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Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols

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Abstract

Although the definition and measurement methods of atmospheric “black carbon” (“BC”) have long been subjects of scientific controversy, the recent discovery of light-absorbing carbon that is not black (“brown carbon, C_{brown}”) makes it imperative to reassess and redefine the components that make up light-absorbing carbonaceous matter (LAC) in the atmosphere. Evidence for the atmospheric presence of C_{brown} comes directly from aerosol absorption measurements near specific combustion sources, from observations of spectral properties of water extracts of continental aerosol, from laboratory studies indicating the formation of light-absorbing organic matter in the atmosphere, and indirectly from the chemical analogy of aerosol species to colored natural humic substances. We show that these species may severely bias measurements of “BC” and “EC” over vast parts of the troposphere, where mass concentration of C_{brown} is high relative to that of combustion soot. We also imply that due to the strongly skewed absorption of C_{brown} towards the UV, single-wavelength light absorption measurements may not be adequate for the assessment of absorption of solar radiation in the troposphere. The possible consequences of these effects on our understanding of tropospheric processes are discussed.

1 Background

Soot, the black material in the smoke from wood and coal fires, has been seen as the archetypical air pollutant throughout history (Brimblecombe, 1987). Its presence in the atmosphere even at the remotest locations was discovered in the 1970s and 1980s (Levin and Lindberg, 1979; Heintzenberg, 1982; Andreae, 1983), and the early studies on the environmental cycle of “black carbon” (BC) were summarized in the monograph *Black Carbon in the Environment* by E. D. Goldberg (1985). A recent review on the geochemistry of “black carbon” in the environment has been provided by Masiello (2004). In this section, we present background information on the evolution of the study of "black carbon" and introduce the relevant concepts and terms. At the end of the section we will provide a set of definitions based on this discussion, which we will use in the rest of the paper, and which we propose for general use.

In recent years, scientific attention has shifted from the role of black carbon as a pollutant to its importance as a driver of global warming (Andreae, 1995; Hansen et al., 1998, 2005; Hansen and Nazarenko, 2004; Ramanathan et al., 2005). Some model calculations suggest that its climate forcing may rival that of methane, and that the present day global warming due to black carbon may be as much as 0.3–0.4°C (Jacobson, 2004; Chung and Seinfeld, 2005), while others find a smaller climate effect from this substance (Jones et al., 2005). Consequently, there is substantial controversy about the benefits of reducing "BC" as a strategy to mitigate global warming (Hansen et al., 2000; Jacobson, 2002; Bond and Sun, 2005). Because the climate effects of "BC" aerosol depend strongly on its physical and chemical properties, as well as on its residence time and distribution in the atmosphere (Jacobson, 2001), a thorough understanding of these properties and accurate techniques for the determination of "BC" in the atmosphere are deemed essential.

"Black carbon" or "soot carbon", the light-absorbing component of aerosols, has been identified as an impure form of near-elemental carbon with a graphite-like structure, which is formed in flaming combustion and in internal combustion engines (White and Germer, 1941; Grisdale, 1953; Medalia and Rivin, 1982; Bockhorn, 1994). In fact, soot particles are the only physically existing and observable particle types that can be readily recognized by their special morphology under the scanning or transmission electron microscope (Oberlin, 1989). Primary soot particles, 10–50 nm spherules, do not exist by themselves – instead they cluster together to form aggregates, which are their most stable form (Wentzel et al., 2003). In fresh smoke, these clusters tend to form open structures, which are then transformed by aging processes, including the uptake of water, into more closely packed particle types (Colbeck et al., 1990; Weingartner et al., 1997; Ruellan et al., 1999; Abel et al., 2003; Onischuk et al., 2003). However, soot associated with the smoldering stage of biomass combustion usually forms much

larger spherical and compacted particles that seem to be more resistant to atmospheric aging processes (Martins et al., 1998b).

The initial chemical composition of soot depends strongly on its sources: some sources can produce almost pure elemental carbon, while others produce soot of which 50% by mass is organic matter (Medalia and Rivin, 1982). Graphite, the ultimate form of pure elemental carbon in the atmosphere, is an absolutely inert material under atmospheric conditions. It can be oxidized in air only at temperatures exceeding 600°C. In graphitic structures each carbon-carbon bond achieves only one third of a double bond character, unlike a strictly aromatic or olefinic linkage. The resonance of the π-electrons among various configurations accounts for its electrical conductivity and broad-band light absorption. This latter property is of utmost importance in the light absorption by soot particles, it thus serves as a basis for the optical methods of their determination.

Graphitic structures in which carbon atoms occupy lattice sites in a two-dimensional honeycomb network (graphene layers) have intense Raman modes, but very weak IR vibrational absorption. These Raman modes enable unambiguous identification of graphitic structures in atmospheric aerosol, possibly as the only method available at a molecular level (Rosen and Novakov, 1977; Mertes et al., 2004). The shapes and intensities of Raman transitions are functions of the graphite crystal size, morphology and sample composition (Sze et al., 2001; Sadezky et al., 2005). High resolution transmission electron microscopy (HRTEM) revealed that the internal structure of combustion soot spherules depends strongly on the chemical and thermal environment under which they are formed and on the time available for annealing (Buseck et al., 1987; Su et al., 2004). Very rapidly formed soot is nearly amorphous, with only some signatures of short-range order (Pósfai et al., 1999; Grieco et al., 2000; Ferry et al., 2002; Wentzel et al., 2003), with fullerenic structures developing at slightly longer residence times in the combustion region. At longer annealing times (seconds to minutes) and higher temperatures, more highly ordered carbon structures develop.

Soot is usually thought to be insoluble in water and organic solvents. While this is definitely true for pure graphite, more atmospherically relevant soot types behave differently (Medalia and Rivin, 1982). For example, extraction of hexane soot with various solvents showed it to contain up to 33 mass-% soluble material, consisting of polyaromatic hydrocarbons (PAHs), oxygenated polyaromatic hydrocarbons, and a small fraction of aliphatic compounds (Akhter et al., 1985).

Although the average elemental composition of combustion soot is usually dominated by carbon (e.g., 92.2 mol-% C and 7.8 mol-% O in kerosene soot), an atmospheric soot particle may be regarded as a complex three-dimensional organic polymer with the capability of transferring electrons, rather than merely an amorphous form of elemental carbon (Chang et al., 1982). The relatively low mass fraction of oxygen in soot may be deceiving, since most of it is actually found on the surface of soot in various functional groups, so that the soot particles do not behave as pure graphitic carbon in most atmospheric processes. The amount of oxygen at the surface of soot particles depends on combustion conditions, with more efficient combustion regimes resulting in higher abundance of oxygen and defective structures at the surface of the particles (Chughtai et al., 2002; Su et al., 2004). This in turn increases the chemical reactivity of the particles (including their thermochemical properties in soot analyzers) and their wettability in the atmosphere. The carbon-to-hydrogen mol ratio has been reported to be about 3–6 in diesel engine and exhaust soots and about 8–20 in carbon blacks (Cachier et al., 1989b; Ebert, 1990; Clague et al., 1999).

Despite the ample variations in morphology and chemistry, we propose to call this combustion-derived particle type "soot carbon" or C_{soot} as long as the identity of this species has been definitely established. However, the measurement techniques that are capable of doing so, such as Raman spectroscopy or electron microscopy, are absolutely impractical for routine monitoring of this important aerosol component.

To address this problem, various measurement methods have been developed and utilized for the quantification of this aerosol component on a routine basis, making use of some characteristic properties of "elemental" carbon (Andreae et al., 1984; Hitzenberger et al., 1999; Schmid et al., 2001; ten Brink et al., 2004). These methods have

created new operational definitions such as black carbon ("BC") or elemental carbon ("EC") depending on the key property they are taking advantage of. "EC" is conventionally the preferred term in conjunction with thermal and wet chemical determinations, which are deemed suitable for the selective measurement of the refractory component. The term "BC" implies that this component is responsible for the absorption of visible light, and is generally used when optical methods are applied for its determination. It is important to note that neither category corresponds in a unique way to a physically observable particle type. Both "BC" and "EC" can only be regarded as "proxies" for the concentration of soot carbon, whose accuracies depend on the similarity between atmospheric soot and the species used for calibration. If atmospheric soot were pure graphite and all the methods were calibrated against graphite, "BC" and "EC" readings would give exactly the mass concentration of soot carbon as intended. Since, however, graphite is only a trace component of atmospheric soot, "BC" and "EC" measurements usually give different results, which have possibly little in common with the "true" mass concentrations of atmospheric soot particles. However, in the literature these discrepancies are usually disregarded and the terms "BC" and "EC" are used interchangeably as synonyms for soot carbon.

To make clear that "EC" is not strictly "elemental" carbon in a chemical sense, but rather an operationally defined component, we shall use the term EC_a ("apparent elemental carbon") in this paper. Similarly, since "BC" is operationally defined as that amount of pure soot (with an absorption cross section of ca. $7.5\,m^2\,g^{-1}$; Bond and Bergstrom, 2006) that would produce the same absorption signal as the sample (Bond et al., 2004), we shall use the term BC_e ("equivalent black carbon") here. When we refer in general to all forms of light absorbing carbonaceous aerosols, we shall use the term "light absorbing carbon" (Malm et al., 1994; Bond and Bergstrom, 2006).

It is conventionally assumed in atmospheric science, especially in climate-related discussions, that "BC" (used synonymously with soot carbon) is the only light-absorbing component of submicron aerosol. In addition, "BC" is very often considered as a single specific entity throughout the atmosphere, originating from combustion as the sole source, and having a black color and uniform chemical composition and physical properties. This view has remained popular in spite of the fact that there exists no single material constant for the refractive index of atmospheric light-absorbing carbon (LAC): its value is dependent on the type of the fuel and the conditions of combustion (Bond and Bergstrom, 2006). The refractive index of LAC, together with size and density are key parameters in the Lorentz-Mie calculation of the mass absorption efficiency (α_{abs}) of a single soot particle. Bond and Bergstrom (2006) have recently re-analyzed the literature data on the refractive index and mass absorption efficiency of uncoated, "naked", soot particles considering only traceable actual measurements, rather than a mixture of measurements, secondary references and models. They suggest that some of the previously reported uncertainty is related to inaccurate analysis of literature data in previous reviews and propose a value of $\alpha_{abs}=7.5\pm1.2\,m^2\,g^{-1}$ for atmospheric soot particles, and that higher absorption cross-sections result from coating processes in the atmosphere.

Recently, it has become clear that certain organic compounds in addition to C_{soot} may also contribute to light absorption in atmospheric fine aerosol. There has been mounting evidence from chemical aerosol measurements, laboratory studies, or direct measurements of the spectral dependence of light absorption (Mukai and Ambe, 1986; Havers et al., 1998b; Hoffer et al., 2005) that there is a continuum of carbonaceous substances in atmospheric aerosols (Fig. 1, from Pöschl, 2003). At one end is the thermally refractory and strongly light absorbing near-elemental "EC" or C_{soot} and at the other extreme are thermally reactive and colorless organic substances, such as hydrocarbons. Although the mass absorption efficiency of light-absorbing organic species at the wavelength of 550 nm is much less than that of C_{soot}, it increases sharply towards lower wavelengths, making their absorption in the UV potentially significant due to their observed high abundance in continental aerosol (Hoffer et al., 2005). This spectral dependence causes the material, or its solution, to appear brown (or yellow). In analogy to soot carbon, we propose to call these species collectively C_{brown}, highlighting their optical properties as well as their uncertain origin and chemical composition.

