Available online at www.sciencedirect.com

SCIENCE DIRECT®

Marine Chemistry 92 (2004) 201–213

MARINE CHEMISTRY

www.elsevier.com/locate/marchem

New directions in black carbon organic geochemistry

C.A. Masiello*

Department of Earth Science, 6100 Main St. MS 126, Rice University, Houston, TX 77005, United States

Received 25 January 2004; received in revised form 27 May 2004; accepted 30 June 2004
Available online 22 October 2004

Abstract

In the past 30 years, the field of black carbon (BC) research has expanded broadly, stretching from its traditional core in the atmospheric sciences into oceanography, soil science, and even anthropology. Results produced in this period of expansion have been exciting: BC has been detected in many important geochemical pools, and interesting new research directions open as we learn about the role of this byproduct of biomass burning in the carbon cycle. Especially important research directions will be the quantification of BC loss processes (both biotic and abiotic), measurement of BC decomposition products in environmentally relevant reservoirs, and exploration of the interactions between BC and its host organo-mineral matrix, including the role of BC in pedogenesis.

However, along with exciting results, we have also seen apparent discrepancies between BC studies. These discrepancies occur at least in part because of a lack of a common language, common methods, and a common model of BC. This paper lays out the framework many BC researchers use to understand the role of BC in the carbon cycle, discussing the ‘combustion continuum’ BC model and the methodological continuum that this model implies.

Keywords: Black carbon; Soot; Charcoal; Carbon cycle; Combustion continuum

---

1. Introduction

Research on the organic geochemistry of black carbon (BC) has reached a turning point since the field was galvanized 20 years ago with the publication of Goldberg, 1985 text, *Black Carbon in the Environment* (Goldberg, 1985). In this influential work, Goldberg put forth the idea of BC as a highly refractory substance remaining after biomass burning and suggested BC had an extremely long environmental lifetime, potentially contributing significantly to the Earth’s slow-cycling carbon pools. The organic geochemistry of BC has become increasingly relevant to a number of carbon cycle and climate questions, including long-term organic matter storage in ocean sediments, soil carbon storage and dynamics, dissolved organic carbon formation and decomposition, paleoclimate and paleohuman behavior, and the Earth’s radiative budget.

---

* Tel.: +1 713 348 5234.
E-mail address: masiello@rice.edu.

0304-4203/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2004.06.043

BC measurements made in the 1980s and 1990s followed the dogma that BC was highly refractory, and continued to point to its potentially important role in slow-cycling carbon pools like ocean sediments and soils (see, for example, Gustafsson and Gschwend, 1998; Haumaier and Zech, 1995; Herring, 1985; Masiello and Druffel, 1998, 2001; Middelburg et al., 1999; Schmidt and Noack, 2000; Skjemstad et al., 2002; Suman, 1996; Suman et al., 1997; Wolbach et al., 1988). Some new data support this 'refractory BC' model, while other data, combined with reconsideration of previous studies, point to a more dynamic role for BC in the global carbon cycle than has previously been considered (Decesari et al., 2002; Kim et al., this volume). A second problem presented by the assumption of a totally refractory nature of BC is the implied very large pool sizes, if loss processes are non-existent or very slow. We know little about BC loss processes and almost nothing about biotic or abiotic agents of BC decomposition.

Finally, there are apparent discrepancies present across the breadth of analytical techniques available for BC analysis, with natural BC concentrations varying more than a factor of 500 for the same sample measured via different methods (Schmidt et al., 2001). These discrepancies are a function of: (1) a lack of a common definition of black carbon; (2) potential underreporting of BC via some methods (i.e., failure to detect material commonly understood to be fire-derived); and (3) potential overdetection of BC by some methods (i.e., detection of material not derived from combustion).

2. Combustion continuum model

BC data is best understood with the combustion continuum model (Fig. 1) in mind. This model was first assembled by John I. Hedges and presented at the 1999 Goldschmidt conference at Harvard University (Hedges et al., 2000). BC is a continuum of combustion products, ranging from slightly charred, degradable biomass to highly condensed, refractory soot. All components of this continuum are high in carbon content, chemically heterogeneous, and dominated by aromatic structures.

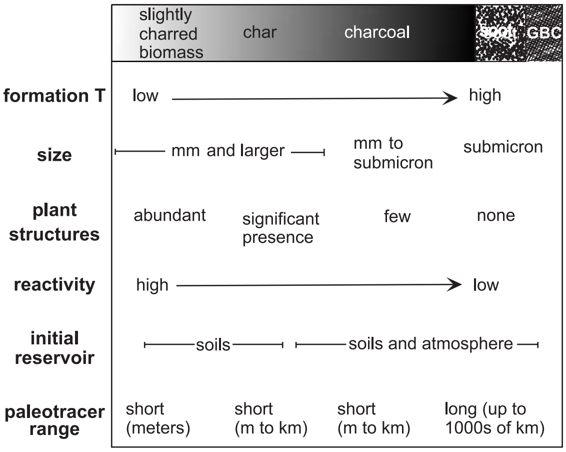

Fig. 1. The black carbon combustion continuum.

The aromaticity of BC increases as charring temperature increases. Experiments using ^{13}C NMR have shown that as pine wood is charred (moving it to the right along the combustion continuum), it loses signal intensity associated with cellulose and gains signal intensity in the aryl and *O*-aryl regions due to an increasingly aromatic chemical structure (Baldock and Smernik, 2002). By the time charring temperatures reach 250 °C, the aryl region of the CP/MAS ^{13}C NMR spectrum composes more than 60% of the total signal intensity, a relative increase of more than 50% from uncharred pine. Accompanying diffuse reflectance infrared Fourier transform (DRIFT) spectra showed loss of both carbohydrate and lignin structures and increases in aromatic and oxygenated aromatic ring structures with charring (Baldock and Smernik, 2002).

At the far end of the combustion continuum, soot has significantly different properties from charcoal. Fundamental to these differences is its production mechanism. Although charcoal retains enough physical and chemical properties to identify its biomass source, soot does not. Soot can be formed both from solid and liquid fuels, and condenses as a secondary product from the hot gases present in flames. The precise mechanism of soot formation has not been described; however, it is generally recognized to form through the production of two-carbon ions or radicals which then join into polycyclic aromatic hydrocarbons (PAHs). PAHs continue to assemble into larger aromatic rings, eventually condensing into solid spheres at a minimum diameter of 1 nm (Kennedy, 1997). This mode of production suggests that the presence of PAHs is intrinsic to the structure of soot particles (Akhter et al., 1985, 1984; Sergides et al., 1987).

