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Estimation of a "radiatively correct" black carbon specific absorption during the Mexico City Metropolitan Area (MCMA) 2003 field campaign

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Abstract. During the Mexico City Metropolitan Area (MCMA) field campaign of 2003, measurements of the shortwave radiation field allowed the inference of the black carbon (BC) specific absorption, α_λ, defined as the monochromatic absorption cross section per unit mass (with units of m^2/g). The averaged values of α_λ derived from the method here are either $8.9\,m^2/g$ or $8.2\,m^2/g$ at 500 nm, depending upon the physical and optical parameters assumed for BC. These results are reasonably consistent with those of Schuster et al. (2005), $9.5\,m^2/g$, and Baumgartner et al. (2002), $7.0\,m^2/g$, both measured at 550 nm. The α_λ values reported in this paper should only be considered effective, "radiatively correct" values because when used in radiative transfer calculations the calculated irradiances match the measured irradiances at 500 nm. The specific absorption so defined can assume a wide range of values, depending upon: (1) the assumptions made prior to the retrieval (e.g., shell/core aerosol configuration), and (2) values chosen for BC density and refractive index. The range of possible values is large, corresponding to a "worst case" uncertainty of about ±70%, assuming that all errors are additive and of the same sign so that no error cancellation occurs.

1 Introduction

Black carbon is found throughout the atmosphere, is mostly of anthropogenic origin, and is thought to be the most important contributor to aerosol absorption of solar radiation. A key measure of the absorption efficiency of BC is the specific absorption, α_λ, defined as the monochromatic absorption cross section per unit mass, typically given in units of m^2/g. The specific absorption is a function of wavelength, as indicated by the subscript λ. Over the years, the literature has reported a large range for values of α_λ, from as low as $2\,m^2/g$ to as high as $25\,m^2/g$ (e.g., Waggoner et al., 1981; Horvath, 1993; Liousse et al., 1993; Petzold et al., 1997; Penner et al., 1998; Moosmüller, 1998; Marley et al., 2001; Arnott et al., 2003; Schuster et al., 2005). As suggested by Liousse et al. (1993) this wide variation may be caused by differences in the aerosol mixing state, with the smaller values favoring external mixtures, while larger values indicate internal mixing of BC. Estimates of aerosol radiative forcing attributable to BC are influenced dramatically by the mixing state of BC, and because of the relationship between mixing state and α_λ, these estimates depend on the value of α_λ as well (e.g., Ackerman and Toon, 1981; Chylek et al., 1995; Fuller et al., 1999; Jacobson, 2000; Jacobson, 2001; Chung and Seinfeld, 2002; Lesins et al., 2002; Riemer et al., 2003; Sato et al., 2003).

Because of the importance of α_λ in determining the magnitude of aerosol radiative forcing, atmospheric measurements of this quantity are critical. In this paper, we present estimates of α_λ based on the observed shortwave radiation field, made within the Mexico City basin during the MCMA field campaign undertaken in April and May of 2003. This basin is an ideal place to study BC aerosols because of the high BC emissions; the high altitude, which enhances the aerosol scattering signal over that of molecular scattering; significant

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variations in relative humidity, from very dry to saturated conditions; and the unique meteorology of the Mexico City basin, which under the right meteorological conditions, may flush pollutants out of the basin on a daily basis (Fast and Zhong, 1998; Gaffney et al., 1999; Whiteman et al., 2000; Molina et al., 2002).

2 Methodology

2.1 Measurements

The primary instrument used for this analysis is the Multi-Filter Rotating Shadowband Radiometer (MFRSR, Harrison et al., 1994). This instrument, as well as most of the other instruments involved in the MCMA campaign, was deployed at the National Center for Environmental Research and Training (Centro Nacional de Investigación y Capacitatión Ambeintal, abbreviated as CENICA), on the Iztapalapa campus of the Unversidad Autónoma Metropolitana (UAM). This site is located at a latitude and longitude of 19.36 N and 99.07 W, respectively, and is atop a building and removed from direct exposure to automobile exhaust. As noted by Johnson et al. (2005), this site is in a mixed commercial-residential area with relatively few industries or congested roads. It is about 9 km southeast from La Merced, a market area often filled with dense traffic, and 2 km south of a large food market frequented by delivery trucks in the morning hours. Given the apparent lack of major aerosol sources in the near vicinity of the site, we assume that the BC aerosols observed here will have had some chance to age compared to those freshly emitted in traffic.

The MFRSR is, as the name implies, a shadowband radiometer that measures two components (diffuse and total) of the shortwave radiation field at the six wavelengths: 415, 500, 615, 673, 870, and 940 nm. The third component of the field – the direct component – is found from the total and diffuse components by subtraction combined with a correction for the cosine response of the instrument. Because all three radiation components are measured with the same sensor, if one component can be calibrated accurately, the other two components will share similar calibration accuracies. Typically, the direct component of the irradiance is calibrated in the field using the Langley method with a calibration accuracy that approaches 1% (Michalsky et al., 2001).

Aerosol optical thicknesses, τ_λ, are derived from the direct component, provided that the path between the sun and the instrument is not obscured by clouds. Whether this criterion is met is easily determined using the Ångström exponent, å (Seinfeld and Pandis, 1998; Schuster et al., 2006). The single scattering albedo, $\varpi_{0,\lambda}$, is the probability ($0 \leq \varpi_{0,\lambda} \leq 1$) that an aerosol scatters, rather than absorbs, a photon that impinges on it. Formally it is the ratio of the aerosol scattering coefficient, b_{scat} (m^{-1}), to the aerosol extinction coefficient, which is the sum of the b_{scat} and absorption coefficient, b_{abs} (m^{-1}), or $\varpi_{0,\lambda}=b_{\text{scat}}/(b_{\text{scat}}+b_{\text{abs}})$. The single scattering albedo can be retrieved from the diffuse and total irradiances using the algorithm of Petters et al. (2003), Kassianov et al. (2005), or Goering et al. (2005). These algorithms work best for large optical thicknesses (e.g., $\tau_\lambda > 0.25$ at 500 nm), a condition that is frequently met in the Mexico City basin. For the work reported here, we tested both the Petters and Kassianov algorithms and obtained nearly similar results for retrieved single scattering albedos, suggesting that the results presented below are independent of the algorithm chosen. These algorithms can only be used if the sky is completely free of clouds, a criterion that was verified using the method of Long and Ackerman (2000). During the entire MCMA campaign, there were only seven periods that satisfied the cloud-free criterion. The dates and time of these periods are listed in the first column of Table 1.