It was observed that particles from smoldering combustion (Patterson and McMahon, 1984), or from industrial combustion of lignite (Bond et al., 1999b) can produce substantial amounts of C_{brown}. Particulate matter collected in the vicinity of a lignite combustion plant appeared light brown to yellowish, but certainly not black as would be expected for pure soot particles (Bond et al., 1998). This was especially true for the initial period of the combustion, when yellow particles were released in great abundance. It was speculated that the weakly absorbing coal tar, consisting of partially aromatized organic matter, can escape from the coal matrix by devolatilization, then undergo thermal processing leading to a progressively greater degree of graphitization. Thus, aromatic compounds emitted from bituminous coal combustion may cover a continuum from a few conjugated aromatic rings (coal tar) to an extended network of aromatic rings (C_{soot}). The higher degree of graphitization means that the energy gap between the highest ground state and the lowest excited state is smaller, which enhances absorption efficiency and simultaneously shifts absorption towards longer wavelengths (lower energy).

Similar processes may take place during the pyrolysis of organic matter, especially during biomass combustion (Mukai and Ambe, 1986). Pyrolysis products can escape without being combusted in flames, and then condense in the cooling plume. Thus they become associated with submicron particles, characteristic of secondary aerosols. Since lignin pyrolysis products are substituted aromatic compounds, they may behave similarly to bituminous coal combustion products. Lignin pyrolysis products were identified in biomass burning aerosol. In addition, there may be some of the solid products of the charring process emitted as aerosol. Most of this char material is expected to end up as supermicron particles, typical of primary aerosols. Because these particles are porous and light, however, their aerodynamic diameter may be much smaller than their geometric diameter, and they may end up in the "submicron" fraction of impactor or stacked filter samples.

Light-absorbing carbonaceous aerosols can also originate from processes other than combustion, particularly from biogenic materials and their low-temperature oxidation and polymerization products .(Andreae and Crutzen, 1997). The bulk characterization of organic carbon in fine continental aerosol, in particular of its water-soluble fraction, revealed that it contains substantial amounts of material with properties closely resembling those of natural humic/fulvic substances (Havers et al., 1998a; Zappoli et al., 1999; Gelencsér et al., 2000a, b; Krivácsy et al., 2000, 2001; Decesari et al., 2001; Kiss et al., 2001). Natural humic/fulvic substances are known to result from the conversion of plant degradation products into polymeric substances with a high degree of aromaticity. Such components make up much of what are usually referred to as humic and fulvic acids, and provide the light absorbing component of dark soils, swamp waters, and black tea. Filters loaded with macroscopic amounts of fulvic or humid acid samples look very dark brown or nearly black (Fig. 2). Tannin/lignin compounds which have similar properties were identified in precipitation (Likens et al., 1983), whereas in cloud water insoluble black particles with the distinguishing infrared absorption bands for both protein and cellulose, and brown particles with the imprint of decomposed proteins were observed (Bank and Castillo, 1987).

Besides originating directly from biomass burning or decomposition, colored polymeric products (HULIS) might also form in heterogeneous reactions from dienes like isoprene in the presence of sulfuric acid (Limbeck et al., 2003). Alternatively, aromatic hydroxy acids, which are emitted in vast quantities by the pyrolysis of lignin during biomass burning may yield colored products in multiphase reactions with OH radicals under typical conditions prevalent in cloud water (Gelencsér et al., 2003).

All these findings point to the important fact that in the atmosphere a single uniform entity of "BC" does not exist: on one hand, C_{soot} already has a wide range of chemical and physical properties which renders any attempt for generalization highly uncertain; on the other hand, there is clearly a substantial fraction of organic matter in fine atmospheric aerosol, which is light-absorbing, but has properties and origins very much different from soot and it is definitely not black. The term "brown carbon" (C_{brown}) that we propose here is meant to represent the latter, though it could include the "tail" of the properties of combustion soot. These moderately-to-weakly absorbing particles could

in part originate from low-temperature combustion processes (e.g., biomass burning or lignite combustion), or could even be produced in the atmosphere in heterogeneous or multiphase processes. Generally speaking, the LAC in aerosol equals the sum of C_{soot} and C_{brown}.

In the following we will review how the existence of C_{brown} may change our understanding of atmospheric LAC and atmospheric light absorption in general. For this purpose we need to know the physical and chemical properties of C_{brown}, particularly in relation to those of soot carbon. Although C_{brown} does denote an existing component of atmospheric aerosol, it possibly covers a wide range of chemical and physical properties that are very difficult to measure, and even more difficult to generalize. In other words, contrary to C_{soot}, for which surrogates such as BC_e or EC_a exist that are widely used for its representation in atmospheric science, no such surrogate can be meaningfully defined for C_{brown}. One might argue that natural humic or fulvic acids may be suitable for representing the fundamental properties of C_{brown}, as has been proven in a series of studies on atmospheric aerosol (Havers et al., 1998a; Zappoli et al., 1999; Krivácsy et al., 2000, 2001; Kiss et al., 2001), and was suggested by Fuzzi et al. (2001). However, terrestrial or aquatic humic and fulvic acids are not single chemical species, but operationally defined classes of compounds, which themselves exhibit an extremely wide range of physico-chemical properties. Therefore, any arbitrarily selected "reference" material as a surrogate is likely to be unsuitable for the representation of the wide variety of C_{brown} in the atmosphere. Nevertheless, in discussing the role of C_{brown} in atmospheric light absorption, we will rely on the properties of HULIS ("HUmic-LIke Substances") observed in the water-soluble fraction of aerosol and sometimes on those of "standard" humic and fulvic acids.

Since the terminology in this field has evolved to be confusing, complex and contradictory, we give here a set of definitions for the way the various terms referring to atmospheric carbon will be used in this paper. Some of these definitions will be discussed in more detail later in the paper.

"Soot carbon" (C_{soot}): Carbon particles with the morphological and chemical prop-

erties typical of the soot aerosol from combustion: Aggregates of spherules made of graphene layers, consisting almost purely of carbon, with minor amounts of bound heteroelements, especially hydrogen and oxygen. This definition does not include the organic substances (oils, etc.) frequently present in or on combustion soot particles.

"Brown carbon" (C_{brown}): Light-absorbing organic matter in atmospheric aerosols of various origins, e.g., soil humics, HULIS, tarry materials from combustion, bioaerosols, etc.

Light-absorbing carbon (LAC): General term for light-absorbing carbonaceous substances in atmospheric aerosol, includes C_{soot} and C_{brown}.

"Elemental carbon" ("EC"): Used here (always in quotes) in the sense that is conventionally and carelessly used in the literature, usually implying a near-elemental soot-carbon-like composition, and usually referring to the fraction of carbon that is oxidized above a certain temperature threshold, and only in the presence of an oxygen-containing atmosphere.

"Apparent elemental carbon" (EC_a): Operationally defined as the fraction of carbon that is oxidized above a certain temperature threshold in the presence of an oxygen-containing atmosphere. May be corrected for charring, depending on the technique used.

"Black carbon" ("BC"): Used here (always in quotes) in the sense that is conventionally and carelessly used in the literature, generally implied to have optical properties and composition similar to soot carbon. In the climate science and in pollutant inventory communities this is the most commonly used term, without consideration of its unclear definition. Also commonly used for the result of a LAC measurement by an optical absorption technique.

"Equivalent black carbon" (BC_e): Operationally defined as the amount of strongly light-absorbing carbon with the approximate optical properties of C_{soot} that would give the same signal in an optical instrument (e.g., the aethalometer) as the sample.

2 Interference of C_{brown} with EC_a/BC_e measurements

2.1 Thermochemical analysis

The accurate sampling and determination of carbonaceous species in atmospheric aerosols has been recognized as one of the most difficult challenges facing atmospheric chemists (Huebert and Charlson, 2000). The most common methods for the determination of OC, BC_e or EC_a are simple thermal, optical, or more recently, thermal-optical methods. The presence of significant concentrations of C_{brown} in tropospheric fine aerosol may cause substantial bias in any of the traditional measurement techniques resulting in erroneous BC_e or EC_a concentration values, which are subsequently carried on to calculations of atmospheric light absorption.

Thermochemical analysis was originally developed for urban aerosols, including particularly diesel soot (Ellis and Novakov, 1982; Cadle et al., 1983; Cachier et al., 1989a; Birch and Cary, 1996). This type of analysis, also referred to as "Evolved Gas Analysis" (EGA), consists of the controlled heating of the sample in a stream of gas, so that organic compounds and soot carbon are successively volatilized and oxidized to CO_2, which is then transferred to a detector and either measured directly or after conversion to CH_4. The total carbon (TC) content of the sample is determined from the integral of the CO_2 emitted over the entire temperature range, while the organic carbon (OC) fraction is defined as the amount of CO_2 released up to a certain threshold temperature. The carbon fraction combusted above this threshold temperature, our EC_a, has usually been called "elemental carbon", because it is assumed that it represents the soot fraction of the aerosol, which is thought to consist mostly of carbon, i.e., have a nearly elemental composition. This is most applicable to diesel soot or lamp black, where black carbon is nearly identical with soot carbon, and has a chemical composition close to elemental carbon. In thermograms of samples where C_{soot} dominates, there is usually a clearly defined peak at high temperatures (>450°C). HR-TEM investigation of diesel soot particles has shown them to have near-spherical structure with onion-like graphene layers. Because the reactivity of carbon phases increases with the amount of free-edge carbon and structural hetero-atoms, diesel soot with its spherical structure and high carbon content is the most refractory environmental carbon phase, and is therefore most readily separated from organic carbonaceous aerosol components (Gustafsson et al., 2001).

However, severe difficulties are encountered when this type of analysis is applied to samples containing brown carbon from biomass burning (Reid et al., 2005b) or humic materials. Firstly, because of the ill-defined chemical nature of C_{brown}, it is volatilized over a wide range of temperatures in thermochemical analysis. Some of it therefore is classified as organic carbon, some as "elemental" carbon (Mayol-Bracero et al., 2002). Furthermore, the chemical composition of the aerosol sample and filter substrate can influence the temperature at which EC_a is evolved (Lin and Friedlander, 1988). In particular, biomass smoke contains inorganic components that catalyze oxidation of C_{soot} and C_{brown}, shifting their combustion to lower temperatures (Novakov and Corrigan, 1995). Generally, it has been found that "EC" in aged and remote aerosols evolves at considerably lower temperatures (450–550°C instead of 550–700°C) than in urban aerosols (Turner and Hering, 1994; Huffman, 1996b). In thermochemical procedures with a fixed temperature sequence, where the distinction between EC_a and OC is made solely based on combustion temperature (e.g., the R&P 5400 Ambient Carbon Particulate Monitor), a misidentification of C_{soot} as organic carbon, and a reduction in the fraction of C_{brown} that is classified as EC_a may result. Conversely, when the last peak in a thermogram is simply interpreted as representing EC_a, without considering the convergence of EC_a and OC combustion temperatures by catalytic effects, EC_a concentrations may be drastically overestimated (by a factor of 2–10) (Novakov and Corrigan, 1995; Mayol-Bracero et al., 2002).

