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The impact of biogenic carbon emissions on aerosol absorption in Mexico City

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Abstract

In order to determine the wavelength dependence of atmospheric aerosol absorption in the Mexico City area, the absorption Ångstrom exponents (AAEs) were calculated from aerosol absorption measurements at seven wavelengths obtained with a seven-channel aethalometer during two field campaigns, the Mexico City Metropolitan Area study in April 2003 (MCMA 2003) and the Megacity Initiative: Local and Global Research Observations in March 2006 (MILAGRO). The AAEs varied from 0.76 to 1.56 in 2003 and from 0.54 to 1.52 in 2006. The AAE values determined in the afternoon were consistently higher than the corresponding morning values, suggesting the photochemical formation of absorbing secondary organic aerosols (SOA) in the afternoon.

The AAE values were compared to stable and radiocarbon isotopic measurements of aerosol samples collected at the same time to determine the sources of the aerosol carbon. The fraction of modern carbon (fM) in the aerosol samples, as determined from ^{14}C analysis, showed that 70% of the carbonaceous aerosols in Mexico City were from modern sources, indicating a significant impact from biomass burning during both field campaigns. The $^{13}C/^{12}C$ ratios of the aerosol samples illustrate the significant impact of Yucatan forest fires (C-3 plants) in 2003 and local grass fires (C-4 plants) at site T1 in 2006. A direct comparison of the fM values, stable carbon isotope ratios, and calculated aerosol AAEs suggested that the wavelength dependence of the aerosol absorption was controlled by the biogenically derived aerosol components.

1 Introduction

Atmospheric aerosols play an important role in global climate because of their ability to both scatter and absorb solar radiation. While aerosol scattering is primarily dependent on particle size, aerosol absorption is largely dependent upon chemical composition. Those aerosols that have no significant absorption in the UVB-UVA-visible spectral region (e.g. sulfate) act to scatter solar radiation, reducing the amount reaching the Earth's surface and resulting in an overall cooling effect. The cooling effect of anthropogenic sulfate aerosols in the Northern Hemisphere has been estimated to be comparable in magnitude to the atmospheric warming produced from increases in carbon dioxide (CO_2) (Kiel and Briegleb, 1993). Other aerosol species (e.g. black carbon) can both scatter and absorb solar radiation resulting in a cooling of the surface while simultaneously warming the atmosphere. Black carbon (BC) aerosols produced from incomplete combustion can reduce the amount of sunlight reaching the Earth's surface by as much as 10% (Ramanathan and Carmichael, 2008). However, they also increase the solar energy absorbed in the atmosphere by as much as 50% in some areas leading to heating of the particles and significant local warming of the boundary layer (Hermann and Hanel, 1997; Ramanathan and Carmichael, 2008). Absorbing aerosols may cause as much warming in the lower atmosphere as the major greenhouse gases, thus being a potentially important contributor to regional climate forcing (Ramanathan et al., 2007). The presence of absorbing aerosols in the troposphere can therefore result in a local heating of the air altering atmospheric stability and affecting large-scale circulation patterns and hydrologic cycles resulting in significant regional climate effects (Kaufman et al., 2002).

1.1 Aerosol absorption

The dominant light-absorbing aerosol species is thought to be BC, commonly known as carbon soot, produced by incomplete combustion of fossil fuels and biomass burning. One of the largest sources of BC is emissions from diesel engines and therefore urban areas are thought to be one of the largest regional sources of absorbing aerosols dominated by this source. The absorption of solar light by freshly emitted BC aerosols is broadband decreasing monotonically with wavelength over the entire spectral region from UV to infrared (Marley et al., 2001).

Other light absorbing species are also present in atmospheric aerosols, including polycyclic and heterocyclic aromatic hydrocarbons and their nitrated derivatives (Jacobson, 1999), amino acids such as tryptophan in biological particles (Pinnick et al., 2004), and polycarboxylic acids known as “humic-like” substances (HULIS) (Cappiello et al., 2003). The polycyclic aromatic hydrocarbons (PAHs) are produced along with BC during combustion of fossil fuels and their nitrated derivatives are formed by atmospheric oxidation in the presence of NO_2. The HULIS are produced from biomass burning (Hoffer et al., 2006), by atmospheric oxidation of BC (Decesari et al., 2002), or by atmospheric oxidation of biogenic hydrocarbons (Limbeck et al., 2003). These organic carbonaceous aerosol species have an enhanced absorption at shorter wavelengths (<400 nm) leading to aerosol absorption profiles greater than that expected from BC aerosols alone (Gelencsér et al., 2003).