Although charcoal and soot share a combustion source and aromatic, hydrogen-poor chemical structures, there also important variations between components of the combustion continuum, particularly related to physical properties. Understanding this variation is essential to accurate interpretation of BC data. Especially important varying properties are size, transport mechanism, and reactivity.

Size is essential in determining transport distances as smaller particles remain air- and waterborne longer. On one end of the combustion continuum are large charcoal particles, whose concentration in sediments reflects the burning history of local ecosystems due to their very short-range transport. Millimeter-size particles, for example, settle out of the atmosphere within 100 m of the fire source (Clark and Patterson, 1997), while submicron soot particles can remain suspended in the atmosphere on the order of months (Ogren and Charlson, 1983), if not subjected to oxidation and wash-out. This variation in transport distances creates multiple signals in sediment cores: the signal left by large charcoal particles, reflecting nearby fires (Clark and Patterson, 1997), and the background atmospheric signal from smaller particles. Evidence for this range of signals can be found in the charcoal record from sediments in the Santa Barbara Basin, where a correlation with local forest fires is only found for charcoal particles with an approximate diameter greater than 60 μm (Mensing et al., 1999).

Size (and therefore transportability) influences the initial reservoir that BC particles enter. The largest BC particles (diameter >1 μm) are unlikely to become airborne, and fall out rapidly if they are lofted up. Unless combustion occurs immediately adjacent to a lake or ocean [within ~1 km (Clark and Patterson, 1997)], the initial reservoir for large BC particles is soil. The ability of particles to remain airborne and avoid soil storage increases as particle size decreases. For BC particles smaller than approximately 2 μm, the initial reservoir is predominantly the atmosphere, as showed by a study of the fate of BC during six biomass burning events in Panama: particles larger than 2 μm made up more than 90% of the BC that fell out of the atmosphere (presumably to soils). For the same six events, particles smaller than 2 μm made up more than 80% of the BC which remained airborne (Suman, 1983, 1986, 1988).

Because soot particles form through assembly of gas-phase precursors, they are very small compared to charcoal. The vast majority of soot particles produced by biomass burning are smaller than 1 μm (Cachier et al., 1995). In polluted urban air, BC particles show a bimodal distribution, with peaks at approximately 0.1 and 1 μm (Seinfeld and Pandis, 1998). Small particles can be transported long distances, making the atmosphere an important initial reservoir for soot BC (Ogren and Charlson, 1983). Long distance transport of small particles makes possible the delivery of BC to remote environments such as the open ocean.

The reactivity of BC also varies along the combustion continuum. Charcoal decomposes much more rapidly than soot when exposed to chemical oxidants in the laboratory (Masiello et al., 2002). Evidence from field experiments suggests that the environmental lability of charcoal also varies dramatically, due to a combination of microbial decay and photo-oxidation (Bird et al., 1999). Laboratory experiments using one plant type (*Pinus resinosa*, Red pine) suggest that extent of charring also influences lability (Baldock and Smernik, 2002).

The possibility of differences in environmental turnover times for different types of BC is a research direction that needs exploration. For example, if some fraction of charcoal decomposes more rapidly under oxic conditions, BC preservation will be a function of sediment diagenetic history, influencing our ability to interpret the paleorecord of biomass burning. In another case, the radiocarbon signature of sedimentary BC is used to understand how much time BC spends in intermediate pools before entering ocean sediments (Masiello and Druffel, 2003). Fractional BC decomposition can affect the interpretation of these ^{14}C measurements.

3. BC methods and BC measurement uncertainty

Recent measurements of BC point to pool sizes that are quite variable. For example in ocean sediments, values for percent sedimentary organic carbon (SOC) accounted for by BC range from 3% to

Table 1
Representative BC concentrations in ocean sediments, rivers, and soils

Site description	%BC per SOC	Citation	Method
Ocean sediments			
Abyssal NE Pacific	15±2	Masiello and Druffel, 1998	H_2CrO_4/H_2SO_4
Abyssal Southern Ocean	21±6	Masiello and Druffel, 1998	H_2CrO_4/H_2SO_4
Santa Monica Basin, NE Pacific coastal oxic	11±4	Masiello and Druffel, 2003	H_2CrO_4/H_2SO_4
Santa Monica Basin, NE Pacific coastal, anoxic	5±2	Masiello and Druffel, 2003	H_2CrO_4/H_2SO_4
Gulf of Maine, NW Atlantic shelf	3–6	Gustafsson and Gschwend, 1998	375 °C/24 h/air
Palos Verdes, CA NE Pacific Shelf	12–18	Gustafsson and Gschwend, 1998	375 °C/24 h/air
Western Mediterranean	5–38	Lim and Cachier, 1996	H_2CrO_4/H_2SO_4
Tropical Atlantic	>50	Verardo and Ruddiman, 1996	HNO_3
Arctic sediments	0.1–17	Guo et al., 2004	375 °C/24 h/air
Rivers			
Santa Clara River, SW North America, particulate BC	8–17	Masiello and Druffel, 2001	H_2CrO_4/H_2SO_4
Mississippi, particulate BC	2–>25	Mitra, 2002	375 °C/24 h/air
Delaware Bay, Chesapeake Bay, NW coastal Atlantic, dissolved BC	9±7	Mannino and Harvey, 2004	375 °C/24 h/air
Soils			
European Chernozem/Mollisols	15–35	Schmidt et al., 2002	UV
U.S. agricultural soils	10–35	Skjemstad et al., 2002	UV+NMR
Tenerife island, various soils	0.4–29	Ribes et al., 2003	375 °C/24 h/air
Brazilian terra preta soils	up to 35	Glaser et al., 2000	BPCA
Native N. American prairies	4–17	Glaser and Amelung, 2003	BPCA
Siberian boreal forest	1.6–4.5	Czimczik et al., 2003	BPCA

Abbreviations for chemical methods: H_2CrO_4/H_2SO_4=chemical oxidation with dichromate/sulfuric acid, HNO_3=chemical oxidation with nitric acid. Thermal method abbreviations follow the convention: heating temperature/time heated/gas used as oxidant. Other abbreviations: UV=oxidation via exposure to high energy ultraviolet radiation, NMR=^{13}C nuclear magnetic resonance, and BPCA=measurement of benzene polycarboxylic acids as molecular markers.

6% for coastal regions like the Gulf of Maine (Gustafsson and Gschwend, 1998), to deep ocean sediment values >50% (Verardo and Ruddiman, 1996) (see Table 1 and Fig. 2). In soils, values range from 2% to 8% in surface layers from a tropical savannah burn sequence in Zimbabwe (Bird et al., 1999) to >30% in US agricultural soils (Skjemstad et al., 2002).

