and $Fe(OH)_3$ accelerated the decomposition of plant-derived constituents, such as polysaccharides and lignin, whereas the influence of $Al(OH)_3$ was less pronounced. Adding BC to rather infertile Oxisols of the Brazilian Amazon basin during pre-Columbian times has created small areas of very fertile soils [*Glaser et al.*, 1998]. These soils are characterized by higher levels of organic matter, phosphorous. and nitrogen. The authors assume that slow oxidation of BC creates carboxylic groups, thereby increasing cation exchange capacity and sustainable soil fertility.

Relatively little is known regarding the effects of coal and its burned residues on soil ecology. Combustion by-products often contain heavy metals and soluble salts and can be potentially harmful to plants and soil organisms [*McCarty et al.*, 1994]. Applied in a field trial, coal fly ash increased plant biomass and crop yields [*Schutter and Fuhrman*, 1999]. However, potential effects of atmospheric deposition of charred organic particles at the field scale are poorly understood.

4.3. BC and Sorption of Pollutants

In aquatic environments, BC can act as carrier of organic pollutants [*Gustafsson and Gschwend*, 1997]. Recent studies of PAH, organic carbon, and soot carbon in surficial continental shelf sediments revealed that the distribution of PAH was highly correlated with soot carbon [*Chiou and Kile*, 1998; *Gustafsson and Gschwend*, 1997; *McGroddy and Farrington*, 1995; *McGroddy et al.*, 1996]. Other organic substances which are characterized by highly aromatic structures include lignin, lignite, or bituminous coal. These substances were found to act as strong sorbents for hydrophobic aromatic compounds in soils and sediments [*Garbarini and Lion*, 1986; *Grathwohl*, 1990; *Kleineidam et al.*, 1999]. Owing to the structural similarities between these substances and BC, it seems likely that also the presence of BC may affect sorption of hydrophobic organic compounds in soils and sediments.

4.4. BC as a Potential Sink in the Global Carbon Cycle

BC is one of the most resistant forms of reduced carbon toward chemical oxidation and is often found in sediments and soils. High estimated production rates of BC [*Kuhlbusch and Crutzen*, 1995] together with high resistance to degradation imply BC could compose a major proportion of all organic carbon buried in sediments. If BC is not being mobilized off the continents at this high rate, it must be either accumulating rapidly in soils and terrestrial sediments or must be mineralized in these environments by severe oxidative mechanisms. In soils, oxidation by microorganisms is reported for BC [*Shneour*, 1966], whereas another author found no degradation [*Shindo*, 1991]. In marine sediments first evidence for significant degradation came from the examination of a relict oxidation front in a turbidite in an abyssal plain [*Middelburg et al.*, 1999].

To assess the impact of BC on the global element cycles (Figure 5), a detailed understanding of the processes involved in
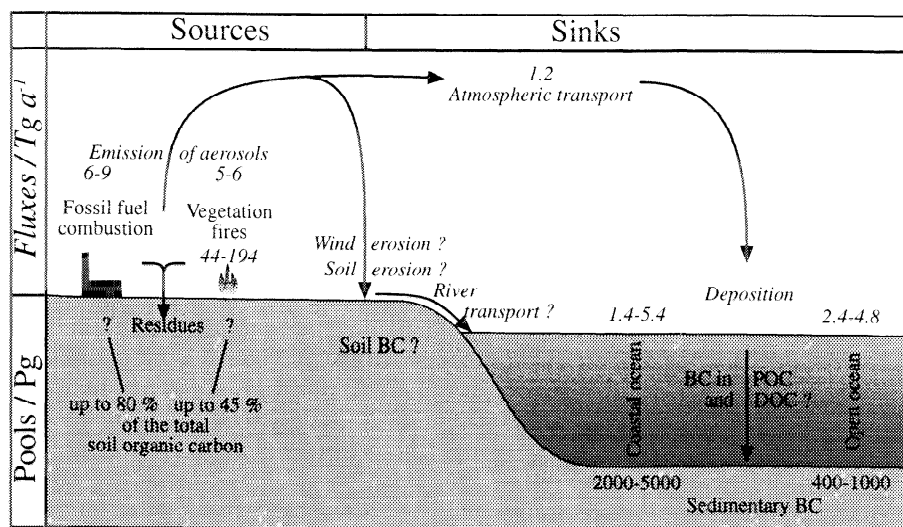
Figure 5. The global biogeochemical cycle of black carbon (BC). On land, BC is produced by vegetation fires and fossil fuel combustion. BC occurs ubiquitously in soils and terrestrial sediments, and via fluvial and atmospheric transport, it is coupled to a common fate of storage in marine sediments. Values for fluxes are shown as italics in teragrams (1 Tg = 10^{12} g) per year, and pools are in petagrams (1 Pg = 10^{15} g). Figure 5 includes data from [*Kuhlbusch and Crutzen* [1996], *Schmidt et al.* [1996, 1999], *Suman et al.* [1997] and *Warneck* [1988].

BC degradation is needed. As part of the global carbon cycle, vegetation fires are thought to represent a sink of atmospheric CO_2 [Kuhlbusch and Crutzen, 1995]. Discrepancies exist, however, in estimates of net and gross carbon fluxes between the oceans, the biosphere, and the atmosphere [Seiler and Crutzen, 1980, and references therein; Gifford, 1994]. The rise in atmospheric CO_2 content since the beginning of the industrial revolution does not account for all the CO_2 released by fossil fuel and biomass burning. The ocean acts as a sink for some of this CO_2, in the form of carbonates and bicarbonates, but this is not enough to account for estimates of CO_2 released. An increased uptake of CO_2 by plants has been suggested as an important sink for the missing carbon. Other terrestrial sinks are being sought, such as BC and oceanic sediments derived from terrestrial runoff.