The wavelength (λ) dependence of aerosol absorption (A) is approximated by a power-law expression;

$$A = \beta\lambda^{-\alpha} \tag{1}$$

where α is the absorption Ångstrom exponent (AAE) and β is the aerosol absorption at 1 μm. The value of α depends on the chemical composition of the absorbing aerosol (Bergstrom et al., 2007). Freshly emitted BC particles from diesel engines have an AAE of 1 (Bergstrom et al., 2002; Marley et al., 2001) while carbonaceous aerosols produced from biomass burning have much stronger wavelength dependence of absorption, with an AAE of 2 (Kirchstetter et al., 2004). The water soluble HULIS isolated from biomass burning aerosols have very high AAEs in the range of 6 to 7 (Hoffer et al., 2006). Fine inorganic dust aerosols have been associated with a wide range of AAEs from values greater than 2 (Bergstrom et al., 2007) to less than 0.5 (Meloni et al., 2006) depending on the source.

An understanding of the wavelength dependence of aerosol absorption is important for several applications. An absorbing aerosol with an AAE of 3 will have an absorption coefficient in the UV that is 8 times larger than that in the visible (Bergstrom et al., 2007). This is not only important for the determination of the aerosol radiative forcing but also for atmospheric photochemical modeling. The UV is the most important spectral range for the promotion of atmospheric photochemical reactions. The presence of UV absorbing aerosols in the troposphere reduces the actinic flux throughout the boundary layer, which reduces the production of photochemical oxidants such as ozone and results in a buildup of the unreacted precursors in the atmosphere (Wendisch et al., 1996; Dickerson et al., 1997). The presence of absorbing aerosols in Mexico City leads to a reduction in the actinic flux below 430 nm by 10–30% (Castro et al., 2001). This reduction in UV radiation results in less surface level ozone produced in the city than would be expected from the precursor concentrations. The unreacted precursors are therefore transported out of the basin ultimately contributing to higher ozone levels in the surrounding region.

Aerosol absorption measurements have been used to determine BC aerosol mass concentrations by using the BC mass absorption efficiencies. Routinely the mass absorption efficiency is determined experimentally at one wavelength and an AAE of 1 is assumed to obtain the mass absorption efficiencies at other wavelengths (Hansen et al., 1984). This assumption can be a major source of error when comparing results of aerosol BC concentrations obtained from different methods. In a recent study, it was concluded that a better understanding of the wavelength dependence of aerosol absorption and how it varies with aerosol composition is needed in order to reconcile BC measurements made with different instrumental methods (Park et al., 2006).

The wavelength dependence of aerosol absorption has also been used to identify and classify different aerosol types (Meloni et al., 2006; Bergstrom et al., 2007). Remote sensing of aerosols by TOMS (Total Ozone Mapping Spectrometer) and OMI (Ozone Monitoring Instrument) type satellites utilizes the ratio of reflected light at two near-UVB and UVA wavelengths (e.g. 340 and 380 nm) to determine the type of absorbing aerosols present in the atmosphere (Torres et al., 1998). Similar methods have been used to identify aerosols in ground-based studies. While urban aerosols that contain large concentrations of BC from the combustion of fossil fuels are associated with an AAE near 1 and aerosols impacted by biomass burning are associated with AAEs around 2, this can vary depending on the wavelength range used. In a recent study, biomass burning aerosols observed in South Africa yielded AAEs of 1.1

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from 325–1685 nm and AAEs of 1.5 from 325–1000 nm (Bergstrom et al., 2007).

A thorough understanding of the wavelength dependence of aerosol absorption is therefore important for the estimation of aerosol radiative forcing as well as for the estimation of atmospheric photochemical oxidant production on local and regional scales. It is also important to the interpretation of satellite retrievals and the identification of absorbing aerosol sources and types, as well as for the comparison of aerosol BC concentration measurements made by different measurement methods. In addition, in order to predict aerosol absorption profiles over the atmospherically relevant spectral range, the measured aerosol absorption must be correlated to the type of absorbing aerosols present.