Some of the natural variation in BC/SOC values occurs because of environmental processes. For example, it is likely that the natural distribution of BC within a soil profile is influenced by pedogenic processes and will thus vary depending on soil type (Glaser et al., 2001; Schmidt et al., 2002). In another example, agriculture can increase the exposure of soil carbon to decomposing conditions and can cause a preferential enrichment of refractory components like BC (Skjemstad et al., 2002). In this way, agricultural soils are a terrestrial analog for marine sediments that have experienced long oxygen exposure times (Hartnett et al., 1998; Hedges et al., 1999). These types of factors preclude a meaningful version of Fig. 2 for soils.

However, a significant fraction of the apparent natural variation in sedimentary and soil BC concentrations is probably related to uncertainty in BC methods. Part of this uncertainty is due to lack of information about what regions of the combustion continuum various methods measure. At least some uncertainty is also related to over- or underdetection of BC (that is, creation of BC during sample analysis, loss of BC during sample analysis, and detection of unburned carbon as BC).

The atmospheric science community has a significant history of intercomparison of BC measurement techniques (e.g., Countess, 1990; Guillemin et al., 1997; Hitzenberger et al., 1999), but BC method intercomparisons involving the oceanographic and soil science communities have only just begun. In a recent study that focused on BC concentrations in a National Institute of Standards and Technology reference material (NIST SRM 1649a), percent

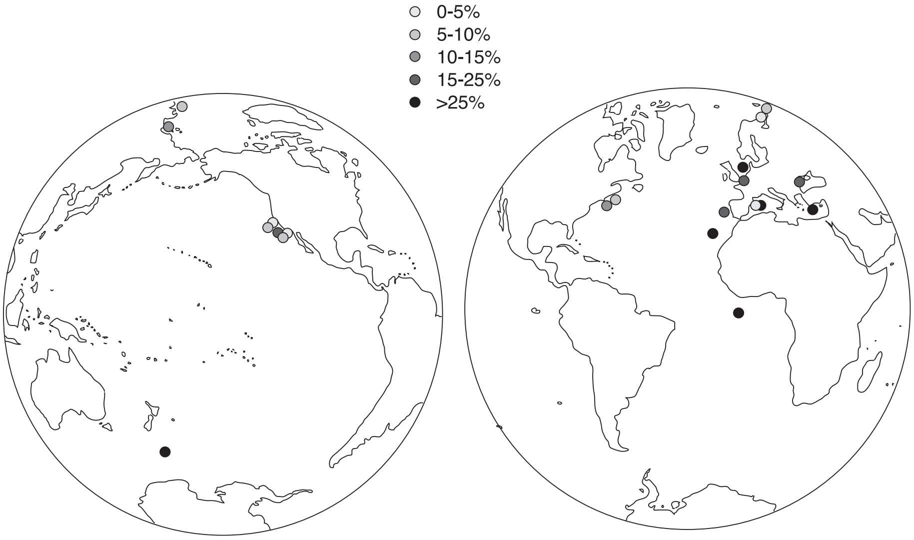

Fig. 2. Percent sedimentary organic carbon composed of black carbon in the world's oceans, measured by various techniques.

organic carbon (OC) identified as BC ranged from 7% to 50%, almost a factor of 10 difference depending only on the method used (Currie et al., 2002). In a second intercomparison that included a broader range of methods to measure BC in soils, the range of values was even more striking, varying by a factor of 500 (Schmidt et al., 2001). Understanding the variation in BC data involves, at least in part, understanding what regions of the combustion continuum different BC methods detect.

3.1. BC methods and the combustion continuum

BC measurement techniques fall into 6 general classes: microscopic (e.g., Clark and Patterson, 1997), optical (e.g. Clarke et al., 1987), thermal (e.g., Cachier et al., 1989a,b; Gustafsson et al., 1997), chemical (e.g., Gillespie, 1990; Verardo, 1997; Wolbach and Anders, 1989), spectroscopic (e.g., Smith et al., 1975; Skjemstad et al., 1999), and molecular marker (e.g., Glaser et al., 1998; Elias, 2001). Additionally, techniques exist which blend these six measurement types (e.g., Huntzicker et al., 1982; Kuhlbusch, 1995). Microscopic techniques measure the number of charcoal pieces visible under an optical microscope. Optical techniques measure the 'blackness' of a sample and provide information useful in understanding the impacts of BC aerosols on the atmosphere's radiative balance. Thermal methods measure BC remaining after oxidation upon heating, and chemical techniques measure BC remaining after chemical extraction. Spectroscopic techniques pinpoint infrared bands or NMR regions characteristic of combustion products and estimate total BC concentration based on the strength of these bands or frequencies after oxidative removal of operationally defined non-BC organics. Molecular marker techniques measure the concentration of a particular compound or class of compounds associated with BC, and use this information to extrapolate BC concentration.

It is clear that each of these techniques measures a different region within the combustion continuum. Microscopic counting techniques, for example, detect only relatively large charcoal particles and cannot pick up any soot or charcoal degradation products. Thermal methods oxidize less refractory charcoal particles, and the harshest thermal methods measure only soot and graphite (Gélinas et al., 2001). Spectroscopic and molecular marker techniques focus on the chemical signature of burning, and because of this hold promise for detection of a wide band of the combustion continuum (Glaser et al., 1998; Simoneit, 2002).

In Fig. 3, I speculate on which regions of the combustion continuum different types of methods detect. This figure helps to explain a number of apparent contradictions within the BC literature. It is not meaningful, for example, to compare yields of BC

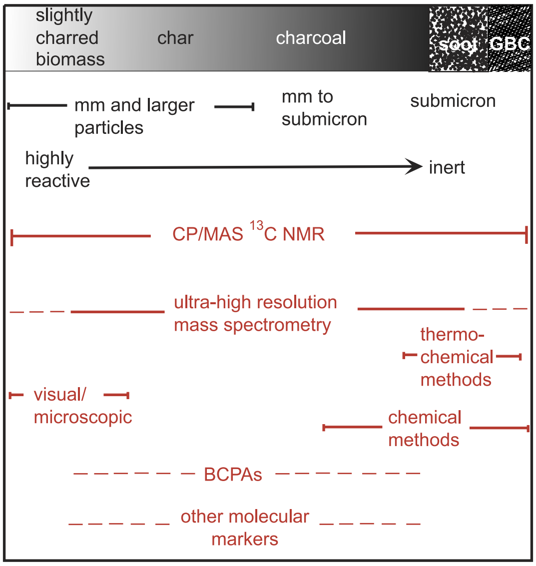

Fig. 3. The black carbon methods continuum. Regions of the combustion continuum detected by each technique are estimated based on published results with a variety of standards and sample types. BPCA abbreviates benzene polycarboxylic acids (Glaser et al., 1998).

