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Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon

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[1] The wavelength dependence of light absorption by aerosols collected on filters is investigated throughout the near-ultraviolet to near-infrared spectral region. Measurements were made using an optical transmission method. Aerosols produced by biomass combustion, including wood and savanna burning, and by motor vehicles, including diesel trucks, are included in the analysis. These aerosol types were distinguished by different wavelength (λ) dependences in light absorption. Light absorption by the motor vehicle aerosols exhibited relatively weak wavelength dependence; absorption varied approximately as λ^{-1}, indicating that black carbon (BC) was the dominant absorbing aerosol component. By contrast, the biomass smoke aerosols had much stronger wavelength dependence, approximately λ^{-2}. The stronger spectral dependence was the result of enhanced light absorption at wavelengths shorter than 600 nm and was largely reduced when much of the sample organic carbon (OC) was extracted by dissolution in acetone. This indicates that OC in addition to BC in the biomass smoke aerosols contributed significantly to measured light absorption in the ultraviolet and visible spectral regions and that OC in biomass burning aerosols may appreciably absorb solar radiation. Estimated absorption efficiencies and imaginary refractive indices are presented for the OC extracted from biomass burning samples and the BC in motor vehicle-dominated aerosol samples. The uncertainty of these constants is discussed. Overall, results of this investigation show that low-temperature, incomplete combustion processes, including biomass burning, can produce light-absorbing aerosols that exhibit much stronger spectral dependence than high-temperature combustion processes, such as diesel combustion. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 1610 Global Change: Atmosphere (0315, 0325); *KEYWORDS:* aerosol light absorption, biomass burning, organic carbon

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1. Introduction

[2] Atmospheric aerosol particles directly modify the earth's radiation balance by absorbing and scattering solar radiation. Recent modeling and field studies indicate that aerosol light absorption is an important component of climate forcing. For instance, the direct radiative forcing of light-absorbing aerosols may be greater than that of methane and equal to about one third of that of carbon dioxide [*Jacobson*, 2001]. Observations from an experiment in the Indian Ocean showed that aerosol-induced changes in regional radiative fluxes can be an order of magnitude larger than the global mean forcing by aerosols or greenhouse gases [*Krishnan and Ramanathan*, 2002, and references therein]. Changes in regional stability caused by atmospheric heating of light-absorbing aerosols may alter large-scale circulations and the hydrological cycle, enough so, apparently, to account for observed temperature and precipitation changes in China and India [*Menon et al.*, 2002]. These findings underscore the need to understand the role of aerosol light absorption in climate change, which requires inclusion of realistic representations of aerosols and their radiative forcings. However, recent assessments of climate change point out the need for better measurements of aerosol atmospheric mass concentrations and optical properties in order to reduce uncertainties in climate models [*Houghton et al.*, 2001; V. Ramanathan et al., A National Research Imperative White Paper, National Aerosol-Climate Interactions Program, 2002, available at http://www-nacip.ucsd.edu/NACIPWhitePaperMay2102.pdf].

[3] Black carbon (BC), a major component of soot, is the most efficient light-absorbing aerosol species in the

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visible spectrum. Climate models typically treat BC as the only light-absorbing aerosol component. Light absorption by BC is generally considered to vary weakly with wavelength [e.g., *Bergstrom et al.*, 2002]. Other aerosol components, exhibiting stronger absorption spectral dependence, contribute to absorption at shorter light wavelengths. Laboratory [*Lindberg et al.*, 1993] and remote sensing [*Dubovik et al.*, 2002] measurements have shown that aerosols over desert regions appreciably absorb light of blue and shorter wavelengths (i.e., wavelengths less than 500 nm). Certain organic compounds also absorb in the blue and ultraviolet spectral regions [*Jacobson*, 1998, 1999]. Pyrogenic aerosols may absorb because of colored organic compounds [*Mukai and Ambe*, 1986], referred to as "brown carbon'" by *Formenti et al.* [2003]. It has been shown that smoldering combustion of pine needles produces soluble particles (i.e., not BC) that exhibit a strong absorption spectral dependence [*Patterson and McMahon*, 1984]. Similarly, low-temperature coal combustion has been shown to produce particles with strong absorption wavelength dependence [*Bond*, 2001; *Bond et al.*, 1999a].

[4] The role of organic carbon (OC) in light absorption has not been thoroughly investigated. Aerosol light absorption is commonly measured at a single wavelength where BC is expected to be the primary absorber of light, for example, at 570 nm using the particle soot absorption photometer (PSAP) [*Bond et al.*, 1999b] or at 880 nm using the aethalometer [*Hansen et al.*, 1984]. To the extent that OC absorbs visible light, it may be a nonnegligible contributor to direct aerosol radiative forcing. If the light absorption spectral dependence of aerosols is underestimated in models, the aerosol positive radiative forcing will be understated [*Bond*, 2001]. Furthermore, aerosol extinction of ultraviolet sunlight may reduce tropospheric ozone concentrations via reduced photolysis rates [*Jacobson*, 1999; *Vuilleumier et al.*, 2001; *Martin et al.*, 2003]. Since the global mean radiative forcing of tropospheric ozone is comparable to that of BC [*Houghton et al.*, 2001], aerosol extinction in the ultraviolet spectral region may affect climate change in addition to atmospheric photochemistry and air quality.

[5] In this study, we measured the spectral dependence of, and the role of OC in, aerosol light absorption. Experiments included two aerosol sources that contribute significantly to atmospheric mass concentrations: motor vehicles, including diesel trucks and buses; and biomass combustion, including burning savanna and wood. Results discussed herein indicate that these aerosol types exhibited distinct light absorption characteristics related to their composition. Results are presented along with a review of related findings from previous studies and discussions of uncertainty.

2. Experiments

2.1. Measurement Methods

[6] We used a light transmission method to characterize the spectral light absorption by aerosol samples collected on quartz fiber filters. Measurements were made using three similar instruments. The first two were optical spectrometers: Perkin Elmer model Lambda 2, which operated throughout the near-ultraviolet to the near-infrared spectral region at 10 nm resolution with a Tungsten lamp, and Ocean Optics model S2000, which operated in the visible and near-infrared spectral regions at sub nanometer resolution with a Tungsten Halogen light source. A sample holder was constructed to accommodate the measurement of light transmission through quartz filter samples in the spectrometer. The third instrument was a multiple wavelength light transmission instrument (MULTI) that was built at Lawrence Berkeley National Laboratory (LBNL). This instrument is similar to that of the laser transmission method (LTM) described by *Rosen and Novakov* [1983], which is the predecessor of the widely used aethalometer. The MULTI was equipped with an array of light emitting diodes (LEDs) to which aerosol samples were sequentially exposed. The intensities of light transmitted through aerosol samples were measured with a silicon photodiode (Hamamatsu, model S1226-44BQ) that had a spectral response range of 190 to 1000 nm. Initially, six discrete LEDs centered at 370, 400, 470, 570, 660, and 850 nm were used; later measurements were made with ten LEDs centered at 375, 400, 470, 525, 590, 616, 660, 780, 880, and 940 nm. The optical emission spectra of the LEDs were measured and confirmed with a spectrometer. Some of the samples included in this study were analyzed using more than one of the optical instruments and the results were the same in each case. This is indicated in Table 1.