The average value of $\varpi_{0,\lambda}$ over these seven cases is 0.90. For the same days, the average $\varpi_{0,\lambda}$ derived from the AERONET (Aerosol Robotic Network; Holben et al., 1998) sun photometer located in Mexico City is 0.89 at 500 nm, as determined by linear interpolation between inferred single scattering albedos at 441 nm and 673 nm. It is also possible to derive $\varpi_{0,\lambda}$ from surface measurements. Baumgartner et al. (2000) measured b_{scat} and b_{abs} using a nephelometer and particle soot absorption photometer (PSAP), respectively. Before these measurements were made, the aerosols were heated to ensure that the relative humidity was less than 40%. Atmospheric soundings that bracket the time period over which inferences of $\varpi_{0,\lambda}$ were made indicate that the boundary layer was quite dry, with relative humidities below the aerosol mixing height generally less than 30%. For such low humidities, the aerosol is likely to be dry. This dry condition permits the use of Baumgartner et al.'s surface measurements without concern for humidity effects. Using these measurements, given in Fig. 2 of Baumgartner et al. (2000), and including only values for relative humidities less than 30%, $\varpi_{0,\lambda}$ is found to be 0.88 at 550 nm. The agreement between these three different ways of finding $\varpi_{0,\lambda}$ suggests that our $\varpi_{0,\lambda}$ are credible.

2.2 Determination of α_λ

The method used here to estimate α_λ is based on a technique first discussed by Schuster et al. (2005), with an important difference mentioned below. The method relies on the simple equation:

$$\alpha_\lambda = \frac{(1-\varpi_{0,\lambda})\tau_\lambda}{M_{\text{BC}}} = \frac{\tau_{\lambda,\text{abs}}}{M_{\text{BC}}} \quad (1)$$

where $\tau_{\lambda,\text{abs}}$ is the aerosol absorption optical depth. The major assumption underlying this equation is that BC is the only atmospheric absorber at the wavelength λ, which is generally valid outside the UV and near-UV spectral ranges (Heintzenberg et al., 1997). The aerosol optical thickness is inferred from the MFRSR direct normal irradiances, and $\varpi_{0,\lambda}$ is

Table 1. The seven case studies selected for retrievals of α_λ (for λ=500 nm) and the results from BC physical and optical parameter sets I and II.

Date, time period (hours, LST)	τ_λ	å	$\varpi_{0,\lambda}$	C_V=C_f+C_c (μm^3/μm^2)	f_V I II	M_{BC} (mg/m^2) I/II	α_λ (m^2/g) I/II	Re[$\tilde{m}_s$] I/II
14 April 2003 (08:26–10:19)	0.313	1.73	0.901	0.1443	0.01136 0.01369	3.3/4.0	9.5/8.7	1.33/1.33
15 April 2003 (07:33–10:26)	0.331	1.50	0.889	0.1350	0.01600 0.01936	4.3/5.2	8.5/7.8	1.40/1.40
16 April 2003 (08:02–10:27)	0.375	1.57	0.859	0.1569	0.01938 0.02347	6.1/7.4	8.7/8.0	1.39/1.39
18 April 2003 (08:19–10:32)	0.267	1.48	0.965	0.1461	0.00375 0.00448	1.1/1.3	8.5/7.9	1.32/1.32
26 April 2003 (07:36–10:40)	0.390	1.69	0.901	0.1300	0.01621 0.01971	4.2/5.1	9.2/8.4	1.46/1.46
27 April 2003 (07:49–11:59)	0.310	1.69	0.924	0.1354	0.00984 0.01191	2.7/3.2	8.8/8.1	1.39/1.39
30 April 2003 (07:54–11:00)	0.335	1.58	0.886	0.1208	0.01724 0.02093	4.2/5.1	9.2/8.4	1.44/1.44
average	0.332		0.904			3.7/4.5	8.9/8.2	1.39/1.39

found from the diffuse and total MFRSR irradiances and the single scattering albedo algorithms mentioned above. It then remains to find M_{BC}.

To find this quantity, we must make the following assumptions: (1) the aerosol is spherical and internally mixed in a shell/core manner (Jacobson, 2000; Bond et al., 2006), with the core of the aerosol consisting of BC. This shell/core configuration differentiates our method from that of Schuster et al. (2005), which handled internal mixing using the Maxwell-Garnett approximation; (2) the physical and optical properties (density, ρ_{BC}; refractive index, $\tilde{m}_{BC}$) of the BC are known; (3) the shell is non-absorbing; (4) the columnar aerosol volume distribution of the aerosol is known; and (5) the mass fractions of the various aerosol chemical constituents do not vary with the aerosol size. The first assumption of an internal mixture is difficult to verify although electron micrographs of the aerosol, as well as a single-particle chemical analysis of the aerosols, indicate that the soot is internally mixed with other substances (Johnson et al., 2005). Given the complexity of aerosol shapes and mixing configurations depicted in Johnson et al., the spherical shell/core model of internal mixing is a simplification but is necessary for conventional Mie theory calculations of the aerosol's optical properties. In regard to the second assumption, the reported values for the physical properties and optical of BC vary widely, as reported by Bond and Bergstrom (2006) and Fuller et al. (1999). Lacking in situ measurements we assume plausible values for these properties, discussed below. Assumption three, that the shell does not absorb, is tantamount to assuming that BC is the only absorber at 500 nm. As mentioned above, this is consistent with the assertion of Heintzenberg et al. (1997).