1.2 Carbon isotopic tracers

Carbon isotope measurements provide a powerful tool to identify different types of carbonaceous aerosols. Carbon-14 measurements can distinguish between fossil fuel and non-fossil fuel carbon sources. Carbon-14, produced naturally in the upper atmosphere by the interaction of nitrogen atoms with thermal neutrons, is taken up as $^{14}CO_2$ and enters the carbon cycle labeling all biogenic materials with a relatively constant initial $^{14}C/^{12}C$ ratio of about 1.5×10^{-12} (Currie et al., 1982). Fossil fuels and the BC aerosols produced from their combustion contain no ^{14}C because their age (on the order of 100–200 million years) is much greater than the 5730-year half-life of the radiocarbon. Therefore, the ^{14}C content in atmospheric aerosols, presented as the fraction of modern carbon (fM) provides a direct measure of the relative contributions of carbonaceous materials derived from fossil fuels and that derived from modern biomass sources.

Stable carbon isotope ratios are also useful for the identification of carbonaceous aerosol sources. Terrestrial plants can utilize two different photosynthetic pathways, denoted C-3 and C-4 according to the number of carbon atoms fixed by each pathway (Smith and Epstein, 1971). The difference in atomic masses of the three carbon isotopes, ^{12}C, ^{13}C, and ^{14}C, affects the chemical reactivity and the physical processes sufficiently to cause selective uptake of $^{12}CO_2$ over both $^{13}CO_2$ and $^{14}CO_2$ during photosynthesis. The C-3 plants, which utilize the Calvin-Benson photosynthetic cycle, have a more selective chemistry and fractionate the heavier carbon isotope (^{13}C) by about 12–14 parts per thousand as compared to the less selective C-4 or Hatch-Slack photosynthetic pathway. The C-3 and C-4 plants will therefore be labeled with different $^{13}C/^{12}C$ ratios. The C-3 plants are most abundant and comprise most tree species, shrubs, and cool temperate grasses and sedges, while the C-4 plants consist mostly of warm temperate to tropical grasses (Sage, 2001). The $^{13}C/^{12}C$ ratios (R) are commonly expressed as $\delta^{13}C$ values in per-mil (‰), and represent the difference between the measured R and that of a carbon isotope standard, typically CO_2 prepared from Peedee belemnite (PDB) carbonate. The measured $^{13}C/^{12}C$ ratios of organic matter are generally ^{13}C-depleted compared to the ratio of the PDB standard and are therefore reported as negative values. These resulting $\delta^{13}C$ values are used to estimate the relative contributions from C-3 ($\delta^{13}C=-27\pm6$) and C-4 ($\delta^{13}C=-13\pm4$) (Boutton, 1991) plant sources to atmospheric carbonaceous aerosols.

1.3 Mexico City field studies

The Mexico City metropolitan area (MCMA) is the largest urban center in North America. Due to the high traffic densities and increased energy usage, Mexico City suffers from high levels of particulate BC pollution. The presence of highly absorbing aerosols in Mexico City has lead to a reduction in solar flux of 17.6% (Raga et al., 2001). The mass of absorbing aerosols exported from the MCMA into the surrounding region is estimated to be 6000 metric tons per day or 2 mega-tons per year (Gaffney et al., 1999). Since freshly formed combustion aerosols are hydrophobic, they are expected to be more resistant to washout and have longer lifetimes than more hygroscopic aerosols such as sulfate and nitrate (Gaffney and Marley, 2005; Dua et al., 1999). In addition, since Mexico City is at an altitude of 2250 m (7300 ft), these aerosols are introduced into the atmosphere at altitudes considered to be in the free troposphere elsewhere.

The absorbing aerosols exported from the Mexico City basin are therefore assumed to have longer lifetimes than aerosols released at lower altitudes (Raga et al., 2001). Thus, the MCMA can be a major source of carbonaceous aerosols to the surrounding regions impacting the radiative balance and climate on a regional scale.