[7] Light attenuation (ATN) was calculated from measured sample light transmission (T): ATN = 100 · ln(1/T). In this study, T was defined as $(I_s/I_{s,o}) \cdot (I_{r,o}/I_r)$, where I_s and $I_{s,o}$ are the measured intensities of light transmitted through a quartz filter sample prior to and after removal of carbonaceous material by heating to 800°C in oxygen, and I_r and $I_{r,o}$ are the intensities of light transmitted through a reference quartz filter measured at the same time I_s and $I_{s,o}$, respectively, are measured. Measurements of I_s and $I_{s,o}$ were made using the same quartz filter rather than using another blank quartz filter to measure I_o because (1) light transmission through quartz filters may vary and (2) we wanted to measure aerosol ATN due to carbonaceous material, but not mineral dust. Light-absorbing mineral dust does not evaporate, decompose, or combust at temperatures <800°C, as does BC and OC, and was thus not removed during sample heating. The reference filter was used to correct for possible instrumental variability, such as changes in the brightness of the light source or detector response, during the interval of time between measurements of I_s and $I_{s,o}$.

[8] In the optical transmission method employed here, the aerosol particles were collected using highly reflective quartz fiber filters, as is the case in the aethalometer. Using this method, it was shown that light attenuation is primarily due to particle light absorption [*Rosen and Novakov*, 1983]. We note, however, that several caveats accompany determination of the magnitude of aerosol light absorption (e.g., the absorption coefficient) using transmission methods. First, filter-based transmission measurements exaggerate atmospheric aerosol light absorption because light scattering by the filter fibers provides the embedded particles multiple opportunities to absorb light. For the aethalometer, which uses quartz filters, and the particle soot absorption photometer (PSAP), which uses glass fiber filters, the magnitude of the enhancement reportedly ranges from about 1.8–2.2 [*Weingartner et al.*, 2003; *Bond et al.*, 1999b; *Bodhaine*,

Table 1. Calculated Absorption Ångström Exponents for Various Fine Mode Aerosol Samples[a]

Date					Absorption Ångström Exponent, α[d]		
Collected	Analyzed	Analyzer[b]	Sample Number	Sample Description[c]	Untreated[e]	Extracted[f]	Spectral Region, nm
March 2001	March 2002	Perkin Elmer Spectrometer	1	smoldering redwood needle smoke		2.9	330–1000
August 2003	August 2003	MULTI 6λ	2	firewood smoke[g]	2.2	1.1	370–850
August 2003	March 2004	MULTI 10λ	2	firewood smoke[g]	2.2	1.3	375–940
September 2000	April 2002	Perkin Elmer spectrometer	3	SAFARI 57 (savanna fire)	2.2	1.3	330–1000
August 2000	February 2002	Perkin Elmer spectrometer	4	SAFARI 15 (savanna fire)	1.8[h]	1.2[h]	330–1100
September 2000	September 2002	Ocean Optics spectrometer	5	SAFARI 37 (savanna fire)	1.8	1.3	450–700
September 2000	September 2002	Ocean Optics spectrometer	6	SAFARI 43 (haze, 3170 m)	1.3	1.2	450–950
September 2000	April 2002	Perkin Elmer spectrometer	7	SAFARI 45 (haze, 2370 m)	1.2	1.0	330–1000
June 2001	February 2002	Perkin Elmer spectrometer	8	LBNL, Berkeley, California	1.2	1.1	390–1000
July 2003	July 2003	MULTI 6λ	9	LBNL, Berkeley, California	1.1		370–850
June 2003	July 2003	MULTI 6λ	10	LBNL, Berkeley, California	1.0		370–850
June 1999	April 2002	Perkin Elmer spectrometer	11	LBNL, Berkeley, California	0.9	0.9	330–1000
May 2001	September 2002	Ocean Optics spectrometer	12	LBNL, Berkeley, California[i,j]	0.9	0.9	450–950
May 2001	February 2002	Perkin Elmer spectrometer	13	LBNL, Berkeley, California[j]	0.9[h]	0.8[h]	330–1000
May 2001	January 2004	MULTI 10λ	14	LBNL, Berkeley, California	0.9		375–940
June 2003	July 2003	MULTI 6λ	15	LBNL, Berkeley, California	0.8		370–850
July 2003	August 2003	MULTI 6λ	16	LBNL, Berkeley, California	0.8		370–850
October 2003	October 2003	MULTI 6λ	17	Adjacent to roadway[g]	0.9		370–850
October 2003	February 2004	MULTI 10λ	17	Adjacent to roadway[g]	0.9		375–940
February 1983	February 2002	Perkin Elmer spectrometer	18	Caldecott tunnel	0.9[h]	0.7[h]	370–1000
February 1983	April 2002	Perkin Elmer spectrometer	19	Caldecott tunnel[k]	0.8	0.6	390–1000
February 1983	September 2002	Ocean Optics spectrometer	19	Caldecott tunnel[k]	0.9	0.7	450–950
February 1983	August 2003	MULTI 6λ	19	Caldecott tunnel[k]	0.8		370–850
February 1983	February 2002	Perkin Elmer Spectrometer	20	Caldecott tunnel	0.6[h]	0.7[h]	390–1000

[a] Samples were of fine mode (i.e., $d < 2$ μm) aerosols except for the smoldering redwood needle sample, for which there was no size cut.

[b] See text for a description of the analyzers. MULTI is multiple wavelength light transmission instrument.

[c] Sampling locations are described in the text. SAFARI is Southern African Regional Science Initiative; LBNL is Lawrence Berkeley National Laboratory.

[d] Absorption Ångström exponents were calculated by linear regression of ln(ATN) versus ln(λ) over the specified wavelength region.

[e] Samples were not extracted with acetone.

[f] Samples were extracted with acetone.

[g] Samples 2 and 17 were analyzed using both the six and ten wavelength version of the MULTI.

[h] Samples were preheated to 110°C in air prior to analysis to remove organic vapors that typically adsorb to quartz filters during sample collection.

[i] Sample was collected downstream of a diffusion denuder that scrubbed the sample air of organic vapors.

[j] These two urban air samples (samples 12 and 13) were concurrently collected via the same sampling stack.

[k] Sample 19 was analyzed using both spectrometers and the MULTI.