The columnar aerosol volume distribution, required by the fourth assumption, is obtained from the AERONET database for the specific days in question. The volume distribution found by the AERONET algorithm is expressed as $dV/dlnr$ with units (μm^3/μm^2), such that the integration over all aerosol radii (or more properly, the logarithm of the aerosol radius) yields the total volume concentration of the aerosol per unit area of the atmospheric column, C_V (with units μm^3/μm^2). The inversion method leading to the aerosol volume distribution, as well as the assumptions inherent to the inversion (e.g., spherical particles, various smoothing constraints), have been discussed in Dubovik and King (2000). Formally, the volume distribution is the sum of two lognormal distributions that represent the fine (f) and coarse modes (c) of the total distribution (Dubovik et al., 2002),

$$\frac{dV(r)}{d\ln r} = \frac{C_{V,f}}{\sqrt{2\pi}\sigma_f}\exp\left[-\frac{(\ln r - \ln r_{V,f})^2}{2\sigma_f^2}\right] + \frac{C_{V,c}}{\sqrt{2\pi}\sigma_c}\exp\left[-\frac{(\ln r - \ln r_{V,c})^2}{2\sigma_c^2}\right] \quad (2)$$

In this equation, r is the particle radius, and r_V and σ are the volume median particle radius and the standard deviation, respectively, for either the fine or coarse mode. (The conventional geometric standard deviation, σ_g, is related to the standard deviation listed above by the relationship, σ=lnσ_g.) Typical values of these quantities for the MCMA field experiment are for the fine mode: $C_{V,f}$=0.075 μm^3/μm^2, $r_{V,f}$=0.13 μm, σ_f=0.43; and for the coarse mode: $C_{V,c}$=0.063 μm^3/μm^2, $r_{V,c}$=3.6 μm, σ_c=0.62.

The fifth assumption – constant aerosol composition regardless of aerosol size – is at least partially satisfied. Black

carbon emitted from traffic sources is submicron in size. That these small soot particles make their way to larger particles is clearly seen in the scanning electron micrographs shown in Fig. 5 of Johnson et al. (2005), which show internally mixed soot contained in particles that are larger than 1 μm in size.

Finding M_{BC} begins with the equations

$$(1-\varpi_{0,\lambda})\tau_\lambda = \int_0^\infty \frac{dn(r)}{dr}\sigma_{abs}(\tilde{m}_s, \tilde{m}_{\mathrm{BC}}, r, f_V)dr \quad (3)$$

and

$$\tau_\lambda = \int_0^\infty \frac{dn(r)}{dr}\sigma_{\mathrm{ext}}(\tilde{m}_s, \tilde{m}_{\mathrm{BC}}, r, f_V)dr \quad (4)$$

where *dn(r)/dr* is columnar number distribution obtained from the volume distribution (e.g., $dV/dlnr=r(4/3\pi r^3)\mathrm{d}n(r)/dr$); $\sigma_{\mathrm{abs}}(\tilde{m}_s, \tilde{m}_c, r, f_V)$ and $\sigma_{\mathrm{ext}}(\tilde{m}_s, \tilde{m}_c, r, f_V)$ are the absorption and extinction cross sections as a function of the (complex) refractive indices of the shell, $\tilde{m}_s$, and the BC core, $\tilde{m}_{\mathrm{BC}}$; r is the total radius of the particle, and f_V ($0 \leq f_V \leq 1$) is the volume fraction of the aerosol that consists of BC. Invoking assumptions two and three mentioned above, we assume values for $\tilde{m}_{\mathrm{BC}}$ and the complex part of $\tilde{m}_s$, denoted as $\mathrm{Im}[\tilde{m}_s]$ (these values will be discussed below); *dn(r)/dr* is known from the AERONET retrievals, and from the MFRSR measurements we can infer τ_λ and $\varpi_{0,\lambda}$. With these known factors, Eqs. (3) and (4) become integral equations for f_V and the real part of $\tilde{m}_s$, $\mathrm{Re}[\tilde{m}_s]$. Once f_V is known, M_{BC} follows immediately, $M_{\mathrm{BC}}=C_V f_V \rho_{\mathrm{BC}}$, where again, we use assumption (2) and choose a plausible value for ρ_{BC}, discussed below.

Solving Eqs. (3) and (4) for f_V and the real part of $\tilde{m}_s$ is a straightforward, iterative process. First, we take $\mathrm{Im}[\tilde{m}_s]$ as $-10^{-7}i$. The small imaginary part of the shell refractive index implies negligible absorption and is representative of a sulfate-like compound (Toon et al., 1976), and/or organic compounds that do not absorb at 500 nm. Next, the shell/core Mie code of Ackerman and Toon (1981) is used to compute $\sigma_{\mathrm{abs}}(\tilde{m}_s, \tilde{m}_c, r, f_V)$ and $\sigma_{\mathrm{ext}}(\tilde{m}_s, \tilde{m}_c, r, f_V)$ for ranges of r that encompass the limits of *dn(r)/dr* and plausible values of f_V. Equation (3) and (4) are integrated numerically, compared with $(1-\varpi_{0,\lambda})\tau_\lambda$ and τ_λ, respectively, and this process is repeated until the left- and right-hand sides of the equations are equal. This iteration is robust and converges rapidly.