Seiler and Crutzen [1980] assessed the role of BC as a sink in the global carbon budget. They estimated that the total annual biomass exposed to fire amounts to 9-17 x 10^{15} g dry matter, equivalent to 4-8 x 10^{15} g carbon. Of this total, 5-9 x 10^{15} g is actually burned, resulting in an annual flux of 2-4 x 10^{15} g carbon and indicating a global average burning efficiency of ~50%. Burning in the tropical and subtropical regions accounted for 70% of the global biomass combusted, with only a 30% contribution from the midlatitudes of the Northern Hemisphere. After a wildfire, it was estimated that about 20-30% of the biomass remaining aboveground was present as elemental carbon, and this was mainly BC. The total unburned aboveground biomass was estimated to be 4-11 x 10^{15} g of dry matter, representing 1.8-5 x 10^{15} g of carbon. On this basis they calculated that the BC remaining aboveground after burning represents 0.4-1.5 x 10^{15} g of carbon. In addition, the contribution of particulate BC (elemental charcoal and soot) was estimated at 0.1-0.2 x 10^{15} g carbon. Thus the total annual formation of BC was typically 0.5-1.7 x 10^{15} g carbon, with an average of 1.1 x 10^{15} g carbon. This BC residue represents a significant sink for atmospheric CO_2 and as such should be included in geochemical models of both the carbon and oxygen cycles.

Herring [1985] calculated an annual removal of ~10^{14} g (0.1 x 10^{15} g) of carbon from the atmosphere, using BC fluxes for the last 5 million years in deep-sea sediments of the Northern Pacific Ocean. This flux represents particulate carbon released into the atmosphere by biomass burning and is similar in magnitude to that calculated by Seiler and Crutzen [1980]. Schiffman and Johnson [1989] noted that preparation of sites for reforestation includes burning and may cause slow, long-term increases in detrital carbon as BC. About 4.5 x 10^6 g carbon ha^{-1} as charcoal (charcoal equals 60.7% C in this study) was present on the forest floor of a plantation planted on recently cleared land. This accounted for ~30% of the forest floor carbon.

Subsequent work has indicated that the magnitude of BC production is lower than that calculated by Seiler and Crutzen [1980]. Fearnside [1991] found a lower rate of BC production than Seiler and Crutzen [1980]. In clearing fires in Amazonia they determined that only ~3.6% of the aboveground biomass carbon remained as BC, which is ~20% of the earlier estimate. Crutzen and Andreae [1990] updated estimates of the quantities of biomass being burned in the tropics through activities such as clearing of forests, removal of savanna vegetation, and burning of fuel wood, charcoal, and agricultural waste, in addition to contributions from prescribed burning and forest wildfires. It was estimated between 2.7 and 6.8 x 10^{15} g carbon per year of biomass was exposed to burning of which 1.8-4.7 x 10^{15} g carbon per year was released as CO_2 and 0.2-0.6 x 10^{15} g carbon per year was sequestered as BC. If 70% of BC production occurs in the tropics

[Seiler and Crutzen, 1980], this is equivalent to 0.3-0.9 x 10^{15} g carbon per year globally. This estimate is slightly lower than that of Seiler and Crutzen [1980] but is still significant in terms of global CO_2 fluxes. In a review on the impact of biomass burning on global climate, Andreae [1991] concluded that the range of estimates for the global rate of BC formation is large owing to these uncertainties in quantification. About 0.05-1.7 x 10^{15} g carbon per year is likely to be sequestered as BC, representing between 3 and 30% of the ~7 x 10^{15} g carbon added to the atmosphere annually [Kuhlbusch and Crutzen, 1996; Seiler and Crutzen, 1980]. Esser [1990] recognized the need to consider BC formation from biomass burning in natural environments, such as savannas, grasslands, and forests, when modeling terrestrial sources and sinks of CO_2. The Osnabruck Biosphere Model, a global grid-base model of carbon balance of the terrestrial biosphere, did not consider burning in natural environments and so did not include the BC component. This was identified as an area of refinement required in the model.

From stable and radioisotopic measurements of BC in marine sediments, Masiello and Druffel [1998] concluded that BC, which aged thousands of years in terrestrial soils, contributed to oceanic dissolved and sedimentary organic carbon. From the results of a millionyear marine record, Bird and Cali [1998] inferred that BC from fires in sub-Saharan Africa increased because of anthropogenic activity since Holocene times.

The formation and incorporation of BC into soils and sediments is an important mechanism in the long-term sequestering of carbon and is likely to account for some of the "missing" CO_2 in the global carbon budget. However, degradation rates of BC and the magnitude of this carbon pool remains controversial.

5. Conclusions and Present Challenges

Black carbon (BC) has originated from vegetation burning since the Devonian and recently also from fossil fuel combustion. BC is relatively inert to environmental degradation processes and has been globally distributed via fluvial and atmospheric transport to become a virtually ubiquitous component in soils, lacustrine, and marine sediments. BC seems to be abundant in dark-colored soils and especially those affected by frequent vegetation or fossil fuel burning. Only limited progress, however, has been made calibrating analytical techniques for a better interpretation of experimental data obtained in previous studies.

The key to estimating BC stocks in soils and sediments is to understand the processes involved in BC degradation. Practical progress toward estimating BC degradation rates on a global scale requires analytical approaches that elucidate degradation processes on a molecular level. Studied sites should differ in environmental settings (oxic versus anoxic) and vary widely in timescale of observation. A promising approach would be the combination of short-term laboratory experiments and field trials whereby BC has already been exposed to weathering and biological activity for decades, centuries, or millennia.

To identify BC sources, the analytical focus has mainly been the determination bulk properties, such as micromorphology, elemental composition, isotopy, and chemical structure. Progress in source characterization is likely to come from molecular approaches, e.g. characterization of further source specific molecular markers, and determination of compound-specific properties.

A current challenge complicating the successful quantification of current and historical rates of BC production from different sources is a lack of standardization of both identification of BC

and analytical protocols to quantify BC in the different matrices, including peats, organic and mineral soils, lacustrine, and marine sediments. Presently used analytical methods could produce widely differing results for identical samples. So far, however, systematic comparison exercises have not been published. This challenge is especially difficult because the chemical structure and physical size of BC can be extremely heterogeneous. BC includes a continuum of thermally altered plant material, with aromatization increasing in the order plant tissue < char < charcoal < graphite. However, no generally accepted clear-cut boundaries between these forms of BC exist. Commonly applied methods for measuring BC in the presence of other organic material tend to rely on the resistance of the highly aromatized components of BC to extremely oxidizing conditions, either thermally or chemically. To gain specificity against other organic material present in soils and sediments, many methods provide conservative measures of BC and therefore probably overlook much of the combustion products present.