1995]. Second, it is often assumed that ATN is proportional to the light-absorbing aerosol mass collected on the filter. The aethalometer calibration is based on empirical data that indicated that light attenuation is proportional to BC loading [*Gundel et al.*, 1984], while the PSAP calibration accounts for a diminishing instrumental response to absorption coefficient with increased particle loading [*Bond et al.*, 1999b]. *Weingartner et al.* [2003] reported that the aethalometer calibration should also incorporate this nonlinear loading effect when used to measure absorption coefficient. Third, studies have indicated significant instrumental response to particle light scattering and thus the overestimation of absorption coefficient when the magnitude of the absorption to extinction ratio or the aerosol BC mass fraction is less than 10–20% [*Lindberg et al.*, 1999]. This has been shown using the integrating plate method [*Horvath*, 1997; *Horvath et al.*, 1997], the PSAP [*Bond et al.*, 1999b], and LTM [*Petzold et al.*, 1997]. In contrast to these results, however, *Weingartner et al.* [2003] reported no additional enhancement, beyond the factor 2 already attributed to light scattering by the filter fibers, when measuring the absorption coefficient of external mixtures of light-absorbing and scattering aerosols with an aethalometer. For internal mixtures generated by condensation of organic vapors onto soot particles, Weingartner et al. reported increased attenuation significantly greater than the factor of 2, but did not attribute the enhancement to light scattering by the collected particles. Rather, the enhancement was attributed to light scattering by organic vapors that condensed onto the filter fibers. Additional discussion on the use of light transmission techniques to measure aerosol absorption coefficient has been presented previously [e.g., *Foot and Kilsby*, 1989; *Japar*, 1990; *Campbell et al.*, 1995; *Clarke et al.*, 1996].

[9] While the abovementioned studies suggest caution when using the optical transmission method to measure the magnitude of aerosol absorption, there is evidence that this method provides an accurate measure of the variation in aerosol absorption with wavelength. *Bond* [2001] reported that the scattering artifact had only a minor impact on the measured spectral dependence of aerosol light absorption. *Weingartner et al.* [2003] reported that the aethalometer, the optical transmission method most similar to that used in this study, accurately measured the wavelength dependence of aerosol light absorption. *Horvath* [1997] and *Horvath et al.* [1997] did not indicate the need for a spectrally dependent correction factor for optical transmission measurements. Accordingly, *Bergstrom et al.* [2002] inferred spectrally dependent aerosol optical properties based on measurements made with a light transmission method. In this study, we are mainly concerned with the spectral dependence of aerosol light absorption, although we also estimate absorption coefficients. The reader may wish to keep in mind the abovementioned caveats where absorption coefficients are presented below.

[10] To determine the role of OC on measurements of absorption spectral dependence, two portions of each quartz filter sample were analyzed: one portion was analyzed without any alteration of the collected particles, whereas the second portion was analyzed after it was treated with acetone to extract soluble OC from the particles. The extraction was performed by soaking the sample in 50 mL of acetone for 30 min. Care was taken not to disturb the sample to minimize mechanical removal of the insoluble particles. Following acetone treatment, filter samples were dried under a lamp to promote the evaporation of the acetone from the filters. The mass of carbon extracted from a sample was determined by comparing the carbon contents of the untreated and treated portions of the sample. The carbon content of samples was measured using the evolved gas analysis (EGA) method [*Novakov*, 1981], which has been described recently by *Kirchstetter et al.* [2001]. In EGA, the filter sample is heated at 40°C $\min^{-1}$ from room temperature to 800°C, and the carbonaceous material that evolves from the sample is fully oxidized to carbon dioxide in pure oxygen over magnesium dioxide powder maintained at 800°C. The mole fraction of carbon dioxide is measured with a nondispersive infrared analyzer. A plot of evolved carbon versus temperature, called the carbon thermogram, illustrates carbonaceous materials of different thermal properties. The thermogram is integrated to determine the mass of carbon (μg C) that was in the sample. The carbon mass loading of a sample (μg C cm^{-2}) is determined by dividing the measured carbon mass by the area (cm^2) of the filter sample analyzed. In this study, filter samples of 1.12 and 0.58 cm^2 in area were prepared using circular filter cutters, the areas of which were measured with an uncertainty of about ±1% using stainless steel calipers.

2.2. Sample Description

[11] Here we present data for several recent and archived samples collected in different environments: (1) immediately adjacent to a steeply graded roadway, in Berkeley, California, carrying light-duty gasoline and heavy-duty diesel vehicles traveling up and downhill; (2) at LBNL, downwind of Berkeley, at a height of approximately 10 m above ground, about 25 m from the roadway mentioned above; (3) in the Caldecott roadway tunnel, located in the San Francisco Bay Area, which carries light-duty gasoline and heavy-duty diesel vehicles; (4) aloft in southern Africa during SAFARI 2000; (5) in the plume of smoke from outdoor burning of firewood; and (6) in undiluted smoke from redwood needles smoldered on a heating element. Dates of sample collection and analysis are shown in Table 1.

[12] Aerosol sampling adjacent to the roadway was conducted between 0800 to 1800 h local time when diesel shuttle buses passed by regularly. We expected that samples collected at LBNL, downwind of Berkeley, were strongly influenced by the nearby roadway vehicles, but they may also have been influenced by other emission sources in the city because they were collected at 10 m above ground and for long periods of time (e.g., 12 to 24 hours) including evening and early morning hours. Samples collected in the roadway tunnel were dominated by motor vehicle emissions. Further, a recent apportionment of pollutants emitted from vehicles in the Caldecott tunnel indicated that heavy-duty diesel vehicles dominate BC and other particulate matter emissions, even when these vehicles comprise only 5% of total vehicles [*Kirchstetter et al.*, 1999]. Thus we surmise that samples collected in the tunnel, adjacent to the roadway, and to a large extent at LBNL were influenced primarily by motor vehicles, and, in particular, by diesel vehicles.

[13] SAFARI 2000 samples were collected aboard the University of Washington's Convair-580 research aircraft during the dry, biomass burning season in southern Africa [*Sinha et al.*, 2003; *Kirchstetter et al.*, 2003]. SAFARI samples collected in plumes of savanna fires and in layers of haze aloft are included in this study. Firewood burning included smoldering and flaming conditions, whereas redwood needle combustion was characterized by smoldering exclusively.

3. Results

3.1. Spectral Dependence

[14] The variation of aerosol light absorption with wavelength extending from the near-ultraviolet to the near-infrared is compared for several samples in Figure 1. Light absorption by aerosols collected in biomass burning smoke (savanna and wood) varied more strongly with wavelength than aerosols dominated by motor vehicle emissions (Berkeley and roadway). The stronger spectral dependence was the result of enhanced light absorption at wavelengths shorter than 600 nm. Following the approach of previous investigators, the dependence of aerosol light absorption on wavelength was parameterized using a power law relationship: $\sigma = K \cdot \lambda^{-\alpha}$, where σ is the spectrally dependent mass absorption efficiency, K a constant, λ the light wavelength, and α the absorption Ångström exponent. (Note that ATN is proportional to σ.) Thus the value of α is a measure of the strength of the spectral variation in aerosol light absorption. We show in Figure 1 that $\alpha = 2.5$ approximates the strong spectral dependence of the biomass burning aerosols and $\alpha = 1.0$ describes well the weak spectral dependence of the motor vehicle aerosols.

[15] The spectral dependence of light absorption for all samples was determined by performing a regression of ln(ATN) against ln(λ). Resulting values of α are given in Table 1. On average, $\alpha = 2$ for biomass smoke aerosol samples, excluding the sample of smoldering redwood needles which exhibited much stronger absorption spectral dependence. The samples produced from smoldering redwood needles exhibited the strongest spectral dependence, even after acetone extraction. Burning savanna samples had stronger spectral dependence (average $\alpha = 1.9$) than haze samples aloft (average $\alpha = 1.2$) collected during SAFARI 2000. In contrast to the biomass smoke samples, α averaged 0.9 and 0.8 for the Berkeley and motor vehicle (roadway and tunnel) samples, respectively. As illustrated for the samples included in Figure 1, these absorption Ångström exponents indicate that light absorption by biomass smoke aerosols is characterized by significantly stronger wavelength dependence than urban aerosols influenced by motor vehicles.