In order to better understand the sources of absorbing aerosols in the Mexico City basin and their impact on regional climate, the Mexico City 2003 field study was conducted in April of 2003, as part of the US Department of Energy's (USDOE) Atmospheric Science Program (ASP). This study was conducted in collaboration with the Mexico City Metropolitan Area 2003 (MCMA 2003) air quality study organized by M. J. Molina and L. T. Molina of the Massachusetts Institute of Technology. Aerosol absorption measurements were made as a function of wavelength at the Centro Nacional de Investigación y Capacitación Ambiental (CENICA), on the Iztapalapa campus of the Universidad Autónoma Metropolitana (UAM). Fine (<1 micron) aerosol samples were also collected on quartz fiber filters and these samples were analyzed for carbon isotopic composition ($^{13}C/^{12}C$ ratios and ^{14}C activities) to determine the sources of the absorbing carbonaceous aerosols in the MCMA.

In March 2006, a multiagency field campaign was undertaken in Mexico City called the Megacity Initiative: Local and Global Research Observations (MILAGRO). The MILAGRO study was composed of four collaborative field experiments, including the Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex) sponsored by the USDOE/ASP. The MAX-Mex field study was focused on the investigation of the direct radiative effect of aerosols in the Mexico City plume as a function of time, location, and processing conditions. Aerosol absorption measurements were obtained as a function of wavelength at the Instituto Mexicano del Petroleo (IMP), in the northwestern part of the MCMA. This site, known as T0, was chosen to represent the fresh emissions from the urban center. Fine aerosol samples were collected at site T0 and also at the Technological University of Tecamac, located 18 miles northwest of T0 for the determination of carbon isotopic composition. This second site, known as T1, was expected to represent a mixture of fresh and aged pollutants as they exit the basin.

Results are presented here for AAEs calculated from aerosol absorption measurements at seven wavelengths obtained by a seven-channel aethalometer located in Mexico City during the two field campaigns in April 2003 and March 2006. During both study periods substantial biomass burning events were observed, which were found to affect the aerosol absorption. The AAEs were compared to both stable and radiocarbon isotopic measurements made on the aerosol samples collected at the same time in order to evaluate the sources of carbon that give rise to the observed differences in aerosol absorption properties.

2 Experimental methods

2.1 Sample sites

In 2003, measurements of aerosol absorption were obtained from 3 April (day 93) to 1 May (day 121) on the rooftop of the CENICA laboratory building (19°21′44.541″ N, 99°04′16.425″ W, elevation of 2247 m above sea level) on the Iztapalapa campus of the Universidad Autonóma Metropolitana (UAM) [Calle "Sur 10" No. 230, Colonia La Vicentina, Delegación Iztapalapa, México, D.F.]. The UAM consists of 30 buildings on a campus of restricted traffic flow. It is located in the northeastern section of the MCMA in an area dominated by low cost housing and small industries.

In 2006, measurements were also obtained from 10 March (day 69) to 29 March (day 88) at the Instituto Mexicano de Petroleo Laboratories (IMP) (Eje Central Lazaro Cardenas No. 152, Delegación Gustavo A. Madero, México, Districto Federale). This site, known as T0, is located in the north central part of Mexico City (19°29′ N, longitude 99°09′ W, altitude of 2240 m above sea level) ~16 km (10 mi) north-northeast of the CENICA site. The IMP complex is a restricted campus of 33 buildings located in an industrial and commercial area of Mexico City surrounded by streets that are very heavily trafficked by light duty vehicles and diesel busses. The nearest major roads are approximately 300 m away from the measurement site.

Measurements were also obtained in 2006 from 1 March (day 60) to 29 March (day 88) at the Technological University of Tecamac, State of Mexico, 30 km (18 mi) north of Mexico City. This site, known as T1, is at latitude 19°43′ N and longitude 98°58′ W at an elevation of 2340 m above sea level. The main transportation route is the public road No. 85, which runs south to north through the area from Mexico City to Pachuca. The municipality of Pachuca, which is located 94 km (58 mi) northeast of Mexico City and 64 km (40 mi) northeast of Tecamac, is also a potential source of emissions for Tecamac.