Urgently needed are standard reference materials available across the diverse community of scientists studying environmental BC. Depending on the matrix and the various scientific questions related to BC (degradability, soil fertility, fire history, radiation budget, etc.), there may be a need for different techniques detecting different fractions of BC. Progress in the quantification of BC is likely to come from taking further advantage of noninvasive techniques, such as infrared and nuclear magnetic resonance spectroscopy coupled with the use of stable isotopes (e.g. $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$) and radioisotopes ($\Delta^{14}C$). Also molecular-level indicators can be extremely sensitive indicators of BC types and amounts.

Improved accuracy of BC quantification could allow identification of the sources and histories of BC in soils and sediments. Further efforts to quantify the rates and mechanisms of BC decomposition in soils and sediments are urgently needed. Results could become the key for a number of issues: 1) quantification of the role of BC as a sink of biospheric carbon in the global cycle, 2) determination of the presence of BC in sediments and soils and its effects on increased sorption of PAH, pesticides, and heavy metals, and 3) assessment of long-term effects of BC on soil fertility, nutrient availability, and fluxes of C, N, and S.

References

Akhter, M.S., A.R. Chughtai, and D.M. Smith, The structure of hexane soot, I; Spectroscopic studies, *Appl. Spectrosc.*, *39* (1), 143-153, 1985a.

Akhter, M.S., A.R. Chughtai, and D.M. Smith, The structure of hexane soot, II; Extraction studies, *Appl. Spectrosc.*, *39* (1), 154-167, 1985b.

Almendros, G., F. Martín, and F.J. Gonález-Vila, Effects of fire on humic and lipid fractions in a Dystric Xerochrept in Spain, *Geoderma*, *42*, 115-127, 1988.

Almendros, G., F.J. González-Vila, F. Martín, R. Fründ, and H.-D. Lüde-

mann, Solid state NMR studies of fire-induced changes in the structure of humic substances, *Sci. Total Environ.*, *117/118*, 63-74, 1992.

Altemüller, H.-J., Visuelle Erscheinungs- und Zustandsformen der organischen Bodensubstanz, *Ber. Landwirtsch.*, *206*, 30-44, 1992.

Anderson, R.S., and S.J. Smith, Paleoclimatic interpretation of meadow sediment and pollen stratigraphies from California, *Geology*, *22*, 723-726, 1994.

Andreae, E., Biomass burning: Its history, use, and distribution and its impact on environmental quality and global climate, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J.S. Levine, pp. 3-21, MIT Press, Cambridge, Mass., 1991.

Bailey, J.G., A. Tate, C.F.K. Diessel, and T.F. Wall, A char morphology system with applications to coal combustion, *Fuel*, *69*, 225-239, 1990.

Beck, C.B., K. Coy, and R. Schmidt, Observations of the fine structure of Callixylon wood, *Am. J. Bot.*, *65*, 54-76, 1982.

Beeston, J.W., Aspects of the inertinite formation and deposition in the Denison Troug, Queensland, *Aust. J. Coal. Geol.*, *7*, 33-45, 1987.

Bird, M.I., and J.A. Cali, A million-year record of fire in sub-Saharan Africa, *Nature*, *394*, 767-769, 1998.

Bird, M., and D.R. Gröcke, Determination of the abundance and carbon isotope composition of elemental carbon in sediments, *Geochim. Cosmochim. Acta*, *61*, 3413-3423, 1997.

Bird, M.I., E. Veenendaal, C. Moyo, J. Lloyd, and P. Frost, Stability of elemental carbon in a savanna soil, *Global Biogeochem. Cycles*, *13*, 933-950, 2000.

Burgess, N.D., and D. Edwards, A new Palaeozoic plant closely allied to *Prototaxites Dawson*, *Bot. J. Linn. Soc.*, *97*, 189-203, 1988.

Cachier, H., M.P. Bremond, and P. Buat-Menard, Carbonaceous aerosols from different tropical biomass burning sources, *Nature*, *340*, 371-373, 1989.

Cady, J.G., L.P. Wilding, and L.R Dreefs, Petrographic microscope techniques, in *Methods of Soil Analysis*, edited by A. Klute, pp. 185-218, Am. Soc. Agron., Madison, Wis., 1986.

Cambardella, C.A., and E.T. Elliott, Particulate soil organic matter changes across a grassland cultivation sequence, *Soil Sci. Soc. Am. J.*, *56*, 777-783, 1992.

Chaloner, W.G., Fossil charcoal as an indicator of palaeoatmospheric oxygen level, *J. Geol. Soc. London*, *146*, 171-174, 1989.

Chang, S., and R.A. Berner, Coal weathering and the geochemical carbon cycle, *Geochim. Cosmochim. Acta*, *63*, 3301-3310, 1999.

Chiou, C.T., and D.E. Kile, Deviations from sorption linearity on soils of polar and nonpolar organic compounds at low relative concentrations, *Environ. Sci. Technol.*, *32*, 338-343, 1998.

Chylek, P., V. Srivastava, L. Cahenzli, R.G. Pinnick, R.L. Dod, T. Novakov, T.L. Cook, and B.D. Hinds, Aerosol and graphitic carbon content of snow, *J. Geophys. Res.*, *92*, 9801-9809, 1987.

Chylek, P., B. Johnson, and P.A. Damiano, Biomass burning and black carbon in the GISP2 ice core, *Geophys. Res. Lett.*, *22*, 89-92, 1995.

Clark, J.S., Particle motion and the theory of charcoal analysis: Source area, transport, deposition, and sampling, *Quat. Res.*, *30*, 67-80, 1988a.

Clark, J.S., Stratigraphic charcoal analysis on petrographic thin sections: Application to fire history in northwestern Minnesota, *Quat. Res.*, *30*, 81-91, 1988b.

Clark, J.S., and T.C. Hussey, Estimating the mass flux of charcoal from sedimentary records: Effects of particle size, morphology and orientation, *Holocene*, *6*, 129-144, 1996.

Clark, J.S., and P.D. Royall, Particle-size evidence for source areas of charcoal accumulation in late Holocene sediments of eastern North American lakes, *Quat. Res.*, *43*, 80-89, 1995.

Clark, J.S., H. Cachier, J.G. Goldhammer, and B. Stocks (Eds.), Sediment Records of Biomass Burning and Global Change, *NATO ASI Ser. Ser. I*, *51*, 489pp., 1997.