[16] Many of the samples included in this study were collected with two quartz filters in series. Analysis of backup quartz filters of the firewood smoke and Berkeley

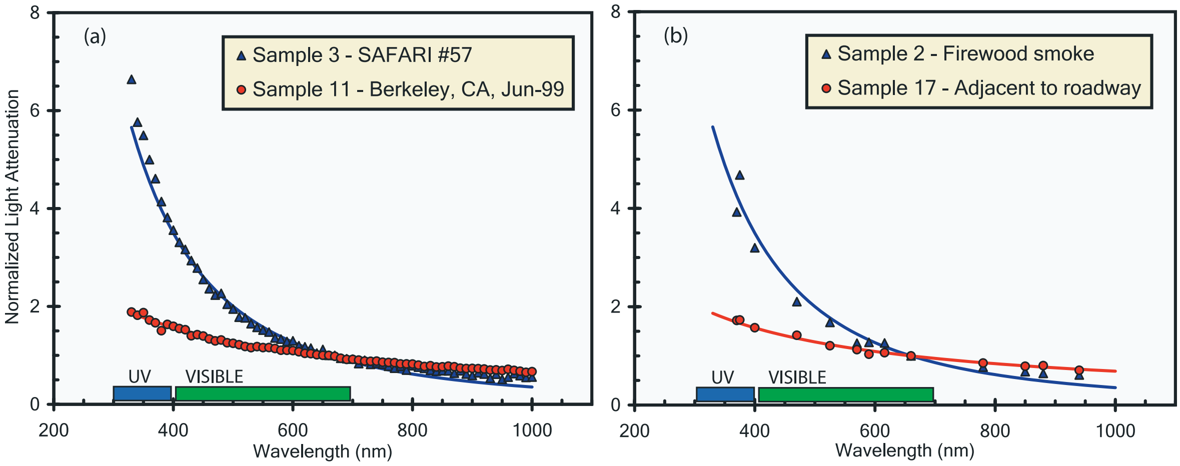

Figure 1. Normalized light attenuation (ATN) for four aerosol samples measured using (a) a Perkin Elmer spectrometer and (b) the multiple wavelength light transmission instrument (MULTI). ATN values were normalized so that spectral absorption trends could be compared independent of sample loading. The solid lines were generated using a power law equation (see text) with λ^{-1} for the Berkeley and roadway samples and $\lambda^{-2.5}$ for the Southern African Regional Science Initiative (SAFARI) and firewood samples. The values of the exponent of λ were chosen to fit the data.

samples indicated that adsorbed organic gases (i.e., the positive sampling artifact [*Kirchstetter et al.*, 2001]) contributed to the measured light absorption by the particle-laden quartz filters for firewood smoke but not for the Berkeley samples. However, the influence of this gaseous light absorption on the value of α for the firewood smoke samples was much too small (<10%) to cause the measured differences between the spectral dependence in aerosol light absorption by the urban and biomass smoke samples.

[17] We found that the power law relationship often understated the spectral dependence in absorption for samples that exhibited strong spectral dependence (i.e., the biomass smoke samples) (as shown in Figure 3c). In the case of biomass smoke samples, the power law relationship fit the data better and larger absorption Ångström exponents were obtained when near-infrared wavelength data were excluded. Thus, considering only the ultra violet and visible spectral regions, the difference between the absorption spectral dependence of the biomass and urban (Berkeley and motor vehicle) samples, as expressed by α, is generally larger than indicated in Table 1.

[18] Our findings are consistent with prior reports of aerosol absorption spectral dependence, which are summarized in Table 2. Prior measurements of soot and urban aerosols indicated weak spectral dependence [e.g., *Rosen et al.*, 1978; *Bergstrom et al.*, 2002; *Horvath et al.*, 1997]. *Bergstrom et al.* [2003] estimated aerosol absorption spectral dependence by inverting spectral solar radiative flux measurements made during two research flights during SAFARI 2000 and found that aerosol absorption varied as λ^{-2} for optically dense aerosol layers (in the "river of smoke" [*Swap et al.*, 2003]), whereas a spectral dependence of λ^{-1} was inferred from measurements made over the ocean away from aerosol source regions. Likewise, *Dubovik et al.* [1998] reported on AERONET radiance data acquired in Brazil, and noted that during two of three biomass burning seasons, aerosol absorption varied as $\lambda^{-2.4}$. *Patterson and McMahon* [1984] reported strong spectral dependence for aerosols produced during smoldering combustion of pine needles.

3.2. Effect of Organic Carbon

[19] Extraction of aerosol samples with acetone removed significant amounts of OC, as exemplified in Figure 2. After removal of OC, biomass smoke samples exhibited greatly reduced absorption spectral dependence (average α = 1.2, reduced from 2.0). By contrast, removal of OC from the tunnel and roadway samples had a lesser effect (average α = 0.7, reduced from 0.8), and removal of OC from the Berkeley aerosol samples did not change the average absorption spectral dependence (α = 0.9).

[20] The effects of extracting aerosol samples with acetone are further illustrated in Figure 3. Shown are examples where acetone extraction (1) had essentially no impact on α or on the measured values of ATN (Berkeley, June 2001), (2) had little impact on α but reduced the magnitude of ATN at all measured wavelengths (Berkeley, May 2001), and (c) reduced α and the magnitude of ATN at wavelengths below about 600 nm only (SAFARI 57). Samples in category 1 indicate that extraction of acetone soluble OC did not alter the magnitude or the spectral dependence of aerosol light absorption in some cases, namely, the motor vehicle-dominated samples. For these samples, we infer that BC was the dominant light-absorbing aerosol component at all wavelengths considered. We attribute the broad spectral decrease in ATN of samples in category 2 to mechanical removal of BC because no other aerosol components absorb light over the entire spectral region considered here and acetone extraction was not expected to dissolve inorganic salts that might have contributed to the ATN of the untreated sample via light scattering. While the intention of acetone extraction was to remove soluble OC only, mechanical removal of particles from the filter was sometimes visibly evident, particularly for heavily loaded filter samples. The spectrally dependent decrease in ATN exemplified in Figure 3c, and exhibited by the savanna and wood burning