In view of the difficulty of ascertaining the identity of EC_a based solely on its thermal behavior, it may be useful to also use potentially available chemical information. The H/C molar ratio in C_{soot} is ca. 0.15 ± 0.05, well below that of organic substances, where it usually exceeds 1.0, except in highly condensed materials (PAH, humics, lignin) where it tends to cluster in the range 0.5–1.5 (Cachier et al., 1989b; Huffman,

1996b; Kim et al., 2003). This could provide a diagnostic feature in thermograms made with instruments having a H_2O channel in addition to the usual CO_2 detector channel (Kuhlbusch et al., 1998). This possibility has remained little explored, even though detectors that provide simultaneous determination of H_2O and CO_2 are widely available, e.g., the LI-6262 or LI-7000 (LI-COR Biosciences, Lincoln, NE 68504, USA). Figure 3 shows a thermogram from a sample of biomass smoke collected in the Amazon during the LBA-SMOCC campaign (Andreae et al., 2004), which had been water-extracted before analysis. There is a clear differentiation between the three peaks based on the H/C ratio: The first peak, which represents the most volatile compounds, has an H/C ratio of ∼4, and probably still contains some absorbed water from the extraction procedure (note that the thermogram shows H_2O, with two H atoms per molecule). The second peak has an H/C ratio near 2, similar to cellulose and lignin compounds, while the third peak, above 500°C, shows a much lower H/C of about 0.4, near but somewhat above that reported for C_{soot}.

Apart from these conceptual difficulties with the demarcation between C_{soot} and C_{brown}, charring of organic compounds including C_{brown} is one of the major artefacts in thermochemical analyses. Some methods carefully optimize experimental conditions in order to minimize the extent of charring, such as the two-step combustion procedure developed by Cachier et al. (1989a). Although in using this method charring can largely be avoided for various organic matrices, the authors themselves found that humic acids undergo charring up to 37±3% by mass. One could argue, however, that the brown carbon from biomass burning is not as subject to significant charring, given that it has been volatilized before in the fire. This is contradicted by the findings that water-soluble organic carbon (WSOC), which is a major component of pyrogenic aerosols and contains a significant amount of C_{brown}, has been shown to be especially prone to charring (Yu et al., 2002, 2004). This also applies to the most abundant organic compound in pyrogenic aerosols, levoglucosan. These issues have been largely ignored, because at the time the method was developed, nothing was known about the presence of HULIS in fine aerosol, but recently it has become obvious that "EC" values measured in the presence of considerable amounts of C_{brown} (as is likely the case for biomass burning aerosol and continental fine aerosol in general) may be overestimated by some variants of thermochemical analysis.

Extraction of the sample with water or organic solvents prior to thermochemical analysis is used in another group of methods (Novakov and Corrigan, 1995; Mayol-Bracero et al., 2002; Kirchstetter et al., 2003). Water extraction removes both inorganic catalytic compounds and at least part of the C_{brown}, providing a closer approximation of the actual C_{soot} content by EC_a. The removal of the WSOC considerably reduces the charring artefact. Organic solvents also remove organic carbon and part of C_{brown}, but do not eliminate the catalytic effect of inorganic ions.

Charring is corrected for in thermal-optical analysis which has been regarded as the most accurate method for the OC/EC_a split. In this method the transmittance or reflectance of the filter sample is monitored during the thermographic analysis (Chow et al., 1993; Birch and Cary, 1996). The transmittance initially decreases with heating due to charring of organic matter, and then increases again, as the char is combusted. The cut-point between OC and EC_a is defined as that point in the thermogram at which transmittance has returned to the value it had before charring. This optical pyrolysis correction assumes that the light extinction per unit mass of pyrolytically produced carbon is the same as the light extinction per unit mass of carbon removed until the reflectance regains its initial value. Since this condition is unlikely to be met, there is an inherent bias in either direction in the demarcation between light-absorbing and elemental carbon. In an analysis of the data set from the IMPROVE aerosol network in the United States, Huffmann (1996a; 1996b) has shown that the charring correction in the thermal-optical reflectance technique and the misinterpretation in the OC-EC_a cutpoint can lead to a large underestimation of EC_a. In a recent comparison between EC_a/OC determinations by the thermal-optical reflectance (TOR) and thermal-optical transmission (TOT) techniques, differences by as much as a factor of 4 were observed for the EC_a concentrations obtained with the two variants of the technique (Chow et al., 2004). These differences could be attributed to charring within the filter matrix that

introduced a bias in the TOT technique (Chen et al., 2004).

In intercomparisons of a large number of techniques for the determination of TC, OC and EC_a, the agreement is usually quite good for TC, but very poor for the determination of the EC_a fraction (Countess, 1990; Hitzenberger et al., 1999; Schmid et al., 2001; ten Brink et al., 2004; Watson et al., 2006[1]). Typically, the EC_a measurements are highly correlated between methods, indicating that the differences are of a systematic nature. While the various thermal-optical and EGA techniques usually agree reasonably well (better than a factor of two discrepancy) for soot, gasoline and diesel engine emissions, and urban particulates (Countess, 1990; Guillemin et al., 1997; Lim et al., 2003), huge differences (up to factors of six, and occasionally even more) are seen for samples from non-urban areas and biomass burning emissions (Chow et al., 2001; Schmid et al., 2001). But even for the new standard reference materials, RM 8785 (Air Particulate Matter on Filter Media), two different thermal-optical protocols (IMPROVE and STN-NIOSH) yielded unreconciled differences of a factor of 2 (Klouda et al., 2005), so that the material has been issued with two different so-called “information concentration values” (based on the two different protocols) for EC_a!

The good agreement between various methods for analyzing diesel exhaust particulates is understandable since, as discussed above, they exhibit a clearly ordered layer structure approaching that of polycrystalline graphite, and contain very little polymeric organic material. This is supported by the studies of Wittmaack (2004, 2005), who found that diesel particles were thermally stable in air up to 470°C, and then oxidized in a narrow temperature interval between 480 and 510°C. However, large uncertainty is associated with the thermal-optical measurements of aerosol containing a large fraction of C_{brown} and pyrolyzable OC. In a recent study, a thermal-optical method was tested on atmospheric aerosol, wood smoke, coal fly ash, and secondary organic aerosol from smog-chamber experiments as source samples, and on organic matrices

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[1] Watson, J. G., Chow, J. C., and Chen, L.-W. A.: Summary of methods and comparison studies for organic and elemental carbon: Implications for visibility and global warming, J. Air & Waste Manage. Assoc., submitted, 2006.

such as wood smoke extract, candle wax and motor oil (Schauer et al., 2003). It was found that all ambient atmospheric aerosol samples pyrolyzed during analysis, as did wood smoke and secondary organic aerosol among the source samples, and wood smoke extract among the organic matrices. Even with the optimized 10-step temperature program it was not possible to fully correct for charring. The outcome was that elemental carbon was measured by the thermal-optical method in samples in which it should not be present. In other cases, the measurement of EC_a was biased by some organic matrices. For example, in the wood smoke extract, 5% of the carbon was falsely assigned as elemental by the thermal-optical method. Another study revealed that for smog-chamber aerosol, which contained no soot, ∼2% of total carbon was erroneously interpreted to be "EC" (in the sense of soot particles) by a thermal-optical method (Chow et al., 1993). EGA thermograms of non-urban aerosols suggest that a significant fraction of OC is combusted in the temperature range normally associated with C_{soot}, and therefore would be incorrectly assigned to the "EC" fraction. Some types of bioaerosol particles, which are likely to be light-absorbing as well, require combustion temperatures well above 600°C (Wittmaack, 2005).

A further example for these problems is provided by the EGA thermograms of commercial samples of humic acid and lignin, both of which are dark brown to black substances (C_{brown}), visually resembling "EC" (Fig. 4). The lignin sample is combusted almost completely below 600°C, and the ratio of the H_2O and CO_2 signals suggests that the H/C molar ratio ranges from about 1–4, with an average of 1.3, which is within the range previously reported for lignins (Kim et al., 2003). The humic acid sample, on the other hand, has a mean H/C of 0.46 for the low temperature peak and a pronounced peak near 600°C, which would in an unknown sample be usually interpreted as evidence of a large C_{soot} fraction. Even the H/C ratio of ca. 0.3 in the latter peak resulting from the combustion of thermally refractory organic material is difficult to distinguish from that of C_{soot}. The presence of comparably hydrogen-deficient fractions in riverine dissolved organic matter has been interpreted as evidence for the presence of "BC" from charred biomass (Kim et al., 2004), but it is plausible that similar materials

can also be produced by (bio)chemical condensation polymerization.

The response of the thermal or thermal-optical techniques to the light-absorbing substances in biomass smoke has not been adequately characterized, but seems to be very dependent on the instrumental settings. Birch and Cary (1996) note that with an "optimized" setting they find only 0.86% EC_a in cigarette smoke, while with a "less than optimal" setting 20–30% of the carbon on cigarette smoke was designated elemental. Furthermore, thermal analysis of starch and cellulose in the presence of NH_4HSO_4 produced 2–3 times the amount of char than was formed in the absence of the inorganic compound, while the charring of levoglucosan decreased in the presence of NH_4HSO_4 (Yu et al., 2002).

An additional complication for thermal-optical measurements is presented by the fact that the spectral absorption of C_{brown} differs from that of black carbon. The absorption cross section of C_{brown} increases very sharply with decreasing wavelength, with a power of –2 to –6, whereas C_{soot} (e.g., from diesel vehicles) shows a λ^{-1} dependence (Kirchstetter et al., 2004; Hoffer et al., 2005; Schmid et al., 2005). At the red wavelength of the HeNe laser (632.8 nm) used in the thermal-optical instrument, C_{brown} absorbs much less than C_{soot}, which may lead to a bias because of the assumption that char and the LAC in the sample have the same optical properties.

2.2 Light absorption measurements

In principle, the relatively strong light absorption of C_{soot} can be utilized to infer C_{soot} from an optical measurement of aerosol light absorption (σ_{abs}) and the mass-specific absorption of C_{soot} (α_{abs}). This approach has the advantage, from a climate perspective, that the primary measurement relates directly the light-absorbing properties of the aerosol, without consideration of whether the absorption is due to C_{soot} or C_{brown}.

However, significant uncertainties are associated with the determination of both σ_{abs} and α_{abs}. For atmospheric applications, the only instrument that can measure the light absorption directly on an airborne aerosol is the photoacoustic spectrometer (PAS) (Truex and Anderson, 1979; Yasa et al., 1979; Petzold and Niessner, 1995; Moosmüller et al., 1997; Arnott et al., 1999). In principle, light absorption by airborne aerosols can also be determined by the so-called "difference method", where absorption is determined from the difference between extinction and scattering as measured by an extinction cell and a nephelometer, respectively (Schnaiter et al., 2005b; Sheridan et al., 2005). While this method is useful for the validation of absorption techniques with high concentrations of relatively "dark" aerosols (single scattering albedo at 550 nm$<\sim$0.8), it results in unacceptably large errors for typical atmospheric conditions, since it determines σ_{abs} from a fairly small difference of two large numbers (extinction and scattering coefficient) (Schnaiter et al., 2005b; Sheridan et al., 2005). Comparison experiments with the PAS and optical extinction cells show excellent agreement for a wide variety of aerosols including diesel soot, biomass smoke particles and ambient aerosol (Petzold et al., 2005; Schnaiter et al., 2005b).