Cohen, M.S., and P.D. Gabriele, Degradation of coal by the fungi *Polyporus versicolor* and *Poria monticola*, *Appl. Environ. Microbiol.*, *44* (1), 23-27, 1982.

Cook, A.C., The spatial and temporal variation of the type and rank of Australian coals, in *Australian Black Coal: Its Occurence, Mining, Preparation and Use*, edited by A.C. Cook, pp. 63-84, Aust. Inst. for Mining and Metall, Illawarra, New South Wales, Australia, 1975.

Cope, M.J., and W.G. Chaloner, Fossil charcoal as evidence of past atmospheric composition, *Nature*, *283*, 647-649, 1980.

Crutzen, P.J., and M.O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, *250*, 1669-1678, 1990.

Crutzen, P.J., and J.G. Goldammer, Fire in the environment: The ecological, atmospheric, and climatic importance of vegetation fires, in *Dahlem Workshop Reports Environmental Sciences Research Report*, 415pp., John Wiley, New York, 1993.

Cwynar, L.C., Recent history of fire and vegetation from laminated sediment of Greenleaf Lake, Algonquin Park, Ontario, *Can. J. Bot.*, *56*, 10-21, 1978.

Dueser, W.G., K. Emeis, V. Ittekot, and E.T. Degens, Fly-ash particles intercepted in the deep Sargasso Sea, *Nature*, *305*, 216-218, 1983.

Ebbesen, T.W., H. Hiura, J.W. Hedenquist, C.E.J. de Ronde, A. Andersen, O. Often, and V.A. Melezhik, Origins of fullerenes in rocks, *Science*, *268*, 1634-1635, 1995.

Emiliani, C., D.A. Price, and D.J. Seipp, Is the post glacial artificial?, *Spec. Publ. Geochem. Soc.*, *3*, 229-231, 1991.

Esser, G., Modelling global terrestrial sources and sinks of CO_2 with special reference to soil organic matter, in *Soils and the Greenhouse Effect*, edited by A.F. Bouwman, pp. 247-261, John Wiley, New York, 1990.

Fakoussa, R.M., Mikroorganismen erschließen Kohle-Ressourcen, *BioEngineering* 4, 21-28, 1992.

Falcon-Lang, H., The impact of wildfire of an Early Carboniferous coastal environment, North Mayo, Ireland, *Palaeogeogr. Paleoclimatol. Paleaoecol.*, *139*, 121-138, 1998.

Fearnside, P.M., Greenhouse gas contributions from deforestation in Brazilian Amazonia, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J.S. Levine, pp. 92-105, MIT Press, Cambridge, Mass., 1991.

Fearnside, P.M., L. Leal, and F.M. Fernandes, Rainforest burning and the global carbon budget: Biomass, combustion efficiency and charcoal formation in the Brazilian Amazon, *J. Geophys. Res.*, *98*, 16,733-16,743, 1993.

Fedoroff, N., M.A. Courty, and M.L. Thompson, Micromorphological evidence of paleoenvironmental change in Pleistocene and Holocene plaeosols, in *Soil Micromorphology: A Basic and Applied Science*, edited by L.A. Douglas, pp. 653-665, Elsevier Sci., New York, 1990.

Foellmer, A., A. Hoppe, and R. Dehn, Anthropogene Schwermetall-anreicherungen in holozänen Auensedimenten der Möhlin (südlicher Oberrheingraben), *Geowissenschaften*, *15*, 61-66, 1997.

Garbarini, D.R., and L.W. Lion, Influence of soil organics on the sorption of toluene and trichloethylene, *Environ. Sci. Technol.*, *20*, 1263-1269, 1986.

Gehring, A.U., G. Guggenberger, W. Zech, and J. Luster, Combined magnetic, spectroscopic and analytical-chemical approach to infer genetic information for a Vertisol, *Soil Sci. Soc. Am. J.*, *61*, 78-85, 1997.

Gifford, R.M., The global carbon cycle: a viewpoint on the missing sink, *Austral. J. Plant Physiol.*, *21*, 1-15, 1994.

Glaser, B., L. Haumaier, G. Guggenberger, and W. Zech, Black carbon in soils: The use of benzenecarboxylic acids as specific markers, *Org. Geochem.*, *29* (4), 811-819, 1997.

Glaser, B., G. Guggenberger, L. Haumeier, and W. Zech, Sustainable soils in the Brazilian Amazon, paper presented at *Humic Substances Downunder. Understanding and Managing Organic Matter in Soils, Sediments and Waters*, 9th IHSS Conference, Int. Humic Substances Soc., Adelaide, South Australia, Australia, 1998.

Golchin, A., J.A. Baldock, P. Clarke, T. Higashi, and J.M. Oades, The effects of vegetation and burning on the chemical composition of soil organic matter in a volcanic ash soil as shown by ^{13}C NMR spectroscopy, II, Density fractions, *Geoderma*, *76*, 175-192, 1997a.

Golchin, A., P. Clarke, J.A. Baldock, T. Higashi, J.O. Skjemstad, and J.M. Oades, The effects of vegetation and burning on the chemical composition of soil organic matter in a volcanic ash soil as shown by ^{13}C NMR spectroscopy. I. Whole soil and humic acid fraction, *Geoderma*, *76*, 155-174, 1997b.

Goldammer, J.G., and B. Seibert, Natural rain forest fires in eastern Borneo during the Pleistocene and Holocene, *Naturwissenschaften*, *76*, 518-520, 1989.

Goldberg, E.D., *Black Carbon in the Environment*, 198 pp., John Wiley, New York, 1985.

Grathwohl, P., Influence of organic matter from soils and sediments from various origins on sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations, *Environ. Sci. Technol.*, *24*, 1687-1693, 1990.

Griffin, J.J., and E.D. Goldberg, The fluxes of elemental carbon in coastal marine sediments, *Limnol. Oceanogr.*, *20*, 456-463, 1975.

Griffin, J.J., and E.D. Goldberg, Morphologies and origin of elemental carbon in the environment, *Science*, *206*, 563-565, 1979.

Griffin, J.J., and E.D. Goldberg, Impact of fossil fuel combustion on sediments of Lake Michigan: A reprise, *Environ. Sci. Technol.*, *17*, 244-245, 1983.