Table 2. Previous Studies Pertaining to Spectral Light Absorption of Aerosols

Reference	Comment	Spectral Region, nm	Absorption Exponent, α
Volz [1956]	attributed UV absorption in precipitation water to soluble organic material	220–900	NA[a]
Romanov and Shuklin [1984]	attributed light extinction in precipitation water to absorption by organic compounds	250–600	NA[a]
Lindberg and Laude [1974], *Lindberg* [1975]	applied Kubelka-Munk theory to diffuse reflectance measurements of rural, desert aerosol	350–1100	1.4–1.7[b]
Lindberg et al. [1993]	technique same as above applied to (1) water and acetone insoluble and (2) acetone soluble component of rural, desert aerosol, and (3) propane soot	300–1000	1.1 (refer to item 1), 3.4 (refer to item 2), 1.2 (refer to item 3)
Foot and Kilsby [1989]	integrating sandwich technique applied to aerosols of different environments: (1) straw burning, (2) Mojave desert dust, and (3) Farnborough, United Kingdom	500–900	1.6[b] (refer to item 1), 1.9[b] (refer to item 2), 0.9[b] (refer to item 3)
Bond [2001], *Bond et al.* [1999a]	domestic combustion of bituminous coal and industrial combustion of lignite, choked combustion produced light absorbing yellow/brown particles with strongest λ dependence and weakest absorption efficiency	450–1000	1.0–2.9
Patterson and McMahon [1984]	smoldering pine needles made brownish aerosols with a MeCl soluble component with strong λ dependence that dominated total absorption, and an insoluble component	400–700	NA[a]
Lyubovtseva and Yaskovich [1982]	absorption in visible and UV spectral regions was attributed to soot and organic components, respectively, in aerosol samples collected in Abastumani mountains	250–800	NA[a]
Bergstrom et al. [2003]	inverted spectral solar flux measurements made during two research flights in SAFARI 2000: (1) in a "river of smoke" and (2) away from aerosol sources	350–1000	2 (refer item 1), 1 (refer item 2)
Dubovik et al. [1998]	sky radiance data for three seasons of biomass burning in Brazil indicated (1) strong absorption selectivity for two seasons and (2) weak selectivity for one season	440–1020	2.4 (refer to item 1), 1.0 (refer to item 2)
Horvath et al. [1997b]	integrating sandwich method, Santiago, Chile, aerosol samples	450–650	0.9
Kozlov et al. [2002]	three λ optical acoustic spectrometer measurements of ambient aerosols in Tomsk, Russia	530–1060	1.2
Schnaiter et al. [2003]	diesel soot, measured in situ extinction, and scattering	450–700	1.2
Marley et al. [2001]	measurement of transmission and reflectance spectra to determine absorption by diesel soot	300–900	1.5[b]
Rosen et al. [1978]	laser transmission method, urban, roadway tunnel, and laboratory-generated soot samples	450–700	~1
Bergstrom et al. [2002]	integrating sandwich method, Tropospheric Aerosol Radiative Forcing Observation Experiment (TARFOX) aerosol samples collected off east coast of United States	450–1000	~1
Fischer [1973]	absorption efficiency of aerosols collected at urban (near Munich) and remote (Tsumeb and Jungfraujoch) sites reportedly had weak spectral dependence	400–1700	NA[a]

[a] NA is not available; see comment.
[b] Values are computed from data presented in the reference.

samples, suggests that acetone extraction removed much of the aerosol component responsible for the strong absorption spectral dependence, while leaving intact the aerosol component fully responsible for absorption at longer wavelengths. The former component is likely the acetone soluble OC (see Figure 2), while the latter component is BC. The decrease in ATN was evident only for wavelengths shorter than about 600 nm; removal of BC would have resulted in a change in ATN at all wavelengths.

[21] In view of these observations, which suggest two distinct light-absorbing aerosol components, the λ^{-1} curve is included in Figure 3c to illustrate the magnitude and spectral trend in ATN that would result if BC alone contributed to light absorption by the SAFARI samples. We assumed the absorption spectral dependence of BC was λ^{-1}, which is reasonable given the findings of this (Table 1) and previous (Table 2) studies. The λ^{-1} curve was then fit to the measured data at $\lambda > 700$ nm, where the ATN values were largely unaffected by the removal of OC. As shown in Figure 3c, the ATN values of the acetone extracted SAFARI sample were closer to those of the λ^{-1} curve than the untreated sample for $\lambda < 700$ nm. In other words, removal of OC from the SAFARI sample rendered its absorption spectral dependence more similar to that of BC than the original, untreated sample. The remaining difference in spectral dependence between the acetone extracted sample and the BC fit (i.e., the difference between $\lambda^{-1.3}$ and λ^{-1}) may have been due to the OC that remained in the sample after treatment with acetone.

[22] Accordingly, we apportioned light absorption to the BC and OC components of the SAFARI biomass smoke samples. The fraction of light OC absorbed was estimated as $(T_{BC} - T_S)/(1 - T_S)$, where T_{BC} is the transmission due to BC alone and T_S is the transmission measured for the untreated sample containing BC and OC. This procedure is illustrated in Figure 4. As in Figure 3c, we calculated transmission due to BC by fitting the measured data at $\lambda >$ 700 nm and assuming that the BC light absorption varied as λ^{-1}. Further, we assumed that BC and OC absorbed light independently of each other. The results shown in Table 3 indicate that OC in the SAFARI smoke samples contributed

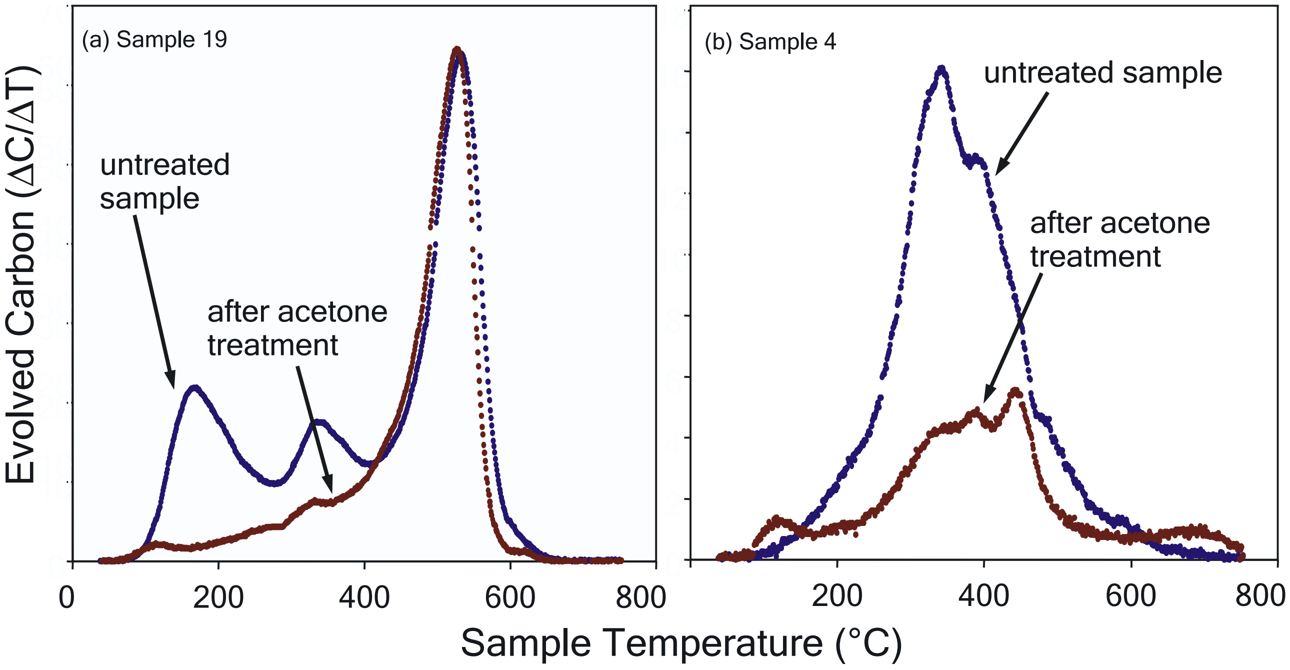

Figure 2. Carbon thermally evolved from filter samples before and after the samples were treated with acetone: (a) diesel vehicle exhaust collected in the Caldecott tunnel and (b) biomass fire smoke in southern Africa. Typically, acetone treatment removed much, but not all, of the sample organic carbon, which generally evolves below 400°C in the thermal evolved gas analysis method applied in this study.