When solving Eqs. (3) and (4), assumptions regarding specific values of $\tilde{m}_{\mathrm{BC}}$ and ρ_{BC} must be made. Measurements of the density of diesel soot (Park et al., 2004; Wu et al., 1997), and the discussion provided in Fuller et al. (1999) and Schuster et al. (2005) suggest a plausible range of ρ_{BC} from 1.7 to 2.1 g/cm^3. Bond and Bergstrom (2006) suggest a more limited range of 1.7 to 1.9 g/cm^3. Although measured density values less than 1.7 g/cm^3 have been reported, an important consideration favoring the higher density values is the need to correlate carbon mass emissions with climate impact. As noted by Fuller et al. and references therein, for this correlation to be meaningful, the density of the tiny spherules that compose soot clusters is important, and not some average density of a soot cluster, which contains voids. Within the 1.7 g/m^3 to 2.1 g/m^3 range, however, we cannot pretend to know the density exactly and consequently, we chose the value, 2.0 g/m^3, so the results may be compared with Schuster et al. (2005). For this same reason we take $\tilde{m}_{\mathrm{BC}}$=2.0–1.0i (Soot G, Fuller et al., 1999).

It is instructive, however, to repeat the specific absorption calculations using the refractive indices and densities as reported by Bond and Bergstrom (2006). In this paper, an exhaustive review and analysis of the literature was undertaken to determine suggested ranges of these quantities. Considering these ranges to be the most credible and updated values for use in radiative transfer calculations, we again find α_λ by taking ρ_{BC} to be 1.8 g/m^3 and $\tilde{m}_{\mathrm{BC}}$ as 1.95–0.79i. The density is the midpoint of the suggested range of 1.7 to 1.9 g/m^3, while $\tilde{m}_{\mathrm{BC}}$ is the highest of the suggested values and implies a minimal void volume in the carbon. To distinguish between these two sets of calculations, we label them as I – for comparison with the results of Schuster et al. (2005); and II – using Bond and Bergstrom "best estimate" values. For the sake of explicitness, the refractive indices and densities of these two sets of calculations are shown in Table 2.

2.3 Specific absorption values

The technique described above was applied to 7 cases during which the sky was free from clouds. Table 1 shows the results for both sets I and II, as well as values of τ_λ , å, and $\varpi_{0,\lambda}$ averaged over the indicated clear sky periods. All results are for a wavelength of 500 nm. It is again important to reiterate that the derived values of α_λ are only appropriate for the time periods when the skies are clear because this requirement is necessary to derive $\varpi_{0,\lambda}$. These time periods occur in the morning hours, before a convective boundary layer develops that encourages the development of convective cloudiness.

For the seven cases considered here and for the BC parameter sets I and II, the eighth column in Table 1 shows α_λ, while the last column shows $\mathrm{Re}[\tilde{m}_s]$. The specific absorptions are depicted by the bar chart in Fig. 1, which shows that the results of set I are larger than set II, but nonetheless fairly close. When averaged over the 7 cases, the averaged values, shown in the bottom row of Table 1, are 8.9 m^2/g and 8.2 m^2/g, for sets I and II respectively, a difference of about 9%.

When averaged over all days, $\mathrm{Re}[\tilde{m}_s]$ is equal to 1.39 for both sets. That $\mathrm{Re}[\tilde{m}_s]$ is virtually the same for both sets is related to the fact that the extinction (τ_λ) depends mostly on the real part of the (effective shell/core) refractive index (King et al., 1978). Furthermore, our value is quite close to the real part of the refractive index obtained from the

Table 2. BC properties used in the two sets of calculations considered here.

	Set I – for comparison with the results of Schuster et al. (2005)	Set II – using "best estimate" values from Bond and Bergstrom (2006)
Refractive index of BC, $\tilde{m}_{BC}$	2.0–1.0i	1.95–0.79i
Density of BC, ρ_{BC}	2.0 g/m^3	1.8 g/m^3

AERONET retrievals, 1.40, when averaged over the same days. An effective shell refractive index of this magnitude suggests the presence of water in the shell, but the boundary layer was very dry and the aerosols were likely to be dry. However, a Re[$\tilde{m}_s$] of this magnitude may be congruent with the large organic carbon (OC) content of the MCMA aerosol. As noted in Salcedo et al. (2006), the average mass composition of OC in the aerosol was about 55%. We do not know exactly which compounds compose the OC content of the MCMA aerosol, nor do we know their refractive indices. To get around a similar problem, Schnaiter et al. (2003) estimated the refractive index of secondary organic aerosols by using known refractive indices of two OC compounds similar to those that might be found in these aerosols. These two values reported by Schnaiter et al. are 1.43 to 1.45. Jacobson (1999) has tabulated the real part of refractive index of many organic compounds; these range from about 1.33 to 1.63. Given these range of values, Re[$\tilde{m}_s$] is consistent with a significant OC component in the MCMA aerosol.

Schuster et al. (2005) report values of α_λ at many AERONET locations using retrievals of aerosol properties from the AERONET sun photometers. The methodology behind their results closely parallels our method, and our set I assumes the same values for the physical properties of BC. The major difference between the two methods is our use of a shell/core model to represent aerosol mixing properties versus Schuster et al.'s use of the Maxwell-Garnett (MG) effective medium approximation (Lesins et al., 2002; Bohren and Huffman, 1983) to find an "effective" refractive index of the aerosol mix. When Schuster at al. used this approximation, the volume fractions of BC and ammonium sulphate, contained in a water host, are iterated until the difference between the calculated and observed (AERONET) values of the index of refraction is minimized. Once the volume fraction is known, M_{BC} is easily calculated.