measured via an optical technique (measuring charcoal) with yields measured via a thermal technique (measuring soot), as the measurement windows of these two methods do not overlap at all. In practice, this means that sediment charcoal accumulation rates should not be compared with sediment BC data measured via chemical or thermal methods. It is also not surprising that the largest differences in concentration occur when BC is measured with the two techniques with the largest and smallest ranges: ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR), which may detect the entire combustion continuum, vs. thermo-chemical techniques, which only detect the most refractory BC fractions (Schmidt et al., 2001). Figs. 1 and 3 also combine to help predict success or failure for some BC studies. For example, a thermal or chemical technique is unlikely to yield any useful information about local biomass burning history, as these techniques do not detect the region of the combustion continuum with a short paleotracer range. Similarly, optical microscope measurements of charcoal provide no direct information on the radiative effects of biomass burning, as optical microscope measurements cannot detect the submicron, airborne particles (although there may be a correlation between charcoal and soot production). Movement beyond speculation in the BC 'methods continuum' will be possible through ongoing methodological intercomparisons (Schmidt et al., 2003).

3.2. Positive and negative artifacts in BC methods

The complexity and chemical heterogeneity of BC make it hard for one method to measure all regions of the combustion continuum without problems of over- or underdetection in at least some matrices. Potential problems include the transformation of non-black organic compounds into BC during thermal or chemical treatments ('charring'), failure to detect significant portions of the combustion continuum, and detection of material which is not fire-derived. Although the BC field currently lacks a comprehensive method intercomparison study, there is some information available on artifacts associated with both thermal and chemical techniques. There is less information available about artifacts in newer techniques.

Depending on their use, thermal techniques can suffer from overdetection due to charring of non-black organic compounds as well as underdetection of charcoal. The behavior of chemical techniques is not as well constrained as thermal techniques; however, existing data suggest positive artifacts in marine sediments for nitric acid-based techniques and less than quantitative detection of BC for dichromate-based techniques.

Charring during thermal analysis has been demonstrated in a number of studies. For convenience, I will abbreviate thermal methods as: heating temperature/heating duration/gas present during heating (for example, 340 °C/2 h/O_2 refers to a sample heated at 340 °C for 2 h in a 100% O_2 atmosphere). In the late 1980s, charring of marine, soil, and terrestrial samples was shown to occur during a relatively low temperature BC measurement technique (340 °C/2 h/O_2) (Cachier et al., 1989a,b). These studies also showed that severity of charring depended on particle size, with BC-free standards such as dry leaf particles producing readings of 58% BC per initial mass of organic carbon (OC) for particles >160 μm, decreasing to 22% BC per OC for leaf particles <20 μm. Reports of erratic yields appeared in the mid-1990s, causing one group to reject thermal analyses (Lim and Cachier, 1996). Further development of a higher temperature thermal method (375 °C/24 h/air) noted the spurious detection of pollen as BC (Gustafsson et al., 1997). These authors also noted that given the relative concentration differences between soot and pollen in their environmental samples, pollen contamination was expected to cause an experimental overestimate of BC on the order of 10–25%.

There is evidence that charring during thermal treatment can be reduced by chemical pretreatment, and that less charring occurs when sample O_2 exposure is maximized. Pretreatment of samples with hydrochloric acid, hydrofluoric acid, and trifluoroacetic acid reduced charring significantly for a 375 °C/24 h/air thermal technique (Gélinas et al., 2001); this work also showed that this technique did not detect any BC in a laboratory char formed at 300 °C from alder wood. Another study (Gustafsson et al., 2002) modified the 375 °C/24 h/air method by using a flow-through tube furnace instead of a muffle furnace and showed that detection of pollen was not necessarily as significant a problem as previously thought, causing an interference as low as 1–2% for some forms of pollen. The same study emphasized the importance of adjusting thermal treatment conditions to insure maximum O_2 diffusion throughout samples during heating to avoid charring, but also cautioned that even with ideal conditions, some marine and/or polysaccharide-rich samples still showed significant charring. The worst-case scenario was BC-free fresh phytoplankton exudates, which yielded a BC per OC reading of 21.7% (Gustafsson et al., 2002). These results suggest that thermal techniques should be applied cautiously to OC-rich samples.

Recently, it has been shown that thermal techniques do not recognize most charcoal as BC. The behavior of a 375 °C/24 h/air version of a thermal technique was tested for a range of charcoals and soots in a variety of matrices (Nguyen et al., 2004). The charcoals selected for the Nguyen et al. (2004) study were produced at many different environmentally representative temperatures and were homogenized to particle sizes less than 70 μm prior to analysis. No BC was detected in 14 of 19 charcoal samples (those produced at less than 850 °C). The remaining 5 charcoals produced at higher temperatures yielded not more than 44% BC. Nguyen et al. (2004) also confirmed previously reported results that soot does not completely survive thermal treatment at 375 °C, and that survivability of soot at 375 °C depends on particle morphology, dispersion, and the presence or absence of a mineral matrix (Accardi-Dey, 2003). Based on the above studies, it seems that when thermal methods are combined with a chemical pretreatment including a demineralization step (Gélinas et al., 2001) and finely ground particles are exposed to well-circulated conditions during heating (Cachier et al., 1989a; Gustafsson et al., 2002), the results can be interpreted as a lower bound for the concentration of soot, charcoal, and graphite.

The body of literature on chemical techniques is not as large as that of thermal techniques, but enough information does exist to identify important areas in need of method development. Commonly used chemical techniques define BC as the material which survives treatment with peroxide (Smith et al., 1975), nitric acid (Verardo, 1997), or a mixture of dichromate and sulfuric acid (Masiello et al., 2002; Wolbach et al., 1989). Some methods combine dichromate and sulfuric acid with a sodium hydroxide pretreatment step (Bird and Gröcke, 1997; Song et al., 2002). Experiments with peroxide have showed substantial degradation of BC and difficulty controlling reaction kinetics (Wolbach and Anders, 1989). Nitric acid has not been widely used, potentially due to a report of large differences between BC concentrations measured via nitric acid and via thermal treatment (Middelburg et al., 1999). The kinetics of nitric acid reactions with BC have not been explored.

Dichromate oxidation showed initial promise in separating kerogen from highly condensed BC standards, provided that reaction kinetics were carefully monitored (Wolbach and Anders, 1989). The basis of the dichromate technique is the assumption that the oxidation of a mixture of labile organic carbon, kerogen, and BC can be modeled as the sum of three first-order reactions, if oxidant is present in excess (Wolbach and Anders, 1989). However, the rate of decomposition of organic matter may vary between terrestrial, coastal marine, deep sea sediments, and rock kerogen sources, requiring different mass yield corrections for each type of sample. Collection of a full suite of kinetics data is quite labor-intensive and is rarely done for all samples measured, or even when sample matrix is varied.