2.2 Aerosol absorption

The absorption of fine aerosols was measured by using a seven-wavelength aethalometer (Thermo-Andersen) with a sample inlet designed to collect aerosols in the size range of 0.1–2 μm. The aethalometer is currently the best method available for the measurement of aerosol AAEs in the field. This is the only instrument that allows for the measurement of aerosol absorption at more than 2 wavelengths and includes the UVB and UVA spectral range. Since most of the enhanced absorption occurs in the UVB and UVA range, instruments that only use visible wavelengths will underestimate the AAEs. However, the use of the aethalometer has been met with some controversy due to errors introduced by depositing the aerosol particles on a filter substrate prior to measurement (Schmid et al., 2005; Arnott et al., 2005).

The aerosols in the air sample are collected within the instrument by continuous filtration through a paper tape strip. The optical attenuation of light transmitted through the deposited aerosol particles is then measured sequentially at seven wavelengths (370, 450, 520, 590, 660, 880, and 950 nm) by changing the source. As the sample is deposited on the paper tape strip, light attenuation increases steadily. At high sample loadings, the high absorption causes the instrument sensitivity to decrease. Therefore, the instrument automatically advances the tape to a new sample spot when light attenuation becomes severe.

Scattering from the filter surface causes a reduction in light intensity not associated with absorption, which results in a positive error in the attenuation measurement. In addition, multiple scattering of light at the filter surface causes an increase in path length, which changes as the filter becomes more heavily loaded (Arnott et al., 2005). Under normal operating conditions, the instrument calculates the BC content of the sample from the optical attenuation measurements, assuming that BC is the main absorbing aerosol species in the samples (Hansen et al., 1982). In this mode the errors associated with the filter substrate become more important and must be corrected. However, as long as the errors are constant over the seven wavelengths used by the instrument, they will not be important in the calculation of aerosol AAEs.

For a given mass of BC, the optical attenuation measured by the aethalometer is given by

$$\mathrm{ATN}(\lambda) = \sigma(1/\lambda) \times [\mathrm{BC}], \tag{2}$$

where [BC] is the mass of black carbon in the sample and σ $(1/\lambda)$ is the wavelength dependent mass absorption efficiency. The aethalometer results of BC aerosol concentrations (μg/m^3) were converted to aerosol optical absorption (m^{-1}) at each wavelength by using the manufacturer's values for σ. The calculated aerosol absorption measurements were recorded at five-minute intervals for each of the seven wavelengths. The results reported here are one-hour averages of the five minute measured values. Measurements obtained just prior to and immediately after the filter tape advance were discarded as outliers (Arnott et al., 2005). The AAEs were calculated by a least squares fit of the seven wavelength aerosol absorption values to Eq. (3).

$$\ln(A) = -\alpha \ln \lambda + \ln \beta \tag{3}$$

2.3 Aerosol sampling

Samples of fine (<1.0 micron) aerosols were collected by using high volume samplers (Hi-Q Environmental Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). The samplers were equipped with brushless, three stage centrifugal fan blowers controlled by an electronic mass flow sensor that detects changes in the operator's pre-set flow rate caused by changes in temperature, barometric pressure, and pressure drop due to particulate loading on filter media. The high-volume sampler compensates for these changes by adjusting the motor speed to maintain the pre-set flow rate at 40 scfm. Three separate LCDs display elapsed time, total volume of air sampled, and instantaneous flow rate.

The aerosol samples were collected on 8 in×10 in glass fiber filters (Whatman) in 2003 and quartz fiber filters (Pall Life Sciences) in 2006. The samples were taken at 12-h intervals from 05:30 to 17:30 and from 17:30 to 05:30 local standard time (LST). The volume of air sampled during the 12-h time period averaged 740 m^3 with an average aerosol loading of 13 mg total carbon content (18 $\mu g/m^3$; σ=5 $\mu g/m^3$).