Gustafsson, Ö., and P.M. Gschwend, Soot as a strong partition medium for polycyclic aromatic hydrocarbons, in *Molecular Markers in Environmental Geochemistry*, edited by R.P. Eganhouse, pp. 365-381, Am. Chem. Soc., Washington, D. C., 1997.

Gustafsson, Ö., and P.M. Gschwend, The flux of black carbon to surface sediments on the New England continental shelf, *Geochim. Cosmochim. Acta*, *62*, 465-472, 1998.

Gustafsson, Ö., F. Haghseta, C. Chan, J. Macfarlane, and P.M. Gschwend, Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability, *Environ. Sci. Technol.*, *24*, 1687-1693, 1997.

Harris, T.M., Forest fire in the Mesozoic, *J. Ecol.*, *46*, 447-453, 1958.

Harvey, R.D., and J.W. Dillon, Maceral distributions in Illinois coals and their palaeoenvironmental implications, *Int. J. Coal Geol.*, *5* (1-2), 141-165, 1985.

Hassink, J., Effects of soil texture and grassland management on soil organic C and N and rates of C and N mineralization, *Soil Biol. Biochem.*, *26* (9), 1221-1231, 1994.

Hatcher, P.G., M. Schnitzer, A.M. Vassallo, and M.A. Wilson, The chemical structure of highly aromatic humic acids in three volcanic ash soils as determined by dipolar dephasing NMR studies, *Geochim. Cosmochim. Acta*, *53*, 125-130, 1989.

Haumaier, L., and W. Zech, Black carbon - Possible source of highly aromatic components of soil humic acids, *Org. Geochem.*, *23*, 191-196, 1995.

Heidenreich, R.D., W.M. Hess, and L.L. Ban, A test object and criteria for high resolution electron microscopy, *J. Appl. Crystallogr.*, *1*, 1-19, 1968.

Herring, J.R., Charcoal flux into sediments of the north Pacific Ocean: the Cenozoic record of burning, in *The Carbon Cycle and atmospheric CO_2: Natural variations Archean to Present, Geophys. Monogr. Ser.*, *32*, edited by E. T. Sundquist and W. S. Broecker, pp. 419-441, AGU, Washington, D. C., 1985.

Hiller, D.A., and G.W. Brümmer, Mikrosondenuntersuchungen an unterschiedlich stark mit Schwermetallen belasteten Böden, 2, Gehalte an Schwermetallen und anderen Elementen in Huminstoffaggregationen, Streustoffen und Holzkohlepartikeln, *Z. Pflanzenernaehr. Bodenkd.*, *160*, 47-55, 1997.

Hofrichter, M., D. Ziegenhagen, S. Sorge, R. Ullrich, F. Bublitz, and W. Fritsche, Degradation of lignite (low-rank-coal) by lignolytic basidiomycetes and their peroxidase system, *Appl. Microbiol. Biotechnol.*, *52*, 78-84, 1999.

Jones, T.P., and W.G. Chaloner, Fossil charcoal, its recognition and palaeoatmospheric significance, *Palaeogeogr. Paleoclimatol. Palaeoecol.*, *97*, 39-50, 1991.

Jones, T.P., W.G. Chaloner, and T.A.J. Kuhlbusch, Proposed biogeological and chemical based terminology for fire-altered plant matter, in *Sedimental Records of Biomass Burning and Global Change*, edited by J.S. Clark et al., pp. 9-22, Springer-Verlag, New York, 1997.

Kalkreuth, W., and D.A. Leckie, Sedimentological and petrographical characteristics of Cretaceous strandplain coals: A model for coal accumulation from the North American Western Interior Seaway, *Int. J. Coal Geol.*, *12*, 381-424, 1989.

Karls, J.F., and E.R. Christensen, Carbon particles in dated sediments from Lake Michigan, Green Bay, and tributaries, *Environ. Sci. Technol.*, *32*, 225-231, 1998.

Kershaw, A.P., Climatic change and aboriginal burning in northeast Australia during the last two glacial/interglacial cycles, *Nature*, *322*, 47-49, 1986.

Kershaw, A.P., G.M. McKenzie, and A. McMinn, The nature and evolution of lithotypes in the Tertiary brown coals of the Latrobe Valley, southeastern Australia, *Int. J. Coal Geol.*, *18*, 233-249, 1993.

Kershaw, A.P., M.B. Bush, G.S. Hope, K.-F. Weiss, J.G. Goldammer, and R. Sanford, The contribution of humans to past biomass burning in the tropics, in *Sedimental Records of Biomass Burning and Global Change*, edited by J.S. et al., pp. 413-442, Springer-Verlag, 1997.

Killops, S.D., and M.S. Massoud, Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic fires, *Org. Geochem.*, *18*, 1-7, 1992.

Kleineidam, S., H. Rügner, B. Ligouis, and P. Grathwohl, Organic matter facies and equilibrium sorption of phenanthrene, *Environ. Sci. Technol.*, *33*, 1737-1644, 1999.

Komarek, E.V., Ancient fires, paper presented at *Tall Timbers Fire*

Ecology Conference, Tall Timbers Res. Stn., Tallahassee, Fla., 1972.

Kononova, M.M., *Soil Organic Matter*, 544 pp., Pergamon, Tarrytown, N. Y., 1966.

Kruge, M.A., A.B. Stankiewicz, J.C. Crelling, A. Montanari, and D.F. Bensley, Fossil charcoal in Cretaceous-Tertiary boundary strata: Evidence for catastrophic firestorm and megawave, *Geochim. Cosmochim. Acta, 58*, 1393-1397, 1994.

Kubiena, W.L., *Micropedology*, 243 pp., Collegiate Press, Ames, Iowa, 1938.

Kuhlbusch, T.A.J., Method for determining black carbon in residues of vegetation fires, *Environ. Sci. Technol., 29*, 2695-2702, 1995.

Kuhlbusch, T.A.J., Black carbon and the carbon cycle, *Science, 280*, 1903-1904, 1998a.

Kuhlbusch, T.A.J., Black carbon in soils, sediments and ice cores, in *Encyclopedia of Environmental Analysis and Remediation*, edited by R.A. Meyers, pp. 813-823, John Wiley, New York, 1998b.

Kuhlbusch, T.A.J., and P.J. Crutzen, 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, *Global Biogeochem. Cylces, 9* (4), 491-501, 1995.