For Mexico City, Schuster et al. (2005) quote a value of α_λ of 9.5±0.9 m^2/g when averaged over the years 2000 and 2001, for a wavelength of 550 nm. Recall that for set I, we used the same BC physical parameters as Schuster et al. For this set, our value 8.9 m^2/g has been derived for a wavelength of 500 nm, and to compare these two values, we must adjust our value to a wavelength of 550 nm. From measurements of aerosol absorption taken at different wavelengths, Bergstrom et al. (2002) show that the wavelength dependence of BC absorption is best described by the well-known relationship λ^{-1} over a wavelength range of 0.4 to 1.0 μm. Kirchstetter et al. (2004) suggest that, for motor vehicle aerosols that have a relatively large BC component, the wavelength dependence is also about λ^{-1} in the visible range. These studies indicate that, for our wavelength extrapolation from 500 to 550 nm, the relationship λ^{-1} is appropriate. With this in mind, converting our "set I" value to 550 nm gives 8.1 m^2/g [=8.9 m^2/g(550 nm/500 nm)$^{-1}$], which is lower than Schuster et al.'s value by about 15%. Our set II value at 550 nm is 7.4 m^2/g.

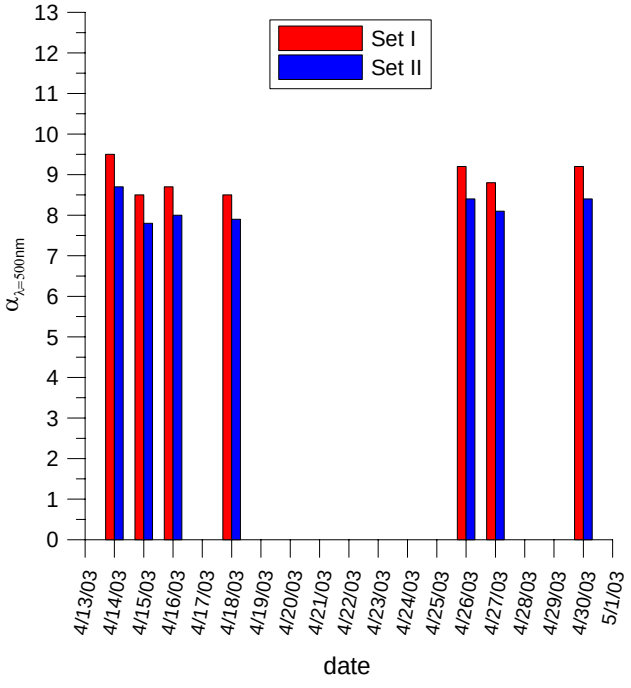

Fig. 1. Bar chart summarizing the values of α_λ, for λ=500 nm, over the course of the MCMA field campaign. Results from sets I and II are shown.

All values mentioned above are less than 10 m^2/g, a value commonly accepted for α_λ at a wavelength of 550 nm. Bond et al. (2006) suggest that aged (i.e., coated) BC aerosols have an (specific) absorption amplification factor of up to 1.5. (Larger values are possible but only for conditions which are unlikely to occur in the atmosphere.) Using Bond

and Bergstrom's (2006) uncoated value of $7.5\pm1.2\,m^2/g$ (550 nm), the range in α_λ from uncoated to coated extends from $7.5\pm1.2\,m^2/g$ up to $11.3\pm1.8\,m^2/g$, and our values, as well as those of Schuster et al. (2005) lie in this range. Our values are also consistent with Fuller et al. (1999) who suggest that the "canonical" value of $10\,m^2/g$ is too large. They arrived at this conclusion by explicitly calculating α_λ for randomly spaced BC occlusions within a host sulphate aerosol, and over a wide range of plausible BC mass mixing ratios, the calculations indicate that $\alpha_\lambda > 10\,m^2/g$ occurs only when two conditions are met: most of the BC is internally mixed, and the host aerosols are sufficiently large, defined as $R_g > 0.06$, where R_g is the geometric mean radius of the size distribution. Our retrievals of R_g for the MCMA based on the algorithm of Kassianov et al. (2005), indicate that R_g is about $0.035\,\mu$m. Alternatively, using the fine component of the AERONET volume distribution yields an R_g of about $0.032\,\mu$m. Both of these radii are smaller that the $0.06\,\mu$m limit, suggesting that α_λ should be less than $10\,m^2/g$ at 550 nm.

2.4 M_{BC}, f_v

In addition to α_λ, Table 1 provides other aerosol characteristics that are derived from our methods, such as M_{BC}. For both sets I and II the averaged M_{BC} values are about $4\,mg/m^2$. These are large BC loadings. As shown in Schuster (2004), columnar BC concentrations in an urban area (Goddard Space Flight Center [GSFC] near Washington, D.C., USA) inferred from AERONET measurements, can range as high as about $7\,mg/m^2$, although most values are less than $3\,mg/m^2$. That the BC columnar concentrations are larger than those typically found at the GSFC seems intuitively credible, given the very large population and emissions of the MCMA.

2.5 Uncertainties

Quantification of the uncertainties associated with the method described here is possible, but still subject to some educated guesswork. Because our method is similar to that discussed by Schuster et al. (2005), much of the uncertainty analysis contained in Schuster et al. is applicable to our method as well. The sources of uncertainty discussed in Schuster at al. include the obvious ones: the physical and optical properties of carbon and the host aerosol, mixing assumptions, and the contamination of the results by absorbing species other than BC. Because these various sources of uncertainty have already been thoroughly discussed in Schuster et al., we will summarize them here. We will also estimate the uncertainty due to the error in the retrieved volume distributions, the departure of the aerosol shape from spherical, and errors in the retrieval of $\varpi_{0,\lambda}$ and τ_λ. In the discussion below, we shall just consider the uncertainties associated with set I; similar arguments would hold for set II. Although the magnitude of the uncertainties might be somewhat different between each set, we must be mindful that these uncertainties cannot be pinned down with exactitude, and an uncertainty estimated for either set is likely to representative of the other set as well.