2.4 Carbon measurements

A low-temperature oxygen plasma was used to oxidize the organic carbon in the samples collected in 2003 to CO_2 (Rowe and Steelman, 2002). A custom-built plasma oxidation apparatus allowed the concomitant collection of CO_2 in a glass tube while the reaction progressed. Glow discharges were produced by radio frequency (RF) capacitive coupling with two external copper electrodes on either end of a 12 cm×4.6 cm glass sample chamber. Vacuum conditions were maintained with a turbomolecular pump and a diaphragm fore pump. Successive oxygen plasmas (1 torr O_2 and 100 W) were used to clean the empty sample chamber until only ≤1 μg carbon was remaining. Each ∼60 cm^2 aerosol filter was inserted into the sample chamber under a positive pressure to prevent the introduction of atmospheric CO_2 or particulates. After a one-hour argon plasma exposure (1 torr Ar and 40 W) to remove adsorbed gases, a one-hour oxygen plasma (1 torr O_2 and 100 W) converted the organic material on the glass fiber filter to CO_2 and H_2O. A second oxygen plasma was performed to ensure quantitative transfer of carbon from the filter. The combined CO_2 was reduced to make a graphite target for accelerator mass spectrometry (AMS) ^{14}C measurement, performed at Lawrence Livermore National Laboratory's Center for Accelerator Mass Spectrometry (CAMS).

The samples collected in 2006 were converted to CO_2 by thermal combustion. Each samples was sealed under vacuum in a quartz tube with copper oxide, metallic copper and silver and combusted at 900°C. The CO_2 produced from combustion was cryogenically isolated from other combustion products and its amount measured manometrically. The CO_2 was then converted to graphite by hydrogen reduction using an iron catalyst. The resulting graphitic carbon was then pounded into an Al target and the $^{14}C/^{12}C$ ratios were measured by accelerator mass spectrometry at Lawrence Livermore National Laboratory. The data were reported as the fraction of modern carbon (fM) in the total carbon of the aerosol sample (Stuiver and Polach, 1977).

Samples of CO_2 were also isolated by thermal combustion of the aerosol samples for the determination of ^{13}C content by stable isotope ratio mass spectrometry. Isotope ratio measurements of CO_2 were made using a Carlo Erba NCS 2500 Elemental Analyzer coupled to a Thermo Finnigan Delta Plus XL triple-collector gas source mass spectrometer. Masses 44, 45, and 46 (CO_2+ions) were measured in the sample and standard gases. Isotope ratios were calculated by comparison with those of two L-glutamic acid references, USGS-40 ($\delta^{13}C=-26.39$) and USGS-41 ($\delta^{13}C=+37.63$) analyzed concurrently with the samples. All references were matrix matched to the aerosol samples by addition of quartz filters to each reference. Vanadium pentoxide was added to all references and samples to ensure complete combustion in the elemental analyzer. Reference CO_2 samples were calibrated to NBS-20 standard (Solenhofen Limestone). The absolute $^{13}C/^{12}C$ ratio in NBS-20 is 0.011:225:3 (Craig, 1957). Results are reported in conventional delta (δ) notation.

$$\delta^{13}C=(R\text{sample}/R\text{standard}-1) \times 1000 \qquad (4)$$

where R is the atom ratio $^{13}C/^{12}C$, and is expressed in units of per mil (‰) deviation relative to the isotopic reference material standard, VPDB, for which $\delta^{13}C$ is defined as 0.00‰ (Coplin et al., 2006). The analytical uncertainties of the $\delta^{13}C$ values reported here are ±0.3‰.

3 Results and discussion

3.1 Aerosol absorption

The aerosol AAEs calculated for Mexico City in April 2003 and March 2001 are shown in Fig. 1. In 2003 the AAE varied from 0.76 to 1.56 with an overall average of 1.05. The AAEs determined at site T0 in 2006 were slightly lower with a range of 0.54 to 1.52 and an average of 0.94. Figure 2 shows the AAEs averaged over the morning (06:00–12:00 LST) and afternoon (12:00–18:00 LST) hours for April 2003 and March 2006. For the majority of days during both studies, the afternoon AAEs were higher than the morning values. This suggests the photochemical formation of secondary absorbing aerosols (SOA) in the afternoon that have excess absorbance in the UV, resulting in higher AAEs than observed from the fresh morning emissions. During 2003, this difference between morning and afternoon AAEs ranged from 0.08 to 0.29 with an average of 0.14, excluding day 99. The afternoon of day 99 was dominated by a particularly turbulent thunderstorm (see Fig. 3) that lofted fine dust, accompanied by heavy cloud cover that significantly reduced solar radiation in Mexico City during the day. Fine dust aerosols have been associated with low AAEs (Meloni et al., 2006). In addition, the reduced solar flux caused by increased cloud cover would result in decreased photochemistry and decreased production of secondary aerosols (Tang et al., 2003). This resulted in the evening AAE being lower than the morning AAE value for day 99.