Kuhlbusch, T.A.J., and P.J. Crutzen, Black carbon, the carbon cycle, and atmospheric carbon dioxide, in *Biomass Burning and Global Change*, edited by J.S. Levine, pp. 160-169, MIT Press, Cambridge, Mass, 1996.

Kuhlbusch, T.A.J., M.O. Andreae, H. Cachier, J.G. Goldammer, J.-P. Lacaux, R. Shea, and P.J. Crutzen, Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle, *J. Geophys. Res., 101*, 23,651-23,665, 1996.

Kumada, K., Carbonaceous materials as a possible source of soil humus, *Soil Sci. Plant Nutr., 29*, 383-386, 1983.

Kumada, K., The nature and genesis of humic acid, in *Chemistry of Soil Organic Matter*, edited by K. Kumada, pp. 181-204, Elsevier Sci., New York, 1987.

Kumada, K., O. Sato, Y. Ohsumi, and S. Ohta, Humus composition of mountain soils in central Japan with special reference to the distributions of P type humic acid, *Soil Sci. Plant Nutr. Tokyo, 13*, 151-158, 1967.

Lapo, A.V., Phyterals of Jurassic coals of Tuva, *Plaeobotanist, 25*, 205-216, 1976.

Lim, B., and H. Cachier, Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous-Tertiary clays, *Chem. Geol., 131*, 143-154, 1996.

Lim, B., and I. Renberg, Lake sediment records of fossil fuel-derived carbonaceous aerosols from combustion, in *Sedimental Records of Biomass Burning and Global Change*, edited by J.S. Clark et al., pp. 442-459, Springer-Verlag, New York, 1997.

MacDonald, G.M., C.P.S. Larsen, J.M. Szeicz, and K.A. Moser, The reconstruction of boreal forest fire history from lake sediments: A comparison of charcoal, pollen, sedimentological and geochemical indices, *Quat. Sci. Rev., 10*, 53-71, 1991.

Masiello, C.A., and E.R.M. Druffel, Black carbon in deep sea sediments, *Science, 280*, 1911-1913, 1998.

McCarty, G.W., R. Siddaramappa, R.J. Wright, E.E. Codling, and G. Gao, Evaluation of coal combustion byproducts as soil liming materials: Their influence on soil pH and enzyme activities, *Biol. Fertil. Soils, 17*, 167-172, 1994.

McGroddy, S. E., and J.W. Farrington, Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts, *Environ. Sci. Technol., 29*, 1542-1550, 1995.

McGroddy, S.E., J.W. Farrington, and P.M. Gschwend, Comparison of the in situ and desorption sediment -- Water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls, *Environ. Sci. Technol., 30*, 172-177, 1996.

McLean, D.M., Impact winter in the global K/T extinctions: No definitive evidences, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J.S. Levine, pp. 493-503, MIT Press, Cambridge, Mass., 1991.

Middelburg, J.J., J. Nieuwenhuize, and P. van Breugel, Black carbon in marine sediments, *Mar. Chem.* 65, 245-252, 1999.

Miltner, A., and W. Zech, Effects of minerals on the transformation of organic matter during simulated fire-induced pyrolysis, *Org. Geochem., 26* (3/4), 175-182, 1997.

Morley, R.J., and K. Richards, Graminae cuticle: A key indicator of late Cenozoic climatic change in the Niger Delta, *Rev. Paleobot. Palynol., 77*, 119-128, 1993.

Nichols, G., and T.P. Jones, Fusain in Carboniferous shallow marine sediments, Donegal, Ireland: the sedimentological effects of wildfire, *Sedimentology, 39*, 487-502, 1992.

Odegaard, B.V., The sedimentary record of spheroidal carbonaceous fly-ash particles in shallow Danish lakes, *J. Paleolimnology, 8*, 171-187, 1993.

Ohta, S., A. Suzuki, and K. Kumada, Experimental studies on the behavior of fine organic particles and water-soluble organic matter in mineral soil horizons, *Soil Sci. Plant Nutr. Tokyo, 32*, 15-26, 1986.

Parthasarathy, G., R. Srinivasan, M. Vairamani, K. Ravikumar, and A.C. Kunwar, Occurence of natural fullerenes in low grade metamorphosed Proterozoic shungite from Karelia, Russia, *Geochim. Cosmochim. Acta, 62*, 3541-3544, 1998.

Patterson, W.A., K.J. Edwards, and D.J. Maguire, Microscopic charcoal as a fossil indicator of fire, *Quat. Sci. Rev., 6*, 3-23, 1987.

Pawluk, S., Soil micromorphology and soil fauna: Problems and importance, *Quaest. Entomologicae, 21*, 473-496, 1985.

Penner, J.E., H. Eddleman, and T. Novakov, Towards the development of a global inventory for black carbon emissions, *Atmos. Environ., 27* (8), 1277-1259, 1993.

Pessenda, L.C.R., R. Aravena, A.J. Melfi, E.C.C. Telles, R. Boulet, E.P.E. Valencia, and M. Tomazello, The use of carbon isotopes (^{13}C, ^{14}C) in soil to evaluate vegetation changes during the Holocene in central Brazil, *Radiocarbon, 38*, 191-201, 1996.

Potter, M.C., Bacteria as agents in the oxidation of amorphous carbon, *Proc. R. Soc. London Ser. B, 80*, 239-259, 1908.

Raison, R.J., Modifications of the soil environment by vegetation fires: A review, *Plant Soil, 51*, 73-108, 1979.

Renberg, I., and M. Wik, Soot particle counting in recent lake sediments: An indirect dating method, *Ecol. Bull., 37*, 53-57, 1985.

Robinson, J.M., Phanerozoic O_2 variation, fire, and terrestrial ecology, *Global Planet. Change, 1*, 223-240, 1989.

Robinson, J.M., W.G. Chaloner, and T.P. Jones, Pre-Quaternary records of wildfire, in *Sedimental Records of Biomass Burning and Global Change*, edited by J.S. Clark et al., pp. 253-270, Springer-Verlag, New York, 1997.

Rose, N.L., A method for the extraction of carbonaceous particles from lake sediment, *J. Paleolimnology, 3*, 45-53, 1990.

Rummery, T.A., The use of magnetic measurements in interpreting the fire histories of lake drainage basins, *Hydrobiologica, 103*, 53-58, 1983.