Additionally, the assumption that all BC is oxidized by dichromate at the same rate does not match existing data (Masiello et al., 2002).

An important area for development in the dichromate technique is the observation of alkyl peaks in some ^{13}C NMR spectra of extracted BC. In addition to aromatic resonances, unquantified alkyl and carboxyl resonances have been seen in spectra of sediments and soils subjected to dichromate oxidation (Song et al., 2002). Carboxyl functionality is not surprising, given that oxidation of BC causes formation of surface –COOH groups. Although some alkyl functionality has been detected in charcoal produced at low temperatures (Baldock and Smernik, 2002) and charcoal produced through short exposure to higher temperatures (Almendros et al., 2003), its presence in a BC spectrum may also indicate detection of non-fire derived organic compounds, and requires further study.

4. Improvements in the global BC budget

The most recent estimate of annual BC production is 0.05–0.27 Gt/year (Kuhlbusch, 1995). Working with a number of vegetation types, Kuhlbusch and Crutzen (1995) thermochemically (NaOH, HNO_3/340 °C/2 h/O_2) measured BC production in experimental burns within their laboratory. They calculated that globally, between 1.4% and 1.7% of carbon exposed to fire is converted to BC, a number similar to the recent ecosystem scale result from natural boreal forest fires of 0.7% (Czimczik et al., 2003), measured via the benzene polycarboxylic acid (BPCA) molecular marker technique (Glaser et al., 1998).

However, the Kuhlbusch and Crutzen (1995) budget was compiled prior to the publication of evidence of very large differences in the detection of BC between methods. With completion of method intercomparisons, it may be possible to expand the Kuhlbusch and Crutzen (1995) budget, especially by incorporating BC measurements into field campaigns in areas representative of a number of different burning regimes. It may also be possible to generate separate estimates of current and paleo-BC production rates. Through measurement coordination with existing biomass burning projects, a next-generation BC budget is a feasible goal.

5. BC loss processes

Measurements of BC production and loss processes are not balanced. The only documented loss process for BC is deposition in ocean sediments; however, the BC production rate (0.05–0.27 Gt/year, Kuhlbusch, 1995) is implausibly large compared to the rate of total organic carbon deposition to the seafloor (0.16 Gt/year, Hedges and Keil, 1995). The lower end of the BC production rate, 0.05 Gt/year, would mean that BC was 30% of sedimentary organic carbon and although it is possible that this could be the case in some abyssal sediments, the vast majority of sedimentary organic carbon is stored in deltas, shelves, and slopes (Hedges and Keil, 1995). Measurements of BC in these regions suggest that BC is only 3–10% of sedimentary organic carbon (Table 1). Methodological uncertainties point to an even greater discrepancy between BC production and loss: the Kuhlbusch (1995) production rate of 0.05–0.27 Gt BC/year was estimated using a thermal treatment step that significantly underestimates the charcoal portion of the combustion continuum.

Evidence for the existence of a large, non-sedimentary BC sink also comes from isotopic studies of highly refractory BC in sediments. A recent study of graphitic black carbon (GBC, measured following Gélinas et al., 2001) detected ^{14}C-free GBC in Northeast Pacific margin coastal sediment transect (Dickens et al., 2004). With careful sedimentation rate calibrations, Dickens et al. (2004) were able to show that this ^{14}C-free GBC was not a product of fossil fuel combustion (known to produce soot with an infinite radiocarbon age) but instead was the result of erosion of very old GBC from rocks into the ocean. Isotopic results in this study point to the possibility that this material is at least in part derived from petrogenic graphite. Further particle size and density analyses confirm that even this most refractory class of BC is not homogenous (Dickens et al., this volume).

This demonstration of a ‘closed loop’ in the BC and carbon cycles implies a larger terrestrial and/or marine BC sink. If BC deposited in ocean sediments comes both from biomass burning and from recycled petrogenic GBC, even less of the annually produced BC can be accounted for in ocean sediments. The existence of a fraction of BC that is geologically recycled and highly refractory also implies a significant, stable GBC pool, simply because materials with extremely slow loss processes will accumulate, even if input rates are very small. Here is the puzzle: if some fraction of the global sedimentary BC pool is really recycled graphite (thus reducing the size of the only known long-term BC sink, ocean sediments), where does the rest of the Earth's annually produced BC go?

Finally, it can be inferred that BC loss processes exist through simple calculations on the rate of BC production and the size of the Earth's soil organic carbon pool. If BC has been produced since the last glacial maximum via biomass burning at the same rate as it is now produced, BC should account for 25–125% of the total soil organic carbon pool (Masiello and Druffel, 2003). Although a few measurements of soil BC/SOC are as large as 25%, even this lower bound is unrealistic for the entire soil carbon pool. Some of this BC may be lost to erosion, but as Dickens et al. (2004) have shown that less is stored in sediments, erosion cannot solve this BC pool size problem (Schmidt, 2004). Furthermore, studies of sedimentary BC under oxic vs. anoxic conditions show decreases in BC concentration when sediments become oxic (Masiello and Druffel, 2003; Middelburg et al., 1999), suggesting the existence of a relatively labile BC fraction that decomposes on the timescale of 1000s of years.

However, even a labile BC loss process with a timescale of thousands of years is too slow to account for environmental observations. A recent study of BC production during Siberian boreal forest fires (Czimczik et al., 2003) makes clear that not enough BC remains after 250 years to account for all the BC produced during a fire. Czimczik et al. (2003) mention in situ degradation, erosion of BC, and translocation within the soil profile as possible BC loss processes, with in situ degradation being the most likely explanation. Although BC degradation is undoubtedly occurring, as of yet, few specific chemical, mechanical, or biological mechanisms have been identified that could cause this.

It is clear from research in the atmospheric chemistry community that even soot, the most inert part of the combustion continuum, can be chemically altered on a very short timescale through reaction with atmospheric oxidants. Although soot is highly aromatic and hydrophobic at formation, reactions with ozone and other atmospheric oxidants create hydrophilic carboxylic acid groups on its exterior. These reactions are so rapid that solubilization of soot particles can occur in 30 min in the presence of 50 ppb of ozone, making it possible to dissolve soot in a solution of distilled water (Chughtai et al., 1991) (for comparison, ozone concentration in rural air in the US ranges diurnally from 20 to 70 ppb, Seinfeld and Pandis, 1998). More recent experiments oxidizing soot in the laboratory have detected aromatic polyacids that closely resemble those detected in biomass burning plumes (Decesari et al., 2002; Mayol-Bracero et al., 2002). Taken together, chemical studies of soot suggest that this fraction of the BC continuum can enter some of the Earth's dissolved organic carbon pools.