Historically, absorption measurements have most frequently been performed with on-line integrating plate techniques (e.g., aethalometer and particle soot absorption photometer, PSAP), which deposit aerosol onto a filter and measure the resulting change in light transmittance through the filter, i.e., not σ_{abs} but the attenuation coefficient σ_{ATN} through the aerosol-laden filter is measured. As a result of the fact that these measurements are not done on airborne aerosols, but on samples deposited on a filter, there are a variety of artefacts mainly due to filter-aerosol interactions (multiple scattering), shadowing of the incident light with increasing filter loading, and aerosol scattering effects (Petzold et al., 1997; Weingartner et al., 2003; Arnott et al., 2005). In a study where several filter-based measurements of the absorption coefficient of biomass smoke were compared, the systematic disagreement between methods was "only" 20–40%, but individual measurements often differed by a factor of three (Reid et al., 1998b).

Although numerous efforts have been made to calibrate aethalometers and PSAPs and to correct for the various artefacts (Hansen et al., 1984; Bodhaine, 1995; Bond et al., 1999a), no generally valid calibration or correction scheme for ambient aerosol has become available due to the complex interaction of physical aerosol properties (size,

single scattering albedo, mixing state) and the filter matrix. Comparisons of simultaneous measurements made using PAS and filter-based techniques (PSAP, aethalometer, integrating plate) show considerable differences (up to a factor of two) under some circumstances, especially when the relative humidity is variable (Moosmüller et al., 1998; Arnott et al., 1999, 2003; Sheridan et al., 2005). The most reliable filter-based instrument for absorption measurements at this time is the multi-angle absorption photometer (MAAP), which simultaneously measures transmittance and reflectance of the filter at multiple angles and uses a two-stream radiative transfer model to determine the filter and aerosol scattering corrections for the absorption measurement (Petzold and Schönlinner, 2004).

Overall we conclude that, depending on which technique is used and what corrections are applied, systematic errors of up to a factor of two must be expected when inferring the true in-situ absorption coefficient from filter-based absorption measurements, unless these are carefully corrected for filter and scattering effects. On the other hand, laboratory comparisons between the PAS and difference method suggest that the PAS can determine aerosol absorption with an accuracy $<$10% (Moosmüller et al., 1998; Arnott et al., 1999, 2003; Sheridan et al., 2005).

Another problem arises from the fact that, when absorption is measured with the intention to derive "black carbon" concentrations, a measured or assumed specific absorption cross section (α_a) must be used to convert light absorption to mass concentration of BC_e. As mentioned above, Bond and Bergstrom (2006) have reviewed the literature and recommended a value of α_{abs}=7.5±1.2 m^2 g^{-1} for airborne, uncoated, "naked" soot particles. However, due to condensation processes and/or cloud processing, atmospheric soot particles acquire non-absorbing coatings (mainly sulfate and/or organic carbon), which lead to absorption enhancements. Mie calculations on soot particles with sulfate coatings indicate enhancements of up to factors of 2–3 for extremely large coating thicknesses (a few mass percent of soot) and relatively large particle size ($>$300 nm) (Martins et al., 1998a; Fuller et al., 1999). This is consistent with recent measurements by Schnaiter et al. (2005a) that showed enhancement factors of up to 2.0±0.2 for 400 nm (diesel) soot particles coated by organic carbon (soot volume fraction <3%). In addition, hygroscopic particle growth may further enhance α_{abs} by up to a factor of about 1.3 at relative humidities up to 95% (Redemann et al., 2001). Hence, for atmospheric conditions we expect α_{abs}=7.5±1.2 $m^2\ g^{-1}$ only to be realistic in near-source regimes; aged soot particles may exceed this value by a factor 2 or more.

For filter-based BC_e methods, one can either convert the measured attenuation into absorption (as described above) and then apply α_{abs} , or apply the attenuation cross section (α_{ATN}) directly to the attenuation coefficient. The range of values for α_{ATN} reported in the literature is between about 1 to 30 $m^2\ g^{-1}$ (Liousse et al., 1993, 1995; Chylek et al., 1995; Colbeck et al., 1997; Petzold et al., 1997; Martins et al., 1998a; Moosmüller et al., 1998; Reid et al., 1998a; Fuller et al., 1999; Kopp et al., 1999; Lavanchy et al., 1999; Dillner et al., 2001; Sharma et al., 2002; Lim et al., 2003; Schnaiter et al., 2003). This exceeds the range of α_{abs} values, since in addition to the inherent variability of α_{abs}, α_{ATN} is affected by the numerous instrument-specific uncertainties that depend on aerosol properties such as chemical composition, particle size and shape, and mixing state (Martins et al., 1998a; Hitzenberger et al., 1999; Reid et al., 2005a; Bond and Bergstrom, 2006). Theoretical considerations as well as laboratory experiments show that, even with the same instrumental setup, α_{ATN} varies considerably as a function of the LAC content of the aerosol, and becomes most variable and uncertain for aerosol with low LAC fractions, in the range commonly encountered in non-urban and remote regions (Horvath, 1997; Lindberg et al., 1999). These problems increase toward lower wavelengths, and therefore most strongly influence measurements made with instruments using green light (e.g., the PSAP at 565 nm) or the shorter-wavelength channels of the 7-wavelength aethalometer AE-31. The aethalometer model AE10, which uses white light at an effective wavelength of 880 nm (Weingartner et al., 2003) is likely to be less affected.

Finally, very often, α_{ATN} is being derived using thermochemical EC_a measurements, and therefore carries with it all the uncertainties discussed above. We feel that this

is one of the primary causes for the huge variations in α_{ATN} observed in calibration studies. In most cases, the importance of this source of uncertainty was, however, not appreciated by the authors, and the relative variations of α_{ATN} were often explained as resulting only from differences in morphology and mixing state of LAC related to different sources and aging processes. In practice, a value of about 10 $m^2\ g^{-1}$ is typically used to derive BC_e from absorption measurements. It can therefore be concluded that, even if the only absorbing substance in aerosols were C_{soot}, an uncertainty of about a factor of two in the estimation of "BC" would result from the variability of α_{ATN} itself. A good example for this is the study by Lim et al. (2003) where BC_e concentrations differing by a factor of two were reported by an aethalometer and a PSAP running in parallel at the same site.

At the same time, one would expect that optical measurements of BC_e by, e.g., an aethalometer or PSAP are less affected by the presence of C_{brown} than thermochemical methods. This is because a typical absorption spectrum of HULIS shows a steep decrease of absorbance into the visible (Havers et al., 1998b; Zappoli et al., 1999; Hoffer et al., 2005), and has a very low specific absorption (<0.05 $m^2\ g^{-1}$) at the operational wavelengths of these instruments (535 and 550 nm, respectively). It should be noted that in the accumulation mode, where the mass concentration of water soluble HULIS is highest (Lukács et al., 2004), Mie theory predicts that even spherical particles of pure graphite would have a significantly lower mass absorption efficiency than those in the Aitken mode. These two effects combined make it probable that over most of the troposphere, the contribution of C_{brown} to atmospheric light absorption relative to that of C_{soot} will be rather low in the wavelength range of 500–550 nm. However, given the strongly skewed absorption of C_{brown} towards the UV, this statement may not be true for atmospheric light absorption integrated over the solar spectrum, i.e. the flux of energy that is absorbed in the troposphere (Hoffer et al., 2005). The possible consequences of this wavelength dependence will be discussed in detail in Sect. 3.

The 7-λ Aethalometer (Model E31, 450 to 950 nm) tries to capitalize on the difference in spectral dependence of C_{brown} and C_{soot} by measuring C_{soot} in the near-infrared regime and deriving C_{brown} from a near UV channel after subtracting the soot absorption component, assuming a λ^{-1} dependence for soot absorption. However, in addition to the numerous systematic uncertainties associated with most filter-based sampling techniques, the concept assumes that the optical properties of C_{brown} are fairly constant. As illustrated in Fig. 1, this cannot be expected due to the variable chemical nature of C_{brown} in general and, for biomass burning in particular, due to the dependence of the optical properties of hydrogenated carbon on the encountered thermal annealing temperatures (Smith, 1984). The situation is further complicated by the presence of non-carbonaceous absorbing aerosol components such as soil dust (mainly hematite), which can play a significant role even in locations quite distant from desert regions (Fialho et al., 2005).

We conclude that especially when a significant fraction of light absorption is due to C_{brown}, a unique relationship between light absorption and “black carbon” cannot be expected to exist (Lindberg et al., 1999). This is the reason why we have introduced the term “equivalent black carbon”, BC_e, which is that amount of C_{soot} that would cause the same amount of light absorption as that observed in the sample, using the value of α_{ATN} and correction factors applied with a particular instrument. More fundamentally, the whole concept of determining a single value of “black carbon” from an absorption measurement on biomass smoke (and presumably also any aerosol sample that contains non-soot light absorbing carbon) must be called into question. Since a given sample consists of a mixture of C_{soot} and C_{brown} in unknown proportions, and both components have different ratios of light absorption to carbon mass, a unique value of “BC” mass concentration cannot be derived from light absorption.

3 Wavelength dependence of absorption and its possible effect on tropospheric photochemistry

Light absorption by particles is often measured at only one wavelength, and is extrapolated to other wavelengths using the power-law relationship for the spectral dependence of absorption:

$$\alpha_{abs} = K \times \lambda^{-Å_{abs}}$$

where α_{abs} is the mass absorption efficiency of the particles ($m^2\ g^{-1}$), K is a constant that includes the aerosol mass concentration, λ (nm) is the wavelength of the light, and $Å_{abs}$ is the Ångström exponent for absorption. Although there is no theoretical justification for this equation, it generally adequately describes spectral absorption of atmospheric aerosol from the near UV to the near infrared regime. For small spherical particles ($2\,r\pi|m|/\lambda \ll 1$) with radius r and wavelength independent refractive index m, $Å_{abs}$ equals to 1.0 (Bond, 2001). For reasonable particle size distributions and a LAC refractive index of m=1.55–0.5i, the theoretical values of Å typically vary between 0.2 and 1.2. Measurements confirm that $Å_{abs}$ values are close to 1 in aerosols in which pure C_{soot} dominates the LAC, as has been shown by several authors for motor vehicle emissions and urban aerosols by in-situ measurements (Rosen et al., 1978; Horvath, 1997; Bergstrom et al., 2002; Schnaiter et al., 2003; Lawless et al., 2004; Bond and Bergstrom, 2006) and inversion of remote sensing data (Dubovik et al., 1998; Bergstrom et al., 2003).