2.5.1 Density of BC

Considering the discussion of Fuller et al. (1999) plausible bounds for BC density range from $1.7\,g/m^3$ to $2.1\,g/m^3$. Bond and Bergstrom (2006) state that the upper end of the plausible range is only $1.9\,g/m^3$. For our set I calculations, we assume a value of $2.0\,g/m^3$ for comparison of the results of Schuster et al. (2005). Assuming that the density of BC in the MCMA is bracketed by $1.7\,g/m^3$ to $2.1\,g/m^3$, the error bounds on α_λ are +18% to −5%. That is, α_λ could be 18% higher or 5% lower than the values we calculate. Schuster et al. estimated ±5%; we think this is a little too low.

2.5.2 Optical properties of BC

The value chosen for the refractive index is $2.0–1.0i$, and this is somewhat above the upper end of reported refractive indices (Bond and Bergstrom, 2006) for both the real and imaginary parts. Reducing either the real or imaginary part of the refractive index from the chosen value reduces the calculated value of α_λ. For example, using a refractive index of $1.85–0.71i$ (a value employed by Bond et al., 2006, and in the middle of the range suggested by Bond and Bergstrom, 2006), in place of $2.0–1.0i$, reduces the α_λ by about 22%. Even lower values for the imaginary part of the refractive index can significantly reduce α_λ. As noted by Schuster at al., using the OPAC (Optical Properties or Aerosols and Clouds) refractive index for soot, $1.75–0.44i$, lowers α_λ by a factor of two, outside the range which is thought plausible. Additional evidence suggests that the OPAC refractive index is not "dark enough" and should be retired (Bond and Bergstrom, 2006), and our results support this assertion. Because the chosen values of both the real and imaginary parts of the refractive index are near the upper bounds thought likely, we estimate a possible positive uncertainty of +10%.

2.5.3 Mixing assumptions and aerosol shape

Scanning electron micrographs of soot-containing particles shown in Johnson et al. (2005) show that the soot is internally mixed. The particles shapes are tortured, and are anything but perfect spheres. Because it is impossible to model the optical properties of such aerosols exactly, we must perforce approximate the aerosols as spheres. Given that we assume a spherical shape, a concomitant issue is the rules that govern the mixing of the BC within the sphere. In our case, we chose a concentric sphere (CS) model with carbon in the center. Other mixing scenarios are possible. Some lead to unrealistic results; for example, Bond et al. (2006) strongly advise against using volume averaging of refractive indices

because this mixing model overestimates absorption. For internal mixtures, Lesins et al. (2002) examined shell/core configurations and refractive index mixing rules such as MG. Optical properties derived from these two scenarios, for the same volume fraction of BC, were typically within 5% of one another. For the f_V of the MCMA aerosol, less than 0.03, calculations done by Fuller et al. (1999) of BC absorption – and shown in their Fig. 12 – indicate that the CS model provides nearly identical absorption to a case where the BC inclusion is randomly distributed throughout the host aerosol, or when the inclusion is located just below the surface. Using this as a guide, we estimate any error in using a CS model to be slightly negative (i.e., the actual absorption could be slightly less than our calculations), but close to zero. This estimate is only justifiable for small BC mixing ratios and spherical aerosols.

That the aerosols are not spherical induces some error into our calculation. Recent work using exact calculations of the optical properties of fractal-like soot aggregations in random orientations (Liu and Mishchenko, 2005) provides some guidance on the extent that aerosol morphology influences α_λ. For example, when the fractal dimension varies from 1.5 (chain-like structures) to 2.4 (more compact and sphere-like), α_λ decreases by about 10%. These results are not strictly applicable to our study because, among other things, Liu and Mishchenko focused only on aggregations of soot monomers, and not the more realistic situation of soot mixed with other compounds. Nonetheless, given these results, we speculate that aerosol shape issues introduce an uncertainty of about $\pm$10%.

2.5.4 Contamination of results by other absorbing species

The air and aerosols in the MCMA contain substances, aside from BC, that absorb sunlight. Surface observations of NO_2 concentrations that occur in the morning hours in Mexico City (Rainer Volkamer, personal communication) show that it is large enough (>40 ppb) to be a significant absorber. These high concentrations would contaminate the retrievals of $\varpi_{0,\lambda}$ at wavelengths where there is significant NO_2 absorption (440 nm for the AERONET sun photometer and 415 nm for the MFRSR). The effect of this absorption is to reduce the inferred value of $\varpi_{0,\lambda}$ compared to the value that would be inferred if the NO_2 absorption were properly taken into account. The OC content of the MCMA aerosol is significant (Salcedo et al., 2006) and this large amount of OC could contribute to increased absorption at the UV and near-UV wavelengths (Jacobson, 1999; Kirchstetter et al., 2004), adding to the contamination of $\varpi_{0,\lambda}$ retrievals. Similarly dust is known to absorb in the UV and near-UV wavelengths (Sokolik and Toon, 1999). The net effect of this contamination, if not accounted for, is to attribute the absorption of NO_2, OC, and dust to BC. This would tend to increase our retrieved values of α_λ.

We have been able to minimize this error by making retrievals at a wavelength equal to 500 nm, where the absorption of NO_2 is small, and the absorption of OC is expected to be very small (Jacobson, 1999; Kirchstetter et al., 2004). Plots of single scattering albedo versus wavelength reveal a definite dust signature in dusty areas (Dubovik et al., 2002), and this signature is absent in the MCMA data, indicating that dust absorption is not likely to be large. Schuster estimated the total contamination bias to be about -10%, that is, the true α_λ values could be lower than calculated by up to this amount. In our case, we estimate that the error is less than -5% because of the use of the 500 nm wavelength, and the apparently small dust loading of the MCMA.