Rumpel, C., H. Knicker, I. Kögel-Knabner, and R.F. Hüttl, Airborne contamination of immature soil (Lusation mining district) by lignite-derived materials: Its detection and contribution to the soil organic matter budget, *Water Air Soil Pollut., 105*, 481-492, 1998.

Saldarriaga, J.G., and D.C. West, Holocene fires in the northern Amazon Basin, *Quat. Res., 26*, 358-366, 1986.

Sanford, R.L., J. Saldarriaga, K.E. Clark, C. Uhl, and R. Herrera, Amazon rain-forest fires, *Science, 227*, 53-55, 1985.

Sase, T., and M. Hosono, Vegetation histories of Holocene volcanic ash soils in Japan and New Zealand -- Relationship between genesis of melanic volcanic ash soils and human impact, *Earth Sci., 50*, 466-482, 1996.

Schiffmann, P.M., and W.C. Johnson, Phytomass and detrital carbon storage during forest regrowth in the southeastern United States Piedmont, *Can. J. Forest. Res., 19*, 69-78, 1989.

Schmidt, M.W.I., H. Knicker, P.G. Hatcher, and I. Kögel-Knabner, Impact of brown coal dust on the organic matter in particle-size fractions of a Mollisol, *Org. Geochem., 25*, 29-39, 1996.

Schmidt, M.W.I., J.O. Skjemstad, E. Gehrt, and I. Kögel-Knabner, Charred organic carbon in German chernozemic soils, *Eur. J. Soil Sci., 50*, 351-365, 1999.

Schmidt, M.W.I., H. Knicker, P.G. Hatcher, and I. Kögel-Knabner, Airborne contamination of forest soils by carbonaceous particles from industrial coal processing, *J. Environ. Qual., 29(3)*, 768-777, 2000.

Schnitzer, M., Bedeutung der organischen Bodensubstanz für die Bodenbildung, Transportprozesse in Böden und die Bodenstruktur, *Ber. Landwirtsch., 206*, 63-81, 1992.

Schultz, E., Size-fractionated measurement of coarse black carbon particles in deposition samples, *Atmos. Environ. Part A, 27*, 1241-1249, 1993.

Schutter, M.E., and J.J. Fuhrman, Microbial responses to coal fly ash under field conditions, *J. Environ. Qual., 28*, 648-652, 1999.

Scott, A.C., Observations on the nature and origin of fusain, *Int. J. Coal Geol., 12*, 443-475, 1989.

Seiler, W., and P.J. Crutzen, Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning, *Clim. Change, 2*, 207-247, 1980.

Sergides, C.A., J.A. Jassim, A.R. Chughtai, and D.M. Smith, The structure of hexane soot, part III, Ozonation studies, *Appl. Spectrosc., 41*, 482-492, 1987.

Shafizadeh, F., The chemistry of pyrolysis and combustion, in *The Chemistry of Solid Wood*, edited by R.M. Rowell, pp. 481-529, Am. Chem. Soc., Washington, D. C;, 1984.

Shindo, H., Elementary composition, humus composition, and decomposition in soil of charred grassland plants, *Soil Sci. Plant Nutr. Tokyo, 37*, 651-657, 1991.

Shindo, H., and M. Urabe, Changes in the humus composition of volcanic ash soils by heating at various temperatures, *Soil Sci. Plant Nutr. Tokyo, 39*, 189-192, 1993.

Shindo, H., T. Higashi, and Y. Matsui, Comparison of humic acids from charred residues of Susuki (Eulalia, *Miscanthus sinensis A.*) and from the A horizons of volcanic ash soils, *Soil Sci. Plant Nutr. Tokyo, 32*, 579-586, 1986.

Shneour, E., Oxidation of graphite carbon in certain soils, *Science, 155*, 991-992, 1966.

Singh, G., A.P. Kerhaw, and R. Clark, Quaternary vegetation and fire history in Australia, in *Fire in the Australian Biota*, edited by A.M. Gill, R.H. Groves, and I.R. Noble, pp. 23-54, Aust. Acad. Sci., Canberra, ACT, 1981.

Skjemstad, J.O., R.P. Le Feuvre, and R.E. Prebble, Turnover of soil organic matter under pasture as determined by ^{13}C natural abundance, *Aust. J. Soil Res., 28*, 267-276, 1990.

Skjemstad, J.O., L.J. Janik, M.J. Head, and S.G. MacClure, 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, 1993.

Skjemstad, J.O., P. Clarke, J.A. Taylor, J.M. Oades, and S.G. McClure, The chemistry and nature of protected carbon in soil, *Aust. J. Soil Res., 34*, 251-271, 1996.

Skjemstad, J.O., P. Clark, A. Golchin, and J.M. Oades, Characterization of soil organic matter by solid state ^{13}C NMR spectroscopy, in *Driven by Nature: Plant Litter Quality and Decomposition*, edited by G. Cadisch, and K. Giller, pp. 253-271, Cab Int., Wallingford, England, 1997.

Skjemstad, J.O., J.A. Taylor, and R.J. Smernik, Estimation of charcoal (char) in soils, *Com. Soil Sci. Plant Analysis, 30*, 2283-2298, 1999.

Smith, D.M., and A.R. Chughtai, The surface structure and reactivity of black carbon, *Colloids Surf. A, 105*, 47-77, 1995.

Smith, D.M., J.J. Griffin, and E.D. Goldberg, Elemental carbon in marine sediments: A baseline for burning, *Nature, 241*, 268-270, 1973.

Smith, D.M., J.J. Griffin, and E.D. Goldberg, Spectrometric method for the quantitative determination of elemental carbon, *Anal. Chem., 47*, 233-238, 1975.

Spycher, G., P. Sollins, and S. Rose, Carbon and nitrogen in the light fraction of a forest soil: Vertical distribution and seasonal patterns, *Soil Sci., 135*, 79-87, 1983.

Stach, E., M.-T. Mackowski, M. Teichmüller, R. Teichmüller, G.H. Taylor, and D. Chandra, *Stach's Textbook of Coal Petrology*, Gebrüder Borntraeger, Stuttgart, Germany,1982.

Suman, D.O., Charcoal production from agricultural burning in Central Panama and its deposition in the sediments of the Gulf of Panama, *Environ. Conserv., 13*, 51-60, 1986.