When absorption is stronger at shorter wavelengths, i.e., the particles appear brownish or yellow, Å will be significantly greater than unity. Values of 2.0 and more were found in aerosol collected near a lignite combustion plant (Bond et al., 1999b), in biomass smoke (Kirchstetter et al., 2004; Schmid et al., 2005; Schnaiter et al., 2005b), environmental tobacco smoke (Lawless et al., 2004), and in rural aerosol (Lindberg et al., 1993). The highest values of Å are found for the yellowish to brownish products of pure smoldering combustion, e.g., tobacco smoke (3.5, Lawless et al., 2004) or water-soluble HULIS from biomass burning (6–7, Hoffer et al., 2005). This steepening of the increase of absorption towards shorter wavelengths can be attributed to the presence of significant amounts of light-absorbing organic compounds, i.e., C_{brown}, in aerosols resulting from low-temperature combustion (Bond, 2001).

This spectral dependence means that caution must be exercised when extrapolating absorption measured at a single wavelength over the solar spectrum, especially when the mass concentration of C_{soot} is low relative to that of C_{brown}. When absorption coefficients are measured at mid-visible wavelengths and the spectral properties of C_{soot} are assumed to represent all ambient light-absorbing carbon, the reduction of downward UV irradiance may be significantly underestimated. Since UV irradiance plays a very important role in tropospheric ozone production and photochemistry in general, its erroneous assessment through oversimplified interpretation of "BC" data may considerably weaken our ability to understand and predict photochemical processes in the troposphere (Albuquerque et al., 2005).

The first explanation for the reduced downward UV-irradiance observed in urban areas was provided by Jacobson (1999) who attributed it to UV-absorbing organic species such as nitrated aromatics, benzaldehydes, benzoic acids, polycyclic aromatic hydrocarbons, and to a lesser extent, nitrated inorganic compounds. In particular, nitrated aromatic compounds, PAHs and benzaldehydes were found to be the most effective UV-A and UV-B absorbers in terms of their imaginary refractive indices and absorption wavelengths. These compounds indeed show very strong wavelength dependence, and because their absorption tails off between the UV and visible wavelengths, global UV irradiance is attenuated much more than total solar irradiance. The decreased UV flux was calculated to reduce ozone mixing ratios in Los Angeles by 5–8%. Model column simulations with the inclusion of enhanced aerosol absorption, however, still underpredicted the observed UV irradiance reductions by 8 and 25% for an urban and rural site, respectively. The absorption by organic aerosol represented about $\frac{1}{4}$ of the total downward UV attenuation, primarily due to non-nitrated and nitrated aromatic compounds in proportions of 10.2–13.5% and 8.8–14.7%, respectively. In radiative transfer model calculations a positive forcing per unit mass of organic carbon of $+21\,\mathrm{W\,m^{-2}}$ per g OC was inferred from this effect alone (Jacobson, 2002).

One may speculate that the UV reduction missing from models may be due to the presence of unspeciated C_{brown}. Its spectral properties observed in atmospheric measurements are intermediate between those of nitrated PAHs and C_{soot}, and it shows a smooth decrease in absorbance towards the visible that can still be approximated by a power law relationship (Bond, 2001; Kirchstetter et al., 2004; Hoffer et al., 2005; Bond and Bergstrom, 2006).

There is another property of C_{brown} which is worthy of note with respect to atmospheric light absorption, namely that a significant fraction of it is soluble in water (Hoffer et al., 2005). In fact, atmospheric observation on the properties of C_{brown} largely came from measurements of the water extract of atmospheric aerosol. It can be well assumed that part of C_{brown} could dissolve into growing cloud droplets upon cloud formation and produce homogeneous absorbing droplets which may affect overall cloud absorption, particularly in the UV. This effect could be most significant in clouds formed on dense biomass smoke plumes, where the concentration of C_{brown} can be substantial (Mayol-Bracero et al., 2002). It was calculated that, e.g., at the wavelength of 475 nm a hydrometeor containing C_{brown} at a concentration of 2×10^{-6} M absorbs about 6 times more radiation than pure water does (Gelencsér et al., 2003). To the best of our knowledge, this effect has never been included in complex atmospheric radiation models.

4 Conclusions

The recent discovery of brown carbon in atmospheric aerosol makes it necessary to revisit the concept of a light-absorbing carbonaceous (LAC) component of atmospheric aerosol, which has been traditionally assumed to be exclusively black combustion soot. Although soot particles are readily recognizable by their typical morphologies, they are far from being uniform either in their chemical or physical properties. Unfortunately, monitoring methods that are commonly used for the determination of the mass concentration of soot carbon can only provide operationally defined quantities such as black carbon ("BC") or elemental carbon ("EC"). However, the operational character of these analytical parameters is very often overlooked, it would therefore be highly desirable to indicate it through the use of terms like "apparent EC" (EC_a) and "equivalent

BC" (BC_e). Even in the case of combustion soot, there is a conceptual ambiguity in the separation of organic and elemental carbon, as well as in the determination of BC_e from light-absorption measurements, which introduces at least a factor of 2 uncertainty to their measurements. More than 50 inter-method and inter-laboratory comparisons for the determination of EC_a or BC_e have been conducted, showing typical differences of a factor of 2 between methods, but sometimes even discrepancies of a factor of 7 (Watson et al., 2006[1]). In spite of this ongoing controversy, "BC" is very often considered a single, well-determined entity throughout the troposphere, especially in emission inventories and radiative transfer models, which has a uniform composition and physical properties approaching those of pure graphite or carbon black (e.g., Hansen et al., 2000; Chung and Seinfeld, 2002; Bond et al., 2004; Schaap et al., 2004; Wang, 2004).

The presence of brown carbon (C_{brown}) in aerosol, for which ample evidence has recently been lined up, raises serious concern about this simplified approach. Here we have shown that C_{brown} may interfere with both EC_a and BC_e measurements and introduce significant bias under specific conditions. This applies in particular to any situation where light absorption is not dominated by C_{soot} from petroleum combustion, i.e., regions where pyrogenic aerosols or light-absorbing biogenic aerosols play an important role – in other words, for most of the globe outside the industrialized regions of the most developed countries.

The fact that these components have progressively stronger absorption in the UV seriously calls into question whether measurements of light absorption at a single wavelength in the mid-visible can be used to infer absorption of solar radiation in the troposphere. In the light of these findings, even the concept of "BC" as a conservative atmospheric tracer for combustion processes must be challenged. Representative measurements of the spectral mass absorption efficiency of C_{brown} must be accomplished, however, before its contribution to atmospheric light absorption can be evaluated. At the same time, further studies are needed on the properties and origin of chromophoric organic species to establish the role they play in the global troposphere. Eventually, the whole concept of "light- absorbing carbon", and the analytical methods

used, need to be carefully reconsidered and "standardized" to provide reliable input for atmospheric models and legislative measures. The development and widespread use of standard reference materials, such as RM 8785 (Air Particulate Matter on Filter Media) (Klouda et al., 2005) should be encouraged.

We conclude that, at the present state of the art, the uncertainties and potential biases in EC_a and BC_e measurements are large, and that there is a poor correlation between measured EC_a or BC_e values and atmospheric light absorption. If these errors are systematic, and unless there is some degree of fortuitous compensation between upward and downward biases, they could call into question even the sign of the direct forcing of anthropogenic aerosols on climate!

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References

Abel, S. J., Haywood, J. M., Highwood, E. J., Li, J., and Busek, P. R.: Evolution of aerosol properties from biomass burning measured during SAFARI 2000, Geophys. Res. Lett., 30, 1783, doi:10.1029/2003GL017342, 2003.

Akhter, M. S., Chughtai, A. R., and Smith, D. M.: The structure of hexane soot – I. Spectroscopic studies, Appl. Spectr., 39, 143–153, 1985.

Albuquerque, L. M. M., Longo, K. M., Freitas, S. R., Tarasova, T., Plana Fattori, A., Nobre, C., and Gatti, L. V.: Sensitivity studies on the photolysis rates calculation in Amazonian atmospheric chemistry – Part I: The impact of the direct radiative effect of biomass burning aerosol particles, Atmos. Chem. Phys. Discuss., 5, 9325–9353, 2005.

Andreae, M. O.: Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosols, Science, 220, 1148–1151, 1983.

Andreae, M. O.: Climatic effects of changing atmospheric aerosol levels, in: World Survey of Climatology, Vol. 16, Future Climates of the World, edited by: Henderson-Sellers, A., pp. 341–392, Elsevier, Amsterdam, 1995.

Andreae, M. O., Andreae, T. W., Ferek, R. J., and Raemdonck, H.: Long-range transport of soot carbon in the marine atmosphere, Sci. Total Environ., 36, 73–80, 1984.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1056, 1997.

Andreae, M. O., Rosenfeld, D., Artaxo, P., Costa, A. A., Frank, G. P., Longo, K. M., and Silva-Dias, M. A. F.: Smoking rain clouds over the Amazon, Science, 303, 1337–1342, 2004.

Arnott, W. P., Hamasha, K., Moosmuller, H., Sheridan, P. J., and Ogren, J. A.: Towards aerosol light-absorption measurements with a 7-wavelength Aethalometer: Evaluation with a photoacoustic instrument and 3-wavelength nephelometer, Aerosol Sci. Technol., 39, 17–29, 2005.

Arnott, W. P., Moosmüller, H., Rogers, C. F., Jin, T., and Bruch, R.: Photoacoustic spectrometer for measuring light absorption by aerosol: Instrument description, Atmos. Environ., 33, 2845–2852, 1999.

Arnott, W. P., Moosmüller, H., Sheridan, P. J., Ogren, J. A., Raspet, R., Slaton, W. V., Hand, J. L., Kreidenweis, S. M., and Collett, J. L.: Photoacoustic and filter-based ambient aerosol light absorption measurements: Instrument comparisons and the role of relative humidity, J. Geophys. Res., 108, 4034, doi:10.1029/2002JD002165, 2003.

Bank, S. and Castillo, R.: Analysis of organic matter from cloud particles, Geophys. Res. Lett., 14, 210–212, 1987.

Bergstrom, R. W., Pilewskie, P., Schmid, B., and Russell, P. B.: Estimates of the spectral aerosol single scattering albedo and aerosol radiative effects during SAFARI 2000, J. Geophys. Res., 108, 8474, doi:10.1029/2002JD002435, 2003.

Bergstrom, R. W., Russell, P. B., and Hignett, P.: Wavelength dependence of the absorption of black carbon particles: Predictions and results from the TARFOX experiment and implications for the aerosol single scattering albedo, J. Atmos. Sci., 59, 567–577, 2002.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Technol., 25, 221–241, 1996.

Bockhorn, H. (Ed.): Soot Formation in Combustion: Mechanisms and Models, Berlin & New York, Springer-Verlag, 596 p, 1994.

Bodhaine, B. A.: Aerosol absorption measurements at Barrow, Mauna Loa and the South Pole, J. Geophys. Res., 100, 8967–8975, 1995.

Bond, T. C.: Spectral dependence of visible light absorption by carbonaceous particles emitted from coal combustion, Geophys. Res. Lett., 28, 4075–4078, 2001.

Bond, T. C., Anderson, T. L., and Campbell, D.: Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, Aerosol Sci. Technol., 30, 582–600, 1999a.

Bond, T. C. and Bergstrom, R. W.: Light absorption by carbonaceous particles: An investigative review, Aerosol Sci. Technol., 40, 27–67, 2006.