2.5.5 Uncertainties in volume distribution retrievals

According to Dubovik et al. (2002), for intermediate particles sizes where the bulk of the particles reside, the retrieval errors of the volume distribution do not exceed 10% in the maxima of the volume distribution. If we assume that the uncertainty of the retrieved aerosol volumes (i.e., integration of the volume distribution) is the same magnitude, then the derived volumes listed in column five, Table 2 would be uncertain to $\pm$10%. (This is a conservative estimate of the error because it does not account for canceling errors during the integration of the volume distribution.) If we again do the calculations and vary the aerosol volume by $\pm$10%, the calculated specific absorptions change by about 4%.

2.5.6 Uncertainties in the retrieval of $\varpi_{0,\lambda}$ and τ_λ

The uncertainty in the retrieval of $\varpi_{0,\lambda}$, $\Delta\varpi_{0,\lambda}$, and an uncertainty in τ_λ, $\Delta\tau_\lambda$, contribute directly to the overall uncertainty of α_λ, $\Delta\alpha_\lambda$, in the following manner: $\alpha_\lambda + \Delta\alpha_\lambda = (1-(\varpi_{0,\lambda}+\Delta\varpi_{0,\lambda}))(\tau_\lambda+\Delta\tau_\lambda)/M_{\mathrm{BC}}$, where the uncertainties in $\varpi_{0,\lambda}$ and τ_λ can be of either sign. Michalsky et al. (2001) states that $\Delta\tau_\lambda$ is $\pm$0.01, while $\Delta\varpi_{0,\lambda}$ is about $\pm$0.03 (Dubovik et al., 2002; Georing et al., 2005). Assuming that the real $\varpi_{0,\lambda}$ is about 0.9, and the real τ_λ is about 0.33 (the average values for the MCMA campaign), we obtain uncertainties of about $\pm$30%. For single scattering albedos that approach one (e.g., the case of 18 April 2003 with $\varpi_{0,\lambda}$=0.965), the uncertainty would be much larger.

2.5.7 Summary of errors

Considering all these factors except particle shape, Schuster et al. (2005) estimated the overall error in M_{BC} retrievals to range from -40% to +15% by simply summing the individual uncertainties together. That is, M_{BC} may be overestimated by 40% or underestimated by 15% and (approximately) visa versa for α_λ because of the inverse relationship between M_{BC} and α_λ. Summarizing our uncertainty analysis for α_λ gives the following values: (a) density, -5% to 18%; (b) optical properties of BC, +10%; (c) mixing assumptions and particle shape, $\pm$10%; (d) contamination by other

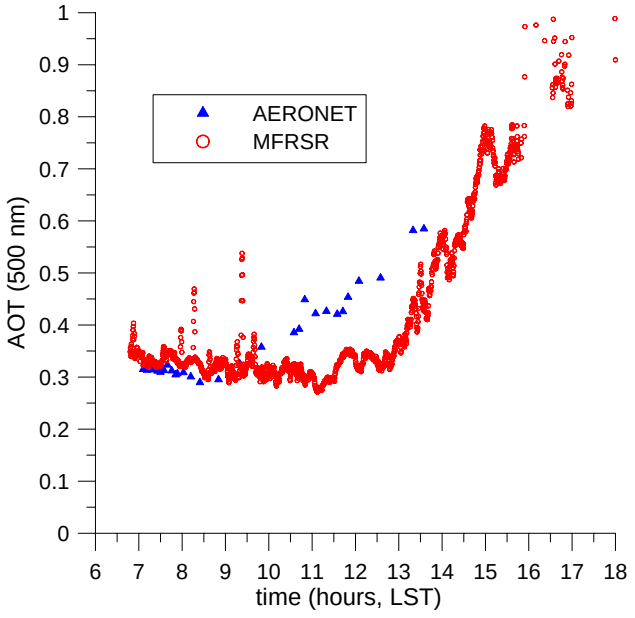

Fig. 2. Aerosol optical thickness (AOT) at 500 nm derived from the MFRSR and AERONET sun photometer in Mexico City. The date is 27 April 2003.

species, −5% to 0%; (e) uncertainties in the retrievals of the volume distribution, ±4%; and (f) uncertainties in the retrievals of $\varpi_{0,\lambda}$ and τ_λ, ±30%. A simple addition of these uncertainties, which emphasizes the worst case scenario because no errors are allowed to cancel, yields an overall uncertainty of from about −55% to about +75%. For convenience, we simply take uncertainty to be ±70%. For a specific absorption of 8.9, this maps into error bars of magnitude of about ±6.2 m^2/g. Most of the overall uncertainty stems from the large uncertainty in retrieving the single scattering albedo.

3 Discussion

When the α_λ values are converted to 550 nm using the conversion rule, λ^{-1}, and when averaged over all seven cases, our method yields 8.1 m^2/g and 7.4 m^2/g for sets I and II, respectively. On the other hand, Schuster et al. (2005) derived a value of 9.5 m^2/g. Baumgartner et al. (2002) measured α_λ at 550 nm equal to 7.0±0.5 m^2/g at the surface using optical methods to measure aerosol absorption and thermal methods to determine EC mass. These values span a plausible range as enunciated in Fuller et al. (1999) and Bond et al. (2006). Fuller et al. states that for isolated carbon spheres, α_λ is about 5 m^2/g, while for aggregates of graphitic carbon grains, α_λ is about 7 m^2/g or less, and for occluded carbon, α_λ is unlikely to exceed 10 m^2/g, except for large, internally mixed aerosols. (Of course, the exact values of these boundaries depend on the size distribution of the aerosol, as well as the optical constants assumed for BC.) As mentioned above, assuming an absorption amplification factor of 1.5 (Bond et al., 2006), it can be inferred from Bond and Bergstrom (2006) that the range in α_λ extends from 7.5±1.2 m^2/g (uncoated) to about 11.3±1.8 m^2/g. The evidence from Johnson et al. (2005) suggests that the aerosols are internally mixed, yet the aerosols over the MCMA are probably not large enough to expect $\alpha_\lambda > 10$ m^2/g. Our results, along with those of Schuster et al. and Baumgartner et al., all lie in a range of about 7–10 m^2/g at 550 nm and are therefore consistent with the findings of Fuller et al. (1999) and Bond et al. (2006).