Although the presence of BC in dissolved organic carbon (DOC) pools has been predicted (Masiello and Druffel, 1998), identifying it has been a methodological challenge. Any chemical technique that requires rinsing a sample cannot be used for this, as dissolved BC would be lost with the supernatant. As thermal techniques without chemical pretreatment do not require rinsing, they may detect BC in DOC; however, thermal techniques without chemical pretreatment can be subject to charring, and their sensitivity to highly oxidized BC may be low. NMR is a tool commonly used to study the functional composition of DOC (e.g., Benner, 2002) and may prove informative about the role of BC in DOC. However, not all NMR experiments can detect BC due to the low concentration of protons in BC, reducing the BC signal in ^{1}H and ^{13}C CP/MAS NMR experiments (Smernik et al., 2002). Newer NMR techniques can address this problem (Smernik et al., 2002), but these techniques have yet to be applied to DOC studies.

Thermal BC measurement techniques have been applied to ultrafiltered dissolved organic matter (UDOM) in the Chesapeake Bay, the Delaware Bay, and in the adjacent Atlantic Margin (Mannino and Harvey, 2004). These results show BC to be 5–12% of DOC. Another technique, electrospray ionization high resolution mass spectrometry, has been applied recently to DOC from a small stream in New Jersey and the Rio Negro. Using this technique, BC degradation products have both been detected and assigned chemical structures (Kim et al., this volume).

New data on BC in terrestrial and marine DOC will help clarify BC's role in DOC and more broadly, will help clarify BC loss processes.

Finally, the interaction of microbes and BC is not well understood. An experiment exposing charcoal produced at a range of temperatures (up to 350 °C) to a microbial inoculum showed very small losses of charcoal after 120 days, confirming the refractivity of BC but suggesting that some microbial degradation is possible (Baldock and Smernik, 2002). Soil microbial communities respond complexly to fire and the presence of charcoal, and significant ecological literature exists on this topic (see for example, Pietkainen and Fritze, 1995; Pietkainen et al., 2000). However, organisms involved in charcoal degradation are unknown, and rates of microbial decomposition of charcoal have yet to be quantified.

6. The interrelationship between BC and kerogen

As BC studies began, BC was carefully defined as a separate material, chemically unique from kerogens. BC was understood to be derived from burning, while kerogen was understood to be a product of very long timescale, low temperature geochemical processes. However, published BC data implicitly contradict this model, requiring reassessment of the relationship between these two carbon pools. BC has been identified in geologic formations (Herring, 1985; Wolbach and Anders, 1989; Wolbach et al., 1989, 1988) and has been shown to be a large component of some sedimentary organic carbon pools (Bird and Cali, 1998; Gustafsson and Gschwend, 1998; Herring, 1985; Masiello and Druffel, 1998; Masiello and Druffel, 2003; Middelburg et al., 1999; Suman et al., 1997; Verardo and Ruddiman, 1996). Many authors describe BC as the 'highly refractory remains of biomass burning', and the idea that at least some BC is highly refractory, combined with its presence in remote ocean sediments, seems to suggest that at least some BC must have a turnover time slow enough to be present in the Earth's kerogen pools.

In this light, it seems surprising that some BC extraction methods (e.g., Wolbach and Anders, 1989) have identified kerogen containing no BC, leaving open the question of why we have not detected BC in the global kerogen pool. Is this because BC is not as significant a component of the Earth's long-term carbon pools as we think? Is this because most BC has a long, but clearly finite lifetime within sediments, preventing its widespread incorporation into kerogen? Or is it possible that BC decomposition products—fragments of oxygenated polyaromatic rings—are present in kerogen, but not detected by current methods? The interrelationship between BC and kerogen is not as clear-cut as has been previously thought, and this area, too, is ready for more geochemical analyses.

7. Conclusions

The field of black carbon research has bloomed in the past 30 years, producing much data relevant to the global carbon cycle. However, as the field has matured, lack of method intercomparisons and lack of a common language have become stumbling blocks, as has our incomplete understanding of positive and negative artifacts. The idea that BC exists as a combustion continuum is a useful model for understanding BC methods and geochemistry. This model also helps understand the appropriateness of different BC techniques for specific studies.

The most pressing geochemical problem in understanding the BC cycle is our lack of knowledge of BC loss processes. In particular, measurements need to be made of BC in the Earth's DOC pools. We also need studies of mechanisms of BC loss, including bacterial, fungal, and abiotic decomposition. BC may also play a role in soil pedogenesis, raising fascinating questions about the relationship between fire and soil formation. Finally, the relationship between BC and kerogen is likely much more complex than has previously been though, requiring re-examination.

Combustion plays a multifaceted role in the Earth's carbon cycle. Improving BC methods and addressing BC loss processes will help us understand how BC interacts with the Earth's slow cycling carbon pools.

Acknowledgments

I would particularly like to acknowledge the guidance of John Hedges while I was a graduate student. His enthusiasm for working with students set a high standard. Conversations with Michael Schmidt, Angela Dickens, Claudia Czimczik, Oliver Chadwick, Ellen Druffel, Jennifer Harden, Sue Trumbore, Bill Reeburgh, Yves Gélinas, Jeff Baldock, Jan Skjemstad, Evelyn Krull, and Sid Mitra improved my understanding of the role of BC in the carbon cycle. I also gratefully acknowledge funding from the Kearney Foundation and the Anne Les AAUW Fellowship.

References

Accardi-Dey, A., 2003. Black carbon in marine sediments: quantification and implications for the sorption of polycyclic aromatic hydrocarbons. PhD thesis, MIT-WHOI.

Akhter, M.S., Chughtai, A.R., Smith, D.M., 1984. The structure of hexane soot: I. Spectroscopic studies. Applied Spectroscopy 39 (1), 143–153.

Akhter, M.S., Chughtai, A.R., Smith, D.M., 1985. The structure of hexane soot: II. Extraction studies. Applied Spectroscopy 39 (1), 154–167.

Almendros, G., Knicker, H., Gonzalez-Vila, F.J., 2003. Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. Organic Geochemistry 34, 1559–1568.

Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Organic Geochemistry 34 (9), 1093–1109.

Benner, R., 2002. Chemical composition and reactivity. In: Hansell, D., Carlson, C. (Eds.), Biogeochemistry of Marine Dissolved Organic Matter. Academic Press, pp. 59–90.

Bird, M.I., Cali, J.A., 1998. A million-year record of fire in sub-Saharan Africa. Nature 394 (6695), 767–769.