Bond, T. C., Bussemer, M., Wehner, B., Keller, S., Charlson, R. J., and Heintzenberg, J.: Light absorption by primary particle emissions from a lignite burning plant, Environ. Sci. Technol., 33, 3887–3891, 1999b.

Bond, T. C., Charlson, R. J., and Heintzenberg, J.: Quantifying the emission of light-absorbing particles: Measurements tailored to climate studies, Geophys. Res. Lett., 25, 337–340, 1998.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion: J. Geophys. Res., 109, D14203, doi:10.1029/2003JD003697, 2004.

Bond, T. C. and Sun, H. L.: Can reducing black carbon emissions counteract global warming?, Environ. Sci. Technol., 39, 5921–5926, 2005.

Brimblecombe, P.: The big smoke: a history of air pollution in London since medieval times, London, New York, Methuen, 185 p, 1987.

Buseck, P. R., Huang, B. J., and Keller, L. P.: Electron-microscope investigation of the structures of annealed carbons, Energy & Fuels, 1, 105–110, 1987.

Cachier, H., Brémond, M.-P., and Buat-Ménard, P.: Carbonaceous aerosols from different tropical biomass burning sources, Nature, 340, 371–373, 1989a.

Cachier, H., Brémond, M. P., and Buat-Ménard, P.: Thermal separation of soot carbon, Aerosol Sci. Technol., 10, 358–364, 1989b.

Cadle, S. H., Groblicki, P. J., and Mulawa, P. A.: Problems in the sampling and analysis of carbon particulate, Atmos. Environ., 17, 593–600, 1983.

Chang, S. G., Brodzinsky, R., Gundel, L. A., and Novakov, T.: Chemical and catalytic properties of elemental carbon, in: Particulate Carbon: Atmospheric Life Cycle, edited by: Wolff, G. T. and Klimisch, R. L., pp. 159–181, Plenum Press, New York, 1982.

Chen, L. W. A., Chow, J. C., Watson, J. G., Moosmuller, H., and Arnott, W. P.: Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis, J. Aerosol Sci., 35, 765–780, 2004.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., and Moosmüller, H.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414–4422, 2004.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH carbon measurements, Aerosol Sci. Technol., 34, 23–34, 2001.

Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI thermal-optical reflectance carbon analysis system – Description, evaluation and applications in United States air quality studies, Atmos. Environ., 27A, 1185–1201, 1993.

Chughtai, A. R., Kim, J. M., and Smith, D. M.: The effect of air/fuel ratio on properties and reactivity of combustion soots, J. Atmos. Chem., 43, 21–43, 2002.

Chung, S. H. and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, J. Geophys. Res., 107, 4407, doi:10.1029/2001JD001397, 2002.

Chung, S. H. and Seinfeld, J. H.: Climate response of direct radiative forcing of anthropogenic black carbon, J. Geophys. Res., 110, D11102, doi:10.1029/2004JD005441, 2005.

Chylek, P., Videen, G., Ngo, D., Pinnick, R. G., and Klett, J. D.: Effect of black carbon on the optical properties and climate forcing of sulfate aerosols, J. Geophys. Res., 100, 16 325–16 332, 1995.

Clague, A. D. H., Donnet, J., Wang, T. K., and Peng, J. C. M.: A comparison of diesel engine soot with carbon black, Carbon, 37, 1553–1565, 1999.

Colbeck, I., Appleby, L., Hardman, E. J., and Harrison, R. M.: The optical properties and morphology of cloud-processed carbonaceous smoke, J. Aerosol Sci., 21, 527–538, 1990.

Colbeck, I., Atkinson, B., and Johar, Y.: The morphology and optical properties of soot produced by different fuels, J. Aerosol Sci., 28, 715–723, 1997.

Countess, R. J.: Interlaboratory analyses of carbonaceous aerosol samples, Aerosol Sci. Technol., 12, 114–121, 1990.

Decesari, S., Facchini, M. C., Matta, E., Lettini, F., Mircea, M., Fuzzi, S., Tagliavini, E., and Putaud, J. P.: Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy, Atmos. Environ., 35, 3691–3699, 2001.

Dillner, A. M., Stein, C., Larson, S. M., and Hitzenberger, R.: Measuring the mass extinction efficiency of elemental carbon in rural aerosol, Aerosol Sci. Technol., 35, 1009–1021, 2001.

Dubovik, O., Holben, B. N., Kaufman, Y. J., Yamasoe, M., Smirnov, A., Tanre, D., and Slutsker, I.: Single-scattering albedo of smoke retrieved from the sky radiance and solar transmittance measured from ground, J. Geophys. Res., 103, 31 903–31 923, 1998.

Ebert, L. B.: Is soot composed predominantly of carbon clusters?, Science, 247, 1468–1471, 1990.

Ellis, E. C. and Novakov, T.: Application of thermal analysis to the characterization of organic aerosol particles, Sci. Total Environ., 23, 227–238, 1982.

Ferry, D., Suzanne, J., Nitsche, S., Popovitcheva, O. B., and Shonija, N. K.: Water adsorption and dynamics on kerosene soot under atmospheric conditions, J. Geophys. Res., 107, 4734, doi:10.1029/2002JD002459, 2002.

Fialho, P., Hansen, A. D. A., and Honrath, R. E.: Absorption coefficients by aerosols in remote areas: a new approach to decouple dust and black carbon absorption coefficients using seven-wavelength Aethalometer data, J. Aerosol Sci., 36, 267–282, 2005.

Fuller, K. A., Malm, W. C., and Kreidenweis, S. M.: Effects of mixing on extinction by carbonaceous particles, J. Geophys. Res., 104, 15 941–15 954, 1999.

Fuzzi, S., Decesari, S., Facchini, M. C., Matta, E., Mircea, M., and Tagliavini, E.: A simplified model of the water soluble organic component of atmospheric aerosols, Geophys. Res. Lett., 28, 4079–4082, 2001.

Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L.: In-situ formation of light-absorbing organic matter in cloud water, J. Atmos. Chem., 45, 25–33, 2003.

Gelencsér, A., Hoffer, A., Molnár, A., Krivácsy, Z., Kiss, G., and Mészáros, E.: Thermal behaviour of carbonaceous aerosol from a continental background site, Atmos. Environ., 34, 823–831, 2000a.

Gelencsér, A., Mészáros, T., Blazsó, M., Kiss, G., Krivácsy, Z., Molnár, A., and Mészáros, E.: Structural characterisation of organic matter in fine tropospheric aerosol by pyrolysis-gas chromatography-mass spectrometry, J. Atmos. Chem., 37, 173–183, 2000b.

Goldberg, E. D.: Black Carbon in the Environment: Properties and Distribution, New York, J. Wiley & Sons, 198 p, 1985.

Grieco, W. J., Howard, J. B., Rainey, L. C., and Vander Sande, J. B.: Fullerenic carbon in combustion-generated soot, Carbon, 38, 597–614, 2000.

Grisdale, R. O.: The formation of black carbon, J. Appl. Phys., 24, 1082–1091, 1953.

Guillemin, M., Cachier, H., Chini, C., Dabill, D., Dahmann, D., Diebold, F., Fischer, A., Fricke, H. H., Groves, J. A., Hebisch, R., Houpillart, M., Israel, G., Mattenklott, M., Moldenhauer, W., Sandino, J. P., Schlums, C., Sutter, E., and Tucek, E.: International round robin tests on the measurement of carbon in diesel exhaust particulates, International Archives of Occupational and Environmental Health, 70, 161–172, 1997.

Gustafsson, O., Bucheli, T. D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J. N., Reddy, C. M., and Eglinton, T. I.: Evaluation of a protocol for the quantification of black carbon in sediments, Global Biogeochem. Cycles, 15, 881–890, 2001.

Hansen, A. D. A., Rosen, H., and Novakov, T.: The aethalometer – an instrument for the real-time measurement of optical absorption by aerosol particles, Sci. Total Environ., 36, 191–196, 1984.

Hansen, J. and Nazarenko, L.: Soot climate forcing via snow and ice albedos, Proc. Natl. Acad. Sci. USA, 101, 423–428, 2004.

Hansen, J., Sato, M., Ruedy, R., Lacis, A., and Oinas, V.: Global warming in the twenty-first century: An alternative scenario, Proc. Natl. Acad. Sci. USA, 97, 9875–9880, 2000.

Hansen, J. E., Sato, M., Lacis, A., Ruedy, R., Tegen, I., and Matthews, E.: Climate forcings in the industrial era, Proc. Natl. Acad. Sci. USA, 95, 12 753–12 758, 1998.

Hansen, J., Sato, M., Ruedy, R., et al.: Efficacy of Climate Forcings, J. Geophys. Res., 110, D18104, doi:10.1029/2005JD005776, 2005.

Havers, N., Burba, P., Klockow, D., and Klockow-Beck, A.: Characterization of humic-like substances in airborne particulate matter by capillary electrophoresis, Chromatographia, 47, 619–624, 1998a.

Havers, N., Burba, P., Lambert, J., and Klockow, D.: Spectroscopic characterization of humic-like substances in airborne particulate matter, J. Atmos. Chem., 29, 45–54, 1998b.

Heintzenberg, J.: Size-segregated measurements of particulate elemental carbon and aerosol light absorption at remote locations, Atmos. Environ., 16, 2461–2469, 1982.

Hitzenberger, R., Jennings, S. G., Larson, S. M., Dillner, A., Cachier, H., Galambos, Z., Rouc, A., and Spain, T. G.: Intercomparison of measurement methods for black carbon aerosols, Atmos. Environ., 33, 2823–2833, 1999.

Hoffer, A., Gelencsér, A., Guyon, P., Kiss, G., Schmid, O., Frank, G., Artaxo, P., and Andreae, M. O.: Optical properties of humic-like substances (HULIS) in biomass-burning aerosols, Atmos. Chem. Phys. Discuss., 5, 7341–7360, 2005.

Horvath, H.: Experimental calibration for aerosol light absorption measurements using the integrating plate method – Summary of the data, J. Aerosol Sci., 28, 1149–1161, 1997.

Huebert, B. J. and Charlson, R. J.: Uncertainties in data on organic aerosols, Tellus Series B-Chemical and Physical Meteorology, 52, 1249–1255, 2000.

Huffman, H. D.: Comparison of the light absorption coefficient and carbon measures for remote aerosols: An independent analysis of data from the IMPROVE Network – I, Atmos. Environ., 30, 73–83, 1996a.

Huffman, H. D.: The reconstruction of aerosol light absorption by particle measurements at remote sites: An independent analysis of data from the IMPROVE Network – II, Atmos. Environ., 30, 85–99, 1996b.

Jacobson, M. Z.: Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption, J. Geophys. Res., 104, 3527–3542, 1999.

Jacobson, M. Z.: Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols, J. Geophys. Res., 106, 1551–1568, 2001.

Jacobson, M. Z.: Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming, J. Geophys. Res., 107, 4410, doi:10.1029/2001JD001376, 2002.

Jacobson, M. Z.: Climate response of fossil fuel and biofuel soot, accounting for soot's feedback to snow and sea ice albedo and emissivity, J. Geophys. Res., 109, D21201, doi:10.1029/2004JD004945, 2004.