The difference in α_λ values between the results of Schuster et al. (2005) and our method is not large compared to the range of values reported in the literature. However, because our method uses the same BC physical/optical constants and the same volume distributions as Schuster et al., it is interesting to investigate why the observed difference exists. It cannot be completely explained by the different ways of dealing with the internal mixture, e.g., shell/core versus MG. Using an aerosol volume distribution appropriate for the GSFC, Schuster et al. found that shell/core and MG approaches are similar, except for lower volume fractions of BC, $f_V < 0.2$. For very small f_V (<0.05), the shell/core method gave higher specific absorptions than MG by at least 10%. These findings indicate that our results should be about 5–10% larger than Shuster et al.'s α_λ values. However, our shell/core values are smaller than Schuster et al.'s values.

It is possible that the short sample period of 7 days during the field campaign does not allow us to sample the full range of conditions found in Schuster et al.'s analysis. Had we been able to perform the analysis over several years as was done in Schuster at al., our values may have become closer to their values. We also must be cognizant of spatial sampling differences. The spatial sampling could be problematic because the distance between the MFRSR and the AERONET instruments is about 16 km, and the possibility that the instruments observe different types of aerosols, different aerosol size distributions, etc., cannot be dismissed. For example, Fig. 2 shows simultaneous observations of aerosol optical thickness at 500 nm, taken at the MFRSR and AERONET sites on 27 April 2003. In the morning hours, these optical thicknesses are similar, but diverge as the day progresses. This increasing discrepancy can be explained by the meteorology of the MCMA (modelled by Fast and Zhong, 1998): the winds that arise during the morning often blow the pollution towards the AERONET site, and this pollution runs into the mountains and would tend to be recirculated over the site, thus increasing the optical thickness at this site over that at the MFRSR site. Whether this increasing optical thickness is associated with a change in aerosol intensive properties (e.g., $\varpi_{0,\lambda}$) cannot be determined without additional measurements.

4 Conclusions

Using data from the MFRSR, as well as aerosol volume distributions obtained from the AERONET sun photometer, we calculated α_λ during the MCMA-2003 field campaign, for a wavelength of 500 nm. The method described here uses inferences of the aerosol optical thickness, τ_λ, and aerosol single scattering albedo, $\varpi_{0,\lambda}$, obtained from the MFRSR to estimate the absorption optical thickness, $\tau_{\lambda,abs}$. Once this quantity is estimated, all that is needed is an estimate of columnar concentration of BC, M_{BC}. This method also relies on the AERONET volume distribution appropriate for the day in question, the assumption of a shell/core model of internal mixing, and specific choices of BC density and refractive index to find M_{BC}. For these quantities, we chose two sets (I and II) of values as listed in Table 2. For set I, the BC physical and optical properties are those stated in Fuller et al. (1999) under the category "Soot G". These values were chosen so that our results could be compared with those of Schuster et al. (2005). The second (II) comes from "best estimates" of these quantities found in Bond and Bergstrom (2006), as listed in Table 2. When averaged over 7 clear periods of the MCMA-2003 field campaign, consisting of a total of about 10 h in the morning over the month of April 2003, the values of α_λ are 8.9 $\mathrm{m^2/g}$ (I) or 8.2 $\mathrm{m^2/g}$ (II) at 500 nm. The estimated level of worst case uncertainty for our method is $\pm$70%. This estimate assumes all errors are additive and of the same sign.

When converted to a wavelength of 550 nm using a λ^{-1} conversion rule, the values of α_λ are 8.1 $\mathrm{m^2/g}$ and 7.4 $\mathrm{m^2/g}$, for sets I and II, respectively. For the aerosol size distributions observed in the MCMA, these values lie within the range of likely α_λ values as demarcated by Fuller et al. (1999), Bond and Bergstrom (2006), and Bond et al. (2006).

Schuster et al. (2005) have derived an α_λ value of 9.5 $\mathrm{m^2/g}$ at 550 nm using methods similar to our method, and Baumgartner et al. (2002) report a surface value of 7.0$\pm$0.5 $\mathrm{m^2/g}$ at 550 nm, obtained using an entirely different technique. All reported values, including our own, lie in a range between about 7 and 10 $\mathrm{m^2/g}$ for aerosols that are moderately aged. Refining the optically based α_λ values discussed in this paper will require more precise information about the refractive indices and densities of BC, and/or a method of finding the BC load throughout the vertical extent of the atmosphere. As noted by Schuster et al. results such as those presented here have not been validated by elemental carbon measurements throughout the atmospheric column.

It cannot be underemphasized that these results can only be considered as effective, "radiatively correct" results, meaning that given the assumptions discussed in Sect. 2.2, the α_λ and M_{BC} values are those required to force calculated irradiances to be identical with measured irradiances at 500 nm. Using a different set of assumptions would result in different values of α_λ and M_{BC}, but these values would still be consistent with the requirement that calculated and measured irradiances match. It must be noted, however, that to obtain specific absorption values far outside the range specified above would require rather dubious assumptions regarding the physical and optical properties of BC. For example, if for case 6 (α_λ=8.8 $\mathrm{m^2/g}$), we assume that the refractive index is 2.1–1.2i in place of 2.0–1.0i, then to obtain a specific absorption at the upper end of the expected range (about 13 $\mathrm{m^2/g}$), the chosen density value would have to be about 1.4 $\mathrm{g/m^3}$ (assuming no other source of uncertainties). This value, as well as the refractive index value, lie outside the ranges thought plausible.

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