significantly to light absorption at wavelengths extending from the near-ultraviolet to the mid-visible. Implicit in these calculations is the assumption that light attenuation not attributable to BC was due entirely to OC. Acetone extraction accounted for most (50 to 80%) of the difference in transmission between the untreated samples and that calculated for BC, as illustrated in Figure 4. In this apportionment exercise, the remaining enhancement was attributed to OC remaining in the SAFARI samples after acetone treatment (i.e., the OC not soluble in acetone).

[23] Our finding that OC contributes to light absorption by aerosols from biomass burning is consistent with the results of *Patterson and McMahon* [1984], who measured distinctly different spectral absorption dependences for two different aerosol fractions emitted during pine needle combustion: a methylene chloride soluble fraction that exhibited strong spectral dependence and dominated total aerosol absorption during smoldering combustion, and a nonsoluble fraction with weak spectral dependence that dominated aerosol light absorbance during flaming combustion. While not specific to biomass burning, other studies have indicated that OC contributes to aerosol light absorption. For example, *Lindberg et al.* [1993] reported a strong absorption spectral dependence for rural aerosol (we estimate α = 3.4 using their data). Also, *Volz* [1956], *Lyubovtseva and Yaskovich* [1982], and *Romanov and Shuklin* [1984] attributed light absorption to OC in aerosol and precipitation water samples.

3.3. Estimation of Optical Constants

[24] We calculated optical constants for BC from urban and motor vehicle samples and OC extracted from biomass samples. Attenuation coefficients of BC and acetone extracted OC, respectively, were computed as ATN/M_{BC} and ΔATN/ΔM_{OC}. ATN and M_{BC} are the measured ATN and BC loading (g C cm^{-2}) for samples that exhibited negligible change in light absorption due to extraction of OC (urban and motor vehicle samples). ΔATN and ΔM_{OC} are the differences in ATN and OC loading (g C cm^{-2}) of samples calculated from measurements prior to and after extraction of soluble OC. Attenuation coefficients of acetone extracted OC were computed only for samples that exhibited significant change in light absorption due to acetone treatment, but no change that could be attributed to mechanical removal of insoluble particles, as discussed above (savanna and wood fire samples). The masses of BC and extracted OC were measured using the thermal EGA method described above. Results are shown in Figure 5 for motor vehicle, urban, and three biomass burning samples. Also shown are the attenuation coefficients employed in the spectrum aethalometer: ATN = 14625 × λ^{-1}. On average, the computed attenuation coefficients of the motor vehicle and urban samples were in good agreement with those of the aethalometer. Calculated attenuation coefficients for the OC extracted from the three biomass smoke samples were very similar, barring the two outlying data points at 330 and 340 nm, which were likely because of a low signal-to-noise ratio in the spectrometer data at these short wavelengths.

[25] Table 4 reports estimated mass absorption efficiencies and imaginary refractive indices. Here we remind the reader of the important caveats described above regarding use of optical transmission methods to measure absorption constants. To estimate mass absorption efficiencies (σ), we divided average attenuation coefficients presented in Figure 5 by a factor of 2 to account for the largest of the artifacts known to affect filter-based transmission measurements, namely, that due to multiple reflection of light by the highly

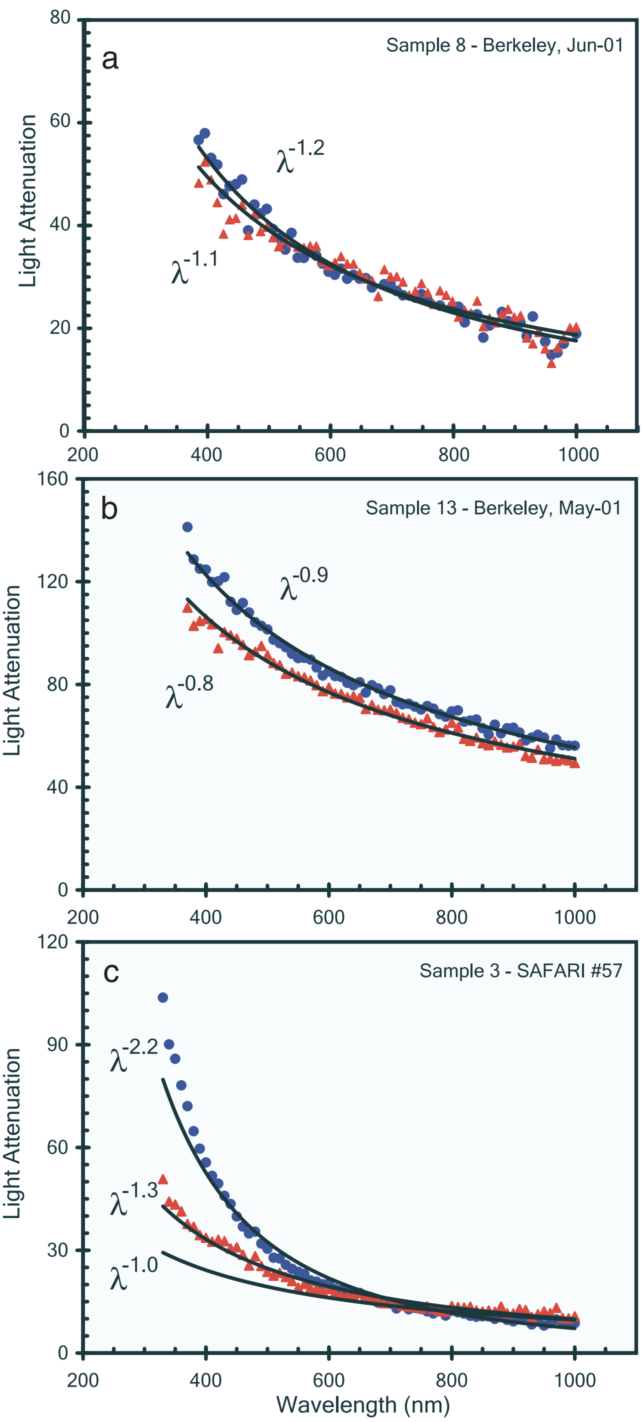

Figure 3. The effects of acetone treatment on sample light attenuation (ATN): (a) sample 8, Berkeley, June 2001, (b) sample 13, Berkeley, May 2001, and (c) sample 3, SAFARI 57. Circles (blue) indicate untreated samples and triangles (red) indicate acetone treated samples. Solid lines and indicated Ångström exponents were determined by statistical regression to fit the data with a power law equation. In the bottom panel of the figure, a λ^{-1} trend line is also shown (see text).