Bird, M.I., Gröcke, D.R., 1997. Determination of the abundance and carbon isotope composition of elemental carbon in sediments. Geochimica et Cosmochimica Acta 61 (16), 3413–3423.

Bird, M.I., Moyo, C., Veenendaal, E., Lloyd, J., Frost, P., 1999. Stability of elemental carbon in a savanna soil. Global Biogeochemical Cycles 13 (4), 923–932.

Cachier, H., Bremond, M.P., Buat-Ménard, P., 1989a. Thermal separation of soot carbon. Aerosol Science and Technology 10, 358–364.

Cachier, H.P., Bremond, M.P., Buat-Ménard, P., 1989b. Determination of atmospheric soot carbon by a simple thermal method. Tellus 41B, 379–390.

Cachier, H., Liousse, C., Buat-Ménard, P., Gaudichet, A., 1995. Particulate content of savanna fire emissions. Journal of Atmospheric Chemistry 22 (1-2), 123–148.

Chughtai, A.R., Jassim, J.A., Peterson, J.H., Stedman, D.H., Smith, D.M., 1991. Spectroscopic and solubility characteristics of oxidized soots. Aerosol Science and Technology 15, 112–126.

Clark, J.S., Patterson, W.A.I., 1997. Background and local charcoal in sediments: scales of fire evidence in the paleorecord. In: Clark, J.S., Cachier Goldammer, J.G., Stocks, B. (Eds.), Sediment Records of Biomass Burning and Global Change. Springer-Verlag, Berlin, pp. 23–48.

Clarke, A.D., Noone, K.J., et al., 1987. Aerosol light absorption measurement techniques: analysis and intercomparisons. Atmospheric Environment 21 (6), 1455–1465.

Countess, R.J., 1990. Interlaboratory analysis of carbonaceous aerosols. Aerosol Science and Technology 12, 114–121.

Currie, L.A., Benner, B.A., et al., 2002. A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. Journal of Research of the National Institute of Standards and Technology 107, 279–298.

Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Schulze, E.-D., 2003. How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: stocks, molecular structure, and conversion to black carbon (charcoal). Global Biogeochemical Cycles 17 (1).

Decesari, S., et al., 2002. Water soluble organic compounds formed by oxidation of soot. Atmospheric Environment 36, 1827–1832.

Dickens, A.F., Gélinas, Y., Masiello, C.A., Wakeham, S.G., Hedges, J.I., 2004. Reburial of fossil organic carbon in marine sediments. Nature 427, 336–339.

Dickens, A.F., Gélinas, Y., Hedges, J.I., this volume. Physical separation of combustion and rock sources of graphitic black carbon in sediments. Marine Chemistry.

Elias, V.O., 2001. Evaluating Levoglucan as an indicator of biomass burning in Carajas, Amazonia: a comparison to the charcoal record. Geochimica Cosmochimica Acta 65 (2), 267–272.

Gélinas, Y., Prentice, K.M., Baldock, J.A., Hedges, J.I., 2001. An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. Environmental Science and Technology 35, 3519–3525.

Gillespie, R., 1990. On the use of oxidation for AMS sample pretreatment. Nuclear Instruments and Methods in Physics Research B52, 345–347.

Glaser, B., Amelung, W., 2003. Pyrogenic carbon in native grassland soils along a climosequence in North America. Global Biogeochemical Cycles 17 (2).

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Organic Geochemistry 29 (4), 811–819.

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

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 2001. The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37–41.

Goldberg, E.D., 1985. Black Carbon in the Environment. John Wiley and Sons, New York.

Guillemin, M., et al., 1997. International round robin tests on the measurement of carbon in diesel exhaust particulates. International Archives of Occupational and Environmental Health 70 (3), 161–172.

Guo, L., Semiletov, I., et al., 2004. Characterization of Siberian Arctic coastal sediments: implications for terrestrial organic carbon export. Global Biogeochemical Cycles 18 (doi:10.1029/2003GB002087).

Gustafsson, O., Haghseta, F., Chan, C., MacFarlane, J., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. Environmental Science and Technology 31 (1), 203–209.

Gustafsson, O., Gschwend, P.M., 1998. The flux of black carbon to surface sediments on the New England continental shelf. Geochimica et Cosmochimica Acta 62 (3), 465–472.

Gustafsson, O., et al., 2002. Evaluation of a protocol for the quantification of black carbon in sediments. Global Biogeochemical Cycles 15 (4), 881–890.

Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391 (6667), 572–574.

Haumaier, L., Zech, W., 1995. Black carbon—possible source of highly aromatic components of soil humic acids. Organic Geochemistry 23 (3), 191–196.

Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation—an assessment and speculative synthesis. Marine Chemistry 49 (2–3), 81–115.

Hedges, J.I., et al., 1999. Sedimentary organic matter preservation: a test for selective degradation under oxic conditions. The American Journal of Science 299 (7–9), 529–555.

Hedges, J.I., et al., 2000. The molecularly-uncharacterized component of nonliving organic matter in natural environments. Organic Geochemistry 31, 945–958.

Herring, J.R., 1985. Charcoal fluxes into sediments of the North Pacific Ocean: the Cenozoic record of burning. In: Sundquist, E.T., Broecker, W.S. (Eds.), The Carbon Cycle and Atmospheric CO_2: Natural Variations, Archaean to Present. A.G.U., pp. 419–442.

Hitzenberger, R., et al., 1999. Intercomparison of measurement methods for black carbon aerosols. Atmospheric Environment 33 (17), 2823–2833.

Huntzicker, J.J., Johnson, R.L., et al., 1982. Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method. Particulate Carbon: Atmospheric Lifestyle. G.T. Wolff and R.L. Klimisch.

Kennedy, I.M., 1997. Models of soot formation and oxidation. Progress in Energy and Combustion Science 23, 95–132.

Kim, S., Kaplan, L.A., Benner, R., Hatcher, P.G., this volume. Hydrogen deficient molecules in natural riverine water samples—evidence for existence of black carbon in DOM. Marine Chemistry.

Kuhlbusch, T.A.J., 1995. Method for determining black carbon in residues of vegetation fires. Environmental Science and Technology 29, 2695–2702.

Kuhlbusch, T.A.J., Crutzen, P.J., 1995. Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and a source of O_2. Global Biogeochemical Cycles 9 (4), 491–501.

Lim, B., Cachier, H.P., 1996. Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous–Tertiary clays. Chemical Geology 131, 143–154.

Mannino, A., Harvey, H.R., 2004. Black carbon in estuarine and coastal dissolved organic matter. Limnology and Oceanography 49 (3), 735–740.

Masiello, C.A., Druffel, E.R.M., 1998. Black carbon in deep-sea sediments. Science 280 (5371), 1911–1913.