Suman, D.O., T.A.J. Kuhlbusch, and B. Lim, Marine Sediments: A reservoir for black carbon and their use as spatial and temporal records of combustion, in *Sedimental Records of Biomass Burning and Global Change*, edited by J.S. Clark et al., pp. 271-293, Springer-Verlag, New York, 1997.

Swain, A.M., A history of fire and vegetation in northeastern Minnesota as recorded in lake sediments, *Quat. Res., 3*, 383-396, 1973.

Swain, A.M., Environmental changes during the past 2000 years in north-central Wisconsin: Analysis of pollen, charcoal, and seeds in varved lake sediments, *Quat. Res., 10*, 55-68, 1978.

Takahashi, T., R.A. Dahlgren, and T. Sase, Formation of melanic epipedons under forest vegetation in the xeric moisture regime of northern California, *Soil Sci. Plant Nutr. Tokyo, 40*, 617-628, 1994.

Tate, K.R., G.J. Churchman, R.H. Meinhold, and R.H. Newman, Relationships between the type and carbon chemistry of humic acids from some New Zealand and Japanese soils, *Soil Sci. Plant Nutr. Tokyo, 36*, 611-621, 1990.

Taylor, G.H., and A.C. Cook, Sclerotinite in coal-its petrology and classification, *Geol. Mag., 99*, 41-52, 1962.

Taylor, G.H., S.H. Liu, and C.F.K. Diessel, The cold climate origin of inertinite-rich Gondwana coals, *Int. J. Coal Geol., 11*, 1-22, 1989.

Taylor, G.H., M. Teichmüller, A. Davis, C.F.K. Diessel, R. Littke, and P. Robert, *Organic Petrology*, 704 pp., Gebrüder Borntraeger, Stuttgart, Germany1998.

Thompson, R., and F. Oldfield, *Environmental Magnetism*, Allen and Unwin, Winchester, Mass., 1986.

Tschudy, R.H., C.L. Pillmore, C.J. Orth, J.S. Gilmore, and J.D. Knight, Disruption of the terrestrial plant ecosystem at the Cretaceous-Tertiary boundary, Western Interior, *Science, 255*, 1030-1032, 1984.

Venkatesan, M.I., and J. Dahl, Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary, *Nature, 338*, 57-60, 1989.

Verado, D.J., Charcoal analysis in marine sediments, *Limnol. Oceanogr., 42*, 192-197, 1997.

Verado, D.J., and W.F. Ruddiman, Late pleistocene charcoal in tropical Atlantic deep-sea sediments: Climatic and geochemical significance, *Geology, 24*, 855-857, 1996.

Waddington, J.C.B., A stratigraphic record of the pollen flux to a lake in the Big Woods of Minnesota, *Spec. Pap. Geol. Soc. Am., 123*, 263-282, 1969.

Ward, D.E., Factors influencing the emissions of gases and particulate matter from biomass burning, in *Fire in the Tropical Biota: Ecosystem Processes and Global Challenges*, edited by J.G. Goldammer, pp. 418-436, Springer-Verlag, New York, 1990.

Wardle, D.A., O. Zackrisson, and M.-C. Nilsson, The charcoal effect in Boreal forests: Mechanisms and ecological consequences, *Oecologica, 115*, 419-426, 1998.

Warneck, P., *Chemistry of the Natural Atmosphere*, 614 pp., Academic, San Diego, Calif., 1988.

Watson, A., J.E. Lovelock, and L. Margulis, Methanogenesis, fires and the regulation of atmospheric oxygen, *BioSystems, 10*, 293-298, 1978.

Wik, M., and I. Renberg, Distribution in forest soils of carbonaceous particles from fossil fuel combustions, *Water Air Soil Pollut., 33*, 125-129, 1987.

Wik, J., and I. Renberg, Recent atmospheric deposition in Sweden of carbonaceous particles from fossil-fuel combustion surveyed using lake sediments, *Ambio, 20*, 289-292, 1991.

Wik, J., and I. Renberg, Environmental records of carbonaceous fly-ash particles from fossil-fuel combustion: A summary, *J. Paleolimnology, 15* (3), 193-206, 1996.

Willmann, G., and R.M. Fakoussa, Biological bleaching of water soluble coal macromolecules by a basidiomydete strain, *Appl. Microbiol. Biotechnol., 47*, 95-101, 1997.

Winkler, M.G., Charcoal analysis for palaeoenvironmental interpretation: A chemical assay, *Quat. Res., 23*, 313-326, 1985.

Winkler, M.G., Sensing plant community and climate change by charcoal-isotope analysis, *Ecoscience, 1*, 340-345, 1994.

Winston, R.B., Reassessement of the evidence for primary fusinite and degradofusinite, *Org. Geochem., 20*, 209-221, 1993.

Wolbach, W.S., and E. Anders, Elemental carbon in sediments: Determination and isotopic analysis in the presence of kerogen, *Geochim. Cosmochim. Acta, 53*, 1637-1647, 1989.

Wolbach, W.S., R.S. Lewis, and E. Anders, Cretaceous extinctions: Evidence for wildfires and search for meteoritic material, *Science, 230*, 167-170, 1985.

Wolbach, W.S., I. Gilmour, C.J. Orth, and R.R. Brooks, Global fire at the Cretaceous/Tertiary boundary, *Nature, 334*, 665-669, 1988.

Wolbach, W.S., E. Anders, and M.A. Nazarov, Fires at the K/T boundary: Carbon at the Sumbar, Turkmenia, site, *Geochim. Cosmochim. Acta, 54*, 1133-1146, 1990.

Yarilova, E.A., Comparative characteristic of fabric components in some chernozems of the U.S.S.R., in *Third International Working-Meeting on Soil Micromorphology Wroclaw, 1969*, pp. 357-369, Zeszyty Problemowe Postepow Nauk Rolniczych, Wroclaw, Poland, 1972.

Zackrisson, O., M.C. Nilson, and D.A. Wardle, Key ecological function of charcoal from wildfire in the Boreal forest, *Oikos, 77*, 10-19, 1996.

Zech, W., G. Guggenberger, P. Zalba, and N. Peinemann, Soil organic matter transformation in Argentinian Hapludolls, *Z. Pflanzenernaehr Bodenkd., 160*, 563-571, 1997.

Zepp, R.G., and C. Sonntag, *The Role of Nonliving Organic Matter in the Earths Carbon Cycle*, 342 pp., John Wiley, New York, 1995.

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