reflective quartz substrate. Imaginary indices of refraction (k) were calculated from $\rho\sigma\lambda/4\pi$, where ρ is the particle density. Application of this equation has been discussed elsewhere [*Gosse et al.*, 1997; *Bohren and Huffman*, 1998; *Jennings et al.*, 1979]. We apply it here since indices of refraction for OC are very scarce, if not nonexistent. We choose $\rho = 1.2$ g cm^{-3} for both OC and BC, consistent with reported values [*Lohmann et al.*, 1999; *Turpin and Lim*, 2001]. The ratio σ_{OC}/σ_{BC} decreased from 22% at 350 nm, to 9% at 450 nm, to 1% at 650 nm. Estimated values of k_{BC} were largely insensitive to wavelength over the spectral region considered here, while k_{OC} increased with decreasing wavelength. Whereas the calculated absorption constants for OC are substantially smaller than those for BC, we note that OC may contribute significantly to light absorption by aerosols characterized by a low BC/OC ratio, such as the biomass smoke samples considered here (10 to 20%) and in biomass smoke in general [*Andreae and Merlet*, 2001].

[26] It has been shown that the spectral mass absorption efficiency for small particles is approximately inversely proportional to the light wavelength (i.e., $\alpha \sim 1$) provided the refractive index is approximately wavelength independent [*Bohren and Huffman*, 1998; *Dalzell and Sarofim*, 1969; *van de Hulst*, 1957]. Several authors have explained strong absorption selectivity by the presence of a spectrally dependent imaginary part of the refractive index [e.g., *Dubovik et al.*, 1998; *Bond*, 2001]. Our findings suggest that the spectrally dependent aerosol imaginary refractive index is explained by a relatively constant imaginary refractive index for BC and a spectrally dependent imaginary refractive index for OC. Likewise, *Bond et al.* [1999a] suggested that light-absorbing material other than graphitic carbon is present in lignite burning emissions, and that the refractive index of this component has a wavelength dependence stronger than that of BC.

[27] Optical constants reported in Table 4 for BC are within the range of values previously reported, although we note that previously reported values exhibit wide variability that has been attributed to combustion source and aerosol aging processes [see, e.g., *Marley et al.*, 2001, Table 4]. Possible errors in the absorption constants presented in Table 4 due to light scattering by particles could not be directly assessed because this study made use of archived samples and measurements of scattering coefficient were not available. B. Magi (personal communication, 2004) found that correcting PSAP measurements for the particle scattering artifact reduced absorption coefficients measured aloft during SAFARI 2000 by 6 to 14%. In the absence of light scattering measurements, *Bond et al.* [1999a] estimated that absorption coefficients of aerosols from coal burning, measured with two light transmission instruments, were biased to high values by about 1% for particles collected on glass fiber filters and 4% for measurements with Nuclepore filters. We note that the optical constants reported in Table 4 may have similar biases.

4. Discussion

[28] Knowledge of the spectral dependence of aerosol light absorption is important for accurate representation of aerosols in radiative transfer models. The spectral dependence is required for interpolation and extrapolation of

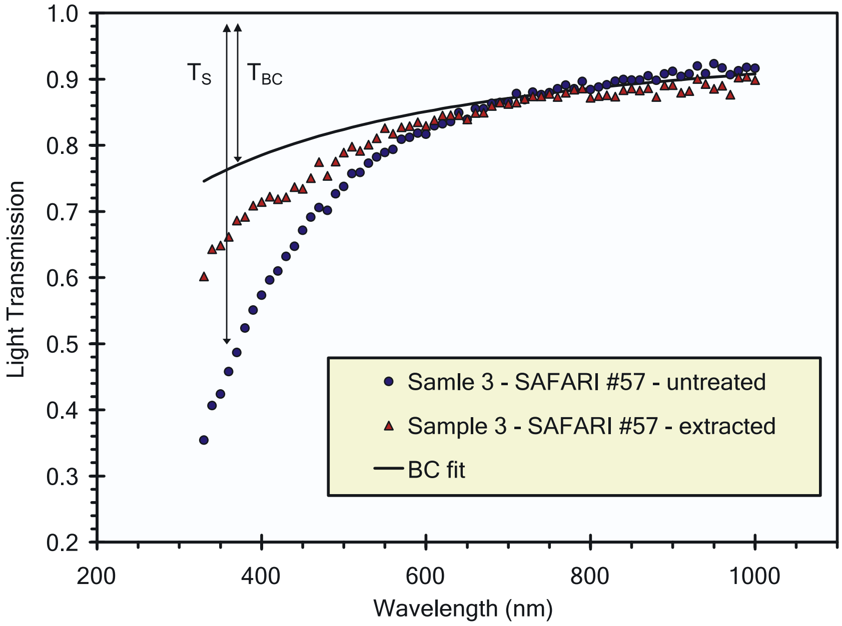

Figure 4. Illustration of apportionment of light absorption to black carbon (BC) and organic carbon (OC) in a biomass smoke sample. T_S is the transmission measured for the sample, and T_{BC} is the transmission due to BC alone.

absorption coefficients beyond measurements, which are often obtained at a single wavelength. In this paper, we presented data and reviewed studies that indicate that a power law relationship applied with a single value for the absorption Ångström exponent does not accurately reflect all aerosol types. In particular, the λ^{-1} dependence typically invoked for aerosol light absorption was found to be accurate for urban aerosols close to motor vehicle sources, but aerosols from biomass smoke can exhibit a much stronger spectral dependence.

[29] Biomass burning is estimated to contribute significantly, and roughly equally compared to fossil fuel combustion, to the global budgets of primary carbonaceous aerosols [*Liousse et al.*, 1996], and carbon particles emitted from biomass burning are thought to have a significant impact on regional and global radiation budgets [*Cachier et al.*, 1996]. Savanna fires contribute a large fraction of biomass emissions worldwide, and fires in Africa account for about two thirds of the savanna burned worldwide [*Hao and Liu*, 1994]. A recent assessment of aerosol emissions found that savanna fires, forest fires and biofuel use contribute comparably to worldwide OC emissions [*Andreae and Merlet*, 2001]. Therefore if the results presented here are generally applicable to savanna and other biomass emissions, a major fraction of global carbonaceous aerosol emissions may have spectral absorption characteristics different from that typically assumed for BC. Further, strong absorption spectral dependence may not be unique to biomass emissions. *Bond* [2001] reported a strong spectral dependence for low-temperature coal combustion ($1.0 \leq \alpha \leq 2.9$) typical of domestic use in many locations. The prevalence of this type of coal combustion is not well known, but domestic combustion of coal is estimated to contribute heavily to BC emissions regionally, for example, in China [*Streets et al.*, 2001], and globally [*Cooke et al.*, 1999].

[30] It has been suggested that measurements of aerosol optical properties have not been sufficiently accurate to describe the effects of aerosols on climate [*Russell and Heintzenberg*, 2000]. The prevalence of nonblack, light-absorbing carbonaceous material is not well known and the assumption that aerosol light absorption is inversely proportional to wavelength may not be valid in many locations. Thus it is important to examine the sensitivity of climate models, and the inversion of radiometric measurements, to different spectral absorption dependences, such as those reported here.