Masiello, C.A., Druffel, E.R.M., 2001. The isotope geochemistry of the Santa Clara River. Global Biogeochemical Cycles 15 (2), 407–416.

Masiello, C.A., Druffel, E.R.M., 2003. Organic and black carbon ^{13}C and ^{14}C through the Santa Monica Basin oxic–anoxic transition. Geophysical Research Letters 30 (4).

Masiello, C.A., Druffel, E.R.M., Currie, L.A., 2002. Radiocarbon measurements of black carbon in aerosols and ocean sediments. Geochimica et Cosmochimica Acta 66 (6), 1025–1036.

Mayol-Bracero, O.L., et al., 2002. Water-soluble organic compounds in biomass burning aerosols over Amazonia: 2. Apportionment of the chemical composition and importance of the polyacidic fraction. Journal of Geophysical Research 107 (D20).

Mensing, S.A., Michaelsen, J., Byrne, R., 1999. A 560-year record of Santa Ana fires reconstructed from charcoal deposited in the Santa Barbara Basin, California. Quaternary Research 51 (3), 295–305.

Middelburg, J.J., Nieuwenhuize, J., vanBruegel, P., 1999. Black carbon in marine sediments. Marine Chemistry 65 (3–4), 245–252.

Mitra, S., 2002. Sources of terrestrially-derived organic carbon in Lower Mississippi River sediments: implications for differential sedimentation and transport at the coastal margin. Marine Chemistry 77, 211–223.

Nguyen, T.H., Brown, R.A., Ball, W.P., 2004. An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. Organic Geochemistry 35, 217–234.

Ogren, J.A., Charlson, R.J., 1983. Elemental carbon in the atmosphere: cycle and lifetime. Tellus 35B, 241–254.

Pietkainen, J., Fritze, H., 1995. Clear-cutting and prescribed burning in coniferous forest: comparison of effects on soil fungal and total microbial biomass, respiration activity and nitrification. Soil Biology & Biochemistry 27 (1), 101–109.

Pietkainen, J., Kiikkila, O., Fritze, H., 2000. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. Oikos 89, 231–242.

Ribes, S., Van Drooge, B., Dachs, J., Gustafsson, O., Grimalt, J., 2003. Influence of soot carbon on the soil–air partitioning of polycyclic aromatic hydrocarbons. Environmental Science and Technology 37 (12), 2675–2680.

Schmidt, M.W.I., 2004. Carbon budget in the black. Nature 427, 305–306.

Schmidt, M.W.I., Noack, A.G., 2000. Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14 (3), 777–793.

Schmidt, M.W.I., Skjemstad, J.O., Czimczik, C.I., Glaser, B., Prentice, K.M., Gélinas, Y., Kuhlbusch, T.A.J., 2001. Comparative analysis of black carbon in soils. Global Biogeochemical Cycles 15 (1), 163–167.

Schmidt, M.W.I., Skjemstad, J.O., Jäger, C., 2002. Carbon isotope geochemistry and nanomorphology of soil black carbon: black chernozemic soils in central Europe originate from ancient biomass burning. Global Biogeochemical Cycles 16 (4).

Schmidt, M.W.I., Masiello, C.A., Skjemstad, J.O., 2003. Final recommendations for reference materials in black carbon analysis. EOS Transactions of the American Geophysical Union 84 (52), 582–583.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change vol. xxvii. Wiley, New York. 1326 pp.

Sergides, C.A., Jassim, J.A., Chughtai, A.R., Smith, D.M., 1987. The structure of hexane soot: Part III. Ozonation studies. Applied Spectroscopy 41 (3), 482–492.

Simoneit, B.R.T., 2002. Biomass burning—a review of organic tracers for smoke from incomplete combustion. Applied Geochemistry 17 (3), 129–162.

Skjemstad, J.O., Taylor, J.A., Smernik, R.J., 1999. Estimation of charcoal (char) in soils. Communications in Soil Science and Plant Analysis 30 (15–16), 2289–2298.

Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J.A., 2002. Charcoal carbon in U.S. agricultural soils. Soil Science Society of America Journal 66, 1249–1255.

Smernik, R.J., Baldock, J.A., Oades, J.M., 2002. Impact of remote protonation on C-13 CPMAS NMR quantitation of charred and uncharred wood. Solid State Nuclear Magnetic Resonance 22 (1), 71–82.

Smith, D.W., Griffin, J.J., Goldberg, E.D., 1975. A spectroscopic method for the quantitative determination of elemental carbon. Analytical Chemistry 47, 233–238.

Song, J., Peng, P., Huang, W., 2002. Black carbon and kerogen in soils and sediments: 1.Quantification and characterization. Environmental Science and Technology 36, 3960–3967.

Suman, D.O., 1983. Agricultural Burning in Panama and Central America: Burning Parameters and the Coastal Sedimentary Record, University of California at San Diego.

Suman, D.O., 1986. Charcoal production from agricultural burning in central Panama and its deposition in the sediments of the Gulf of Panama. Environmental Conservation 13, 51–60.

Suman, D.O., 1988. The flux of charcoal to the troposphere during the period of agricultural burning in Panama. Journal of Atmospheric Chemistry 6, 21–34.

Suman, D.O., 1996. A Five-Century Sedimentary Geochronology of Biomass Burning in Nicaragua and Central America. In: Levine, J.S. (Ed.), Biomass Burning and Global Change. MIT Press, Cambridge, MA. pp. 2 v.

Suman, D.O., Kuhlbusch, T.A.J., Lim, B., 1997. Marine sediments: a reservoir for black carbon and their use as spatial and temporal records of combustion. In: Clark, J.S., Cachier, H., Goldammer, J.G., Stock, B.J. (Eds.), Sediment Records of Biomass Burning and Global Change. Springer Verlag, Berlin.

Verardo, D.J., 1997. Charcoal analysis in marine sediments. Limnology and Oceanography 42 (1), 192–197.

Verardo, D.J., Ruddiman, W.F., 1996. Late Pleistocene charcoal in tropical Atlantic deep-sea sediments: climatic and geochemical significance. Geology 24 (9), 855–857.

Wolbach, W.S., Anders, E., 1989. Elemental carbon in sediments: determination and isotopic analysis in the presence of kerogen. Geochimica et Cosmochimica Acta 53, 1637–1647.

Wolbach, W.S., Gilmore, I., Anders, E., Orth, C.J., Brooks, R.B., 1988. Global fires at the Cretaceous–Tertiary boundary. Nature 334, 665–669.

Wolbach, W.S., Anders, E., Nasarov, M.A., 1989. Fires at the K/T boundary: carbon at the Sumbar, Turkmenia site. Geochimica et Cosmochimica Acta 54, 1133–1146.