Jones, G. S., Jones, A., Roberts, D. L., Stott, P. A., and Williams, K. D.: Sensitivity of global-scale climate change attribution results to inclusion of fossil fuel black carbon aerosol, Geophys. Res. Lett., 32, L14701, doi:10.1029/2005GL023370, 2005.

Kim, S., Kramer, R. W., and Hatcher, P. G.: Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram, Anal. Chem., 75, 5336–5344, 2003.

Kim, S. W., Kaplan, L. A., Benner, R., and Hatcher, P. G.: Hydrogen-deficient molecules in natural riverine water samples – evidence for the existence of black carbon in DOM, Mar. Chem., 92, 225–234, 2004.

Kirchstetter, T. W., Novakov, T., and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, J. Geophys. Res., 109, D21208, doi:10.1029/2004JD0004999, 2004.

Kirchstetter, T. W., Novakov, T., Hobbs, P. V., and Magi, B.: Airborne measurements of carbonaceous aerosols in southern Africa during the dry, biomass burning season, J. Geophys. Res., 108, doi:10.1029/2002JD002171, 2003.

Kiss, G., Varga, B., Gelencsér, A., Krivácsy, Z., Molnár, A., Alsberg, T., Persson, L., Hansson, H. C., and Facchini, M. C.: Characterisation of polar organic compounds in fog water, Atmos. Environ., 35, 2193–2200, 2001.

Klouda, G. A., Filliben, J. J., Parish, H. J., Chow, J. J., Watson, J. G., and Cary, R. A.: Reference material 8785: Air particulate matter on filter media, Aerosol Sci. Technol., 39, 173–183, 2005.

Kopp, C., Petzold, A., and Niessner, R.: Investigation of the specific attenuation cross-section of aerosols deposited on fiber filters with a polar photometer to determine black carbon, J. Aerosol Sci., 30, 1153–1163, 1999.

Krivácsy, Z., Gelencsér, A., Kiss, G., Mészáros, E., Molnár, A., Hoffer, A., Mészáros, T., Sárvári, Z., Temesi, D., Varga, B., Baltensperger, U., Nyeki, S., and Weingartner, E.: Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch, J. Atmos. Chem., 39, 235–259, 2001.

Krivácsy, Z., Kiss, G., Varga, B., Galambos, I., Sárvári, Z., Gelencsér, A., Molnár, A., Fuzzi, S., Facchini, M. C., Zappoli, S., Andracchio, A., Alsberg, T., Hansson, H. C., and Persson, L.: Study of humic-like substances in fog and interstitial aerosol by size-exclusion chromatography and capillary electrophoresis, Atmos. Environ., 34, 4273–4281, 2000.

Kuhlbusch, T. A. J., Hertlein, A. M., and Schütz, L. W.: Sources, determination, monitoring, and transport of carbonaceous aerosols in Mainz, Germany, Atmos. Environ., 32, 1097–1110, 1998.

Lavanchy, V. M. H., Gaggeler, H. W., Nyeki, S., and Baltensperger, U.: Elemental carbon (EC) and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch, Atmos. Environ., 33, 2759–2769, 1999.

Lawless, P. A., Rodes, C. E., and Ensor, D. S.: Multiwavelength absorbance of filter deposits for determination of environmental tobacco smoke and black carbon, Atmos. Environ., 38, 3373–3383, 2004.

Levin, Z. and Lindberg, J. D.: Size distributions, chemical composition, and optical properties of urban and desert aerosols in Israel, J. Geophys. Res., 84, 6941–6950, 1979.

Likens, G. E., Edgerton, E. S., and Galloway, J. N.: The composition and deposition of organic carbon in precipitation, Tellus, 35B, 16–24, 1983.

Lim, H. J., Turpin, B. J., Edgerton, E., Hering, S. V., Allen, G., Maring, H., and Solomon, P.: Semicontinuous aerosol carbon measurements: Comparison of Atlanta Supersite measurements, J. Geophys. Res., 108, 8419, doi:10.1029/2001JD001214, 2003.

Limbeck, A., Kulmala, M., and Puxbaum, H.: Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, Geophys. Res. Lett., 30, 1996, doi:10.1029/2003GL017738, 2003.

Lin, C. and Friedlander, S. K.: A note on the use of glass fiber filters in the thermal analysis of carbon containing aerosols, Atmos. Environ., 22, 605–607, 1988.

Lindberg, J. D., Douglass, R. E., and Garvey, D. M.: Carbon and the optical properties of atmospheric dust, Appl. Opt., 32, 6077–6081, 1993.

Lindberg, J. D., Douglass, R. E., and Garvey, D. M.: Atmospheric particulate absorption and black carbon measurement, Appl. Opt., 38, 2369–2376, 1999.

Liousse, C., Cachier, H., and Jennings, S. G.: Optical and thermal measurements of black carbon aerosol content in different environments: Variation of the specific attenuation cross-section, sigma (s), Atmos. Environ., 27A, 1203–1211, 1993.

Liousse, C., Devaux, C., Dulac, F., and Cachier, H.: Aging of savanna biomass burning aerosols: Consequences on their optical properties, J. Atmos. Chem., 22, 1–17, 1995.

Lukács, H., Gelencsér, A., Pio, C., Legrand, M., Preunkert, S., Schock, M., Puxbaum, H., Kasper-Giebl, A., and Fialho, P.: Comparative study on HULIS concentrations and their seasonal variations across Europe, Paper presented at the 8th International Conference on Carbonaceous Particles in the Atmosphere, Vienna, Austria, 2004.

Malm, W. C., Sisler, L. T., Kaufman, D., Eldred, R. A., and Cahill, T. A.: Spatial and seasonal trends in particle concentrations and optical extinction in the United States, J. Geophys. Res., 99, 1347–1370, 1994.

Martins, J. V., Artaxo, P., Liousse, C., Reid, J. S., Hobbs, P. V., and Kaufman, Y. J.: Effects of black carbon content, particle size, and mixing on light absorption by aerosols from biomass burning in Brazil, J. Geophys. Res., 103, 32 041–32 050, 1998a.

Martins, J. V., Hobbs, P. V., Weiss, R. E., and Artaxo, P.: Sphericity and morphology of smoke particles from biomass burning in Brazil, J. Geophys. Res., 103, 32 051–32 057, 1998b.

Masiello, C. A.: New directions in black carbon organic geochemistry, Mar. Chem., 92, 201–213, 2004.

Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning aerosols over Amazonia: 2. Apportionment of the chemical composition and importance of the polyacidic fraction, J. Geophys. Res., 107, 8091, doi:10.1029/2001JD000522, 2002.

Medalia, A. I. and Rivin, D.: Particulate carbon and other components of soot and carbon black, Carbon, 20, 481–492, 1982.

Mertes, S., Dippel, B., and Schwarzenböck, A.: Quantification of graphitic carbon in atmospheric aerosol particles by Raman spectroscopy and first application for the determination of mass absorption efficiencies, J. Aerosol Sci., 35, 347–361, 2004.

Moosmüller, H., Arnott, W. P., and Rogers, C. F.: Methods for real-time, in situ measurement of aerosol light absorption, J. Air & Waste Manage. Assoc., 47, 157–166, 1997.

Moosmüller, H., Arnott, W. P., Rogers, C. F., Chow, J. C., Frazier, C. A., Sherman, L. E., and Dietrich, D. L., Photoacoustic and filter measurements related to aerosol light absorption during the Northern Front Range Air Quality Study (Colorado 1996/1997), J. Geophys. Res., 103, 28 149–28 157, 1998.

Mukai, H. and Ambe, Y.: Characterization of a humic acid-like brown substance in airborne particulate matter and tentative identification of its origin, Atmos. Environ., 20, 813–819, 1986.

Novakov, T. and Corrigan, C. E.: Thermal characterization of biomass smoke particles, Mikrochim. Acta, 119, 157–166, 1995.

Oberlin, A.: High-resolution TEM studies of carbonization and graphitization, in: Chemistry and Physics of Carbon, edited by: Thrower, P. A., pp. 21–142, M. Dekker, New York, 1989.

Onischuk, A. A., di Stasio, S., Karasev, V. V., Baklanov, A. M., Makhov, G. A., Vlasenko, A. L., Sadykova, A. R., Shipovalov, A. V., and Panfilov, V. N.: Evolution of structure and charge of soot aggregates during and after formation in a propane/air diffusion flame, J. Aerosol Sci., 34, 383–403, 2003.

Patterson, E. M. and McMahon, C. K.: Absorption characteristics of forest fire particulate matter, Atmos. Environ., 18, 2541–2551, 1984.

Petzold, A., Kopp, C., and Niessner, R.: The dependence of the specific attenuation cross-section on black carbon mass fraction and particle size, Atmos. Environ., 31, 661–672, 1997.

Petzold, A. and Niessner, R.: Novel design of a resonant photoacoustic spectrophone for elemental carbon mass monitoring, Appl. Phys. Lett., 66, 1285–1287, 1995.

Petzold, A., Schloesser, H., Sheridan, P. J., Arnott, W. P., Ogren, J. A., and Virkkula, A.: Evaluation of multiangle absorption photometry for measuring aerosol light absorption, Aerosol Sci. Technol., 39, 40–51, 2005.

Petzold, A. and Schönlinner, M.: Multi-angle absorption photometry – a new method for the measurement of aerosol light absorption and atmospheric black carbon, J. Aerosol Sci., 35, 421–441, 2004.

Pöschl, U.: Aerosol particle analysis: challenges and progress, Anal. Bioanal. Chem., 375, 30–32, 2003.

Pósfai, M., Anderson, J. R., Buseck, P. R., and Sievering, H.: Soot and sulfate aerosol particles in the remote marine troposphere, J. Geophys. Res., 104, 21 685–21 693, 1999.

Ramanathan, V., Chung, C., Kim, D., Bettge, T., Buja, L., Kiehl, J. T., Washington, W. M., Fu, Q., Sikka, D. R., and Wild, M.: Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle, Proc. Natl. Acad. Sci. USA, 102, 5326–5333, 2005.

Redemann, J., Russell, P. B., and Hamill, P.: Dependence of aerosol light absorption and single-scattering albedo on ambient relative humidity for sulfate aerosols with black carbon cores, J. Geophys. Res., 106, 27 485–27 495, 2001.

Reid, J. S., Eck, T. F., Christopher, S. A., Koppmann, R., Dubovik, O., Eleuterio, D. P., Holben, B. N., Reid, E. A., and Zhang, J.: A review of biomass burning emissions part III: intensive optical properties of biomass burning particles, Atmos. Chem. Phys., 5, 827–849, 2005a.

Reid, J. S., Hobbs, P. V., Ferek, R. J., Blake, D. R., Martins, J. V., Dunlap, M. R., and Liousse, C.: Physical, chemical, and optical properties of regional hazes dominated by smoke in Brazil, J. Geophys. Res., 103, 32 059–32 080, 1998a.

Reid, J. S., Hobbs, P. V., Liousse, C., Martins, J. V., Weiss, R. E., and Eck, T. F.: Comparisons of techniques for measuring shortwave absorption and black carbon content of aerosols from biomass burning in Brazil, J. Geophys. Res., 103, 32 031–32 040, 1998b.