[31] Strong spectral dependence for light-absorbing dust aerosols has also been reported [e.g., *Foot and Kilsby*, 1989]. *Lindberg et al.* [1993] found dust to be predominantly in the coarse particle mode, for which enhanced light absorption in the blue and ultraviolet spectral regions was attributed to noncarbonaceous, noncombustible materials (e.g., mineral oxides). Inferred aerosol properties from AERONET data for desert regions also show large particles (diameter >1 μm) and pronounced light absorption in the

Table 3. Estimated Contribution of Organic Carbon to Aerosol Light Absorption (Expressed as a Fraction of the Total) for Three Samples of Burning Savanna Smoke Collected in Southern Africa During SAFARI 2000

	Sample Number		
λ, nm	3	4	5
350	0.58	0.26	
400	0.50	0.26	
450	0.41	0.22	0.23
500	0.32	0.19	0.15
550	0.24	0.15	0.07
600	0.17	0.10	0.01
650	0.09	0.07	−0.01
700	0.01	0.05	−0.02

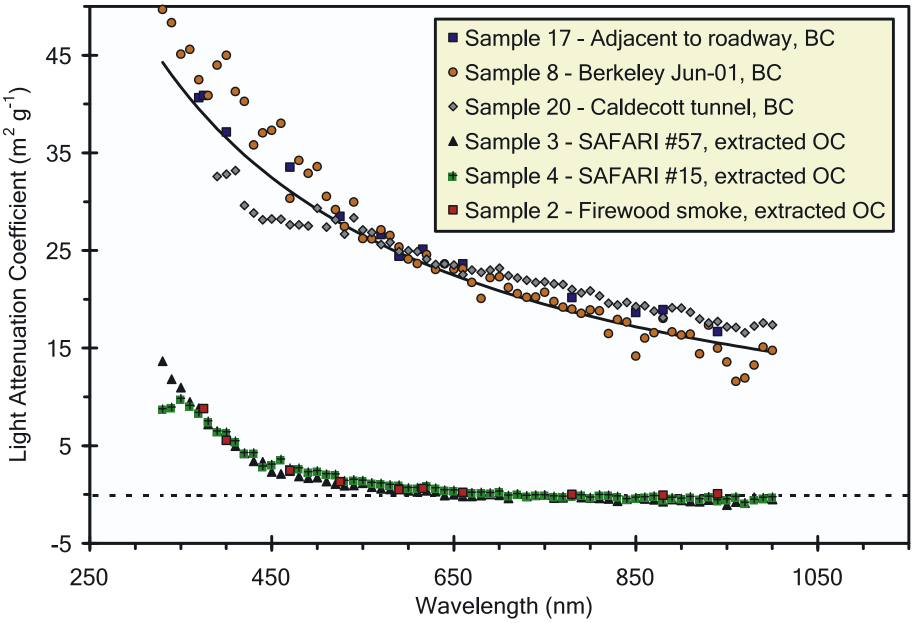

Figure 5. Attenuation cross sections of black carbon (BC) and acetone soluble organic carbon (OC) in several aerosol samples. OC attenuation cross sections were computed by measuring changes in sample attenuation and OC mass content due to acetone treatment (see text). The solid line is the BC calibration curve employed in the spectrum aethalometer.

blue spectral region [*Dubovik et al.*, 2002]. *Bergstrom et al.* [2002] suggested that the difference in spectral absorption between BC and dust, if generally valid, be used to differentiate between dust absorption and BC absorption.

[32] The observations discussed above and the data reported in this paper are limited in number, which highlights the need for continued research to determine the variability in spectral absorption, especially as a function of combustion efficiency, for aerosols produced by different combustion processes and collected in different source regions. The wide range of spectral dependences for light absorption by coal emissions reported by *Bond et al.* [2002] suggests that the optical properties of aerosols, even for a given fuel and combustion apparatus, depend on combustion efficiency and thus may not be uniform regionally or temporally. However, if differences in absorption selectivity can be well characterized, then measurements such as those presented in this study may be useful in determining the dominant source of BC in various regions of the world.

[33] Additional studies could be aimed at identifying the organic compounds that contribute to aerosol light absorption. Sequential extraction of samples in different solvents of increasing polarity has been used to identify organic functional groups with different hygroscopicities [*Maria et al.*, 2002]. Techniques have also been developed for identification of humic-like brown substances [*Havers et al.*, 1998], which are present in biomass burning aerosols [*Gelencser et al.*, 2003; *Mukai and Ambe*, 1986].

[34] The optical transmission method employed in this study is an efficient means of investigating the spectral dependence of aerosol light absorption. Furthermore, as we illustrated for a few samples in this study, application of this method provides a means of apportioning aerosol light absorption to different aerosol constituents. Given its utility, and the scarcity of information about the role of OC in aerosol light absorption, this method warrants further validation. Part of this validation should determine the effect of aerosol mixing state on spectral absorption and if the effect of mixing state is preserved when the aerosols are collected on filters. In view of the uncertainties in using filter-based optical transmission measurements for determining the absolute magnitude of aerosol absorption constants, development of in situ measurement techniques capable of spectral characterization of aerosol absorption should also be pursued. In situ methods of direct measurement of

Table 4. Estimated Optical Constants for Organic Carbon (OC) Extracted From Biomass Smoke Samples and Black Carbon (BC) in Urban and Motor Vehicle Aerosol Samples

	Absorption Efficiency σ,[a] m^2 g^{-1}		Imaginary Refractive Index k	
λ, nm	OC[b]	BC[c]	OC[b]	BC[c]
350	5.0	23	0.168	0.77
400	2.9	19	0.112	0.73
450	1.5	16	0.063	0.71
500	0.9	15	0.045	0.72
550	0.6	14	0.030	0.72
600	0.3	12	0.017	0.71
650	0.1	12	0.005	0.72
700	0.0	11	0.001	0.75

[a] Absorption efficiencies were computed by dividing average attenuation coefficients shown in Figure 5 by a factor of 2 (see text for discussion of this factor and other caveats).

[b] Estimated optical constants for the OC that were extracted from wood burning and SAFARI biomass smoke samples shown in Figure 5. OC optical constants are estimated from measured changes in sample attenuation and OC content due to acetone treatment (see text).

[c] Estimated optical constants for the BC in urban and motor vehicle aerosol samples that are shown in Figure 5.

aerosol light absorption (e.g., photoacoustic methods), or indirect measurement by difference of extinction and scattering (e.g., cavity ring down techniques), may hold promise in this regard.

5. Conclusions

[35] The results of this investigation show that low-temperature combustion processes, including biomass burning, produce light-absorbing aerosols that exhibit much stronger spectral dependence than do high-temperature combustion processes, such as diesel combustion. Divergence from a λ^{-1} spectral dependence indicates the presence of aerosol species other than BC that absorb in the blue and ultraviolet spectral regions. In this study, we found that organic carbon in biomass smoke aerosols contributed to light absorption in the ultraviolet and blue spectral regions.

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