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, Atmos. Chem. Phys., 5, 799–825, 2005b.

Rosen, H., Hansen, A. D. A., Gundel, L., and Novakov, T.: Identification of optically absorbing component in urban aerosols, Appl. Opt., 17, 3859–3861, 1978.

Rosen, H. and Novakov, T.: Raman-scattering and characterization of atmospheric aerosol particles, Nature, 266, 708–710, 1977.

Ruellan, S., Cachier, H., Gaudichet, A., Masclet, P., and Lacaux, J. P.: Airborne aerosols over central Africa during the experiment for regional sources and sinks of oxidants (EXPRESSO), J. Geophys. Res., 104, 30 673–30 690, 1999.

Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., and Poeschl, U.: Raman micro spectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information, Carbon, 43, 1731–1742, 2005.

Schaap, M., Van Der Gon, H., Dentener, F. J., Visschedijk, A. J. H., Van Loon, M., ten Brink, H. M., Putaud, J. P., Guillaume, B., Liousse, C., and Builtjes, P. J. H.: Anthropogenic black carbon and fine aerosol distribution over Europe, J. Geophys. Res., 109, D18207, doi:10.1029/2003JD004330, 2004.

Schauer, J. J., Mader, B. T., Deminter, J. T., et al.: ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon, Environ. Sci. Technol., 37, 993–1001, 2003.

Schmid, H., Laskus, L., Abraham, H. J., et al.: Results of the "carbon conference" international aerosol carbon round robin test stage I, Atmos. Environ., 35, 2111–2121, 2001.

Schmid, O., Artaxo, P., Arnott, W. P., Chand, D., Gatti, L. V., Frank, G. P., Hoffer, A., Schnaiter, M., and Andreae, M. O.: Spectral light absorption by ambient aerosols influenced by biomass burning in the Amazon Basin. I: Comparison and field calibration of absorption measurement techniques, Atmos. Chem. Phys. Discuss., 5, 9355–9404, 2005.

Schnaiter, M., Horvath, H., Möhler, O., Naumann, K. H., Saathoff, H., and Schöck, O. W.: UV-VIS-NIR spectral optical properties of soot and soot-containing aerosols, J. Aerosol Sci., 34, 1421–1444, 2003.

Schnaiter, M., Linke, C., Möhler, O., Naumann, K.-H., Saathoff, H., Wagner, R., and Schurath, U.: Absorption amplification of black carbon internally mixed with secondary organic aerosol, 110, D19204, doi:10.1029/2005JD006046, 2005a.

Schnaiter, M., Schmid, O., Petzold, A., Fritzsche, L., Klein, K.-F., Andreae, M. O., Helas, G., Thielmann, A., Gimmler, M., Möhler, O., Linke, C., and Schurath, U.: Measurement of wavelength-resolved light absorption by aerosols utilizing a UV-VIS extinction cell, Aerosol Sci. Technol., 39, 249–260, 2005b.

Sharma, S., Brook, J. R., Cachier, H., Chow, J., Gaudenzi, A., and Lu, G.: Light absorption and thermal measurements of black carbon in different regions of Canada, J. Geophys. Res., 107, 4771, doi:10.1029/2002JD002496, 2002.

Sheridan, P. J., Arnott, W. P., Ogren, J. A., Andrews, E., Atkinson, D. B., Covert, D. S., Moosmuller, H., Petzold, A., Schmid, B., Strawa, A. W., Varma, R., and Virkkula, A.: The Reno Aerosol Optics Study: An evaluation of aerosol absorption measurement methods, Aerosol Sci. Technol., 39, 1–16, 2005.

Smith, F. W.: Optical constants of a hydrogenated amorphous carbon film, J. Appl. Phys., 55, 764–771, 1984.

Su, D. S., Müller, J. O., Jentoft, R. E., Rothe, D., Jacob, E., and Schlögl, R.: Fullerene-like soot from EuroIV diesel engine: consequences for catalytic automotive pollution control. Topics in Catalysis, 30–31, 241–245, 2004.

Sze, S. K., Siddique, N., Sloan, J. J., and Escribano, R.: Raman spectroscopic characterization of carbonaceous aerosols, Atmos. Environ., 35, 561–568, 2001.

ten Brink, H., Maenhaut, W., Hitzenberger, R., Gnauk, T., Spindler, G., Even, A., Chi, X. G.,

Bauer, H., Puxbaum, H., Putaud, J. P., Tursic, J., and Berner, A.: INTERCOMP2000: the comparability of methods in use in Europe for measuring the carbon content of aerosol, Atmos. Environ., 38, 6507–6519, 2004.

Truex, T. J. and Anderson, J. E.: Mass monitoring of carbonaceous aerosols with a spectrophone, Atmos. Environ., 13, 507–509, 1979.

Turner, J. and Hering, S.: The additivity and stability of carbon signatures obtained by eveolved gas analysis, Aerosol Sci. Technol., 21, 294–305, 1994.

Wang, C.: A modeling study on the climate impacts of black carbon aerosols, J. Geophys. Res., 109, D03106, doi:10.1029/2003JD004084, 2004.

Weingartner, E., Burtscher, H., and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot particles, Atmos. Environ., 31, 2311–2327, 1997.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers, J. Aerosol Sci., 34, 1445–1463, 2003.

Wentzel, M., Gorzawski, H., Naumann, K. H., Saathoff, H., and Weinbruch, S.: Transmission electron microscopical and aerosol dynamical characterization of soot aerosols, J. Aerosol Sci., 34, 1347–1370, 2003.

White, A. H. and Germer, L. H.: The structure of black carbon, J. Chem. Phys., 9, 492–502, 1941.

Wittmaack, K.: Characterization of carbon nanoparticles in ambient aerosols by scanning electron microscopy and model calculations, J. Air & Waste Manage. Assoc., 54, 1091–1098, 2004.

Wittmaack, K.: Combustion characteristics of water-insoluble elemental and organic carbon in size selected ambient aerosol particles, Atmos. Chem. Phys., 5, 1905–1913, 2005.

Yasa, Z., Amer, N. M., Rosen, H., Hansen, A. D. A., and Novakov, T.: Photoacoustic investigation of urban aerosol particles, Appl. Opt., 18, 2528–2530, 1979.

Yu, J. Z., Xu, J. H., and Yang, H.: Charring characteristics of atmospheric organic particulate matter in thermal analysis, Environ. Sci. Technol., 36, 754–761, 2002.

Yu, J. Z., Yang, H., Zhang, H. Y., and Lau, A. K. H.: Size distributions of water-soluble organic carbon in ambient aerosols and its size-resolved thermal characteristics, Atmos. Environ., 38, 1061–1071, 2004.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M. C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, A., Mészáros, E., Hansson, H.-C., Rosman, K., and Zebühr, Y.: Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, Atmos. Environ., 33, 2733–2743, 1999.

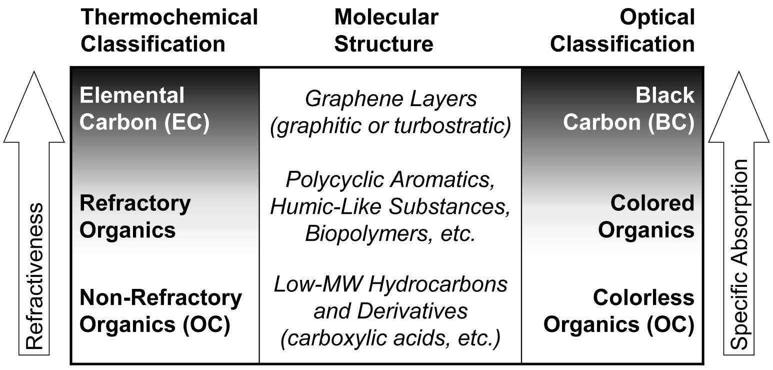

Fig. 1. Classification and molecular structure of carbonaceous aerosol components (from Pöschl, 2003).

Fig. 2. Filters loaded with commercial samples of humic acid (Fluka 53680) and lignin (Aldrich 37,095-9).

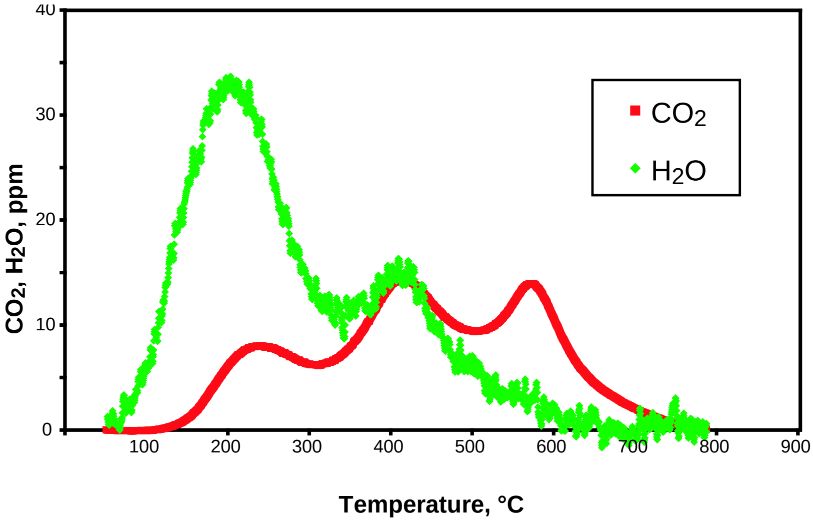

Fig. 3. Carbon and hydrogen thermogram of a water-extracted sample of pyrogenic aerosol from the Amazon region.

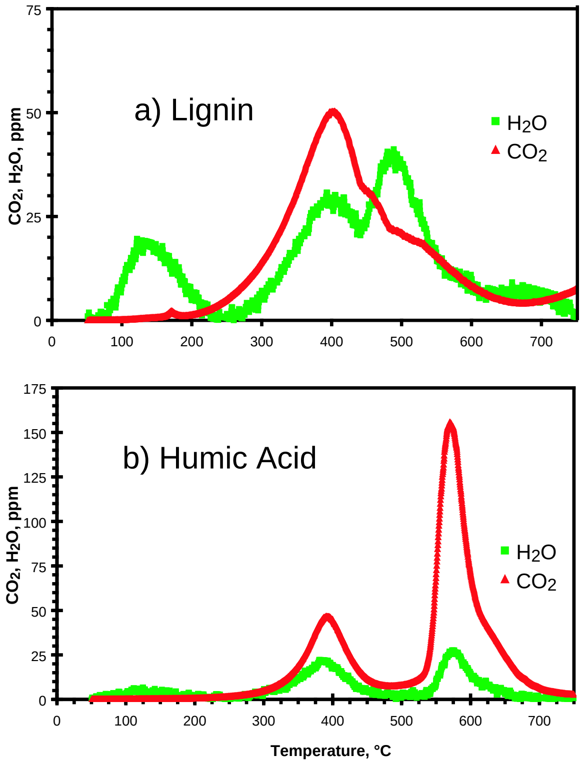

Fig. 4. Carbon and hydrogen thermograms of commercial samples of **(a)** lignin (Aldrich 37,095-9) and **(b)** humic acid (Fluka 53680).