The last week of March 2006 (after day 82) was again dominated by heavy thunderstorms accompanied by large amounts of dust lofting and heavy cloud cover (see Fig. 3). This period resulted in AAEs that were lower than the rest of the study period in 2006 and were also essentially the same for both morning and afternoon hours. During the remaining period, excluding the days 82 through 88, the difference between morning and afternoon absorption exponents ranged from 0.06 to 0.22 with an average of 0.13, resembling the results obtained in 2003.

The values of the AAEs averaged over the nighttime hours (18:00–06:00 LST) were consistently intermediate between morning and evening values during both field studies. This is due to a combination of the venting of the aged pollutants in the basin at night (de Foy et al., 2006) and fresh evening emissions replacing them. The resulting nighttime aerosols remaining in the basin are a mixture of some photochemically aged aerosols from the previous afternoon and freshly emitted aerosols at night yielding AAEs that fall between those typical of fresh emissions and those of photochemically aged aerosols.

The highest AAEs observed in 2003 occurred during the last week of April (days 116 to 120), with hourly averages ranging from 0.9 to 1.6 and an overall average of 1.2 (see Fig. 1). Satellite data has shown that plumes from widespread biomass fires in the Yucatan heavily impacted the Valley of Mexico during the entire month of April 2003 with the highest impacts on Mexico City during the last week of April (Massie et al., 2006). True-color satellite images clearly show smoke plumes that originate from the Mexico-Guatemala border impacting Mexico City on 18 April (day 108), which was also a period of high absorption exponents (Massie et al., 2006). Therefore, a substantial amount of the background carbonaceous aerosol affecting Mexico City during the later study period in 2003 was due to long-range transport of aged biomass burning particulate matter from the Yucatan. These results agree with previous studies that show aerosols associated with biomass burning typically have higher AAEs than aerosols produced by the combustion of fossil fuels (Hoffer et al., 2006; Kirchstetter et al., 2004).

3.2 Carbon-14 measurements

The fM values measured in the fine aerosol samples collected in Mexico City are shown in Fig. 4. At the CENICA site in April 2003, the fM ranged from 0.56 to 0.86 with an average of 0.70. The fM in samples collected in March 2006 ranged from 0.42 to 0.75 with an average of 0.60 at site T0 and from 0.55 to 0.96 with an average of 0.76 at site T1. Overall, the absorbing aerosols produced in the Mexico City basin consisted of approximately 70% biogenic materials. These biogenic aerosol components can be derived either from biomass burning or from SOA formation from biogenic precursors.

The reported values of fM for some other urban areas are listed in Table 1. Early measurements made in Los Angeles and Denver previous to the year 2000 resulted in lower fM values reflecting a higher percentage of fossil fuel derived materials (Hildeman et al., 1994; Klinedinst and Currie, 1999). The major sources in the Los Angeles area at this time were estimated to be meat cooking operations (17%), diesel vehicles (14%), paved road dust (14%), fireplaces (12%), and non-catalyst equipped gasoline vehicles (11%). More recent measurements in the US have resulted in larger fM values reflecting a lower percentage of fossil-derived absorbing carbon. This is possibly a result of implementing tighter controls on motor vehicle emissions and the addition of biofuels throughout the US (Gaffney and Marley, 2000) compounded by little control of open burning.

The very high fM values reported for Launceston, Tasmania in Table 1 were attributed to residential wood burning in the wintertime with 1/3 of households using wood heaters or open fireplaces (Jordan et al., 2006). The high fM values observed in Nashville and Tampa during the summertime were attributed to secondary organic aerosol formation (Lewis and Stiles, 2006; Lewis et al., 2004).

The fM values measured at site T0 in 2006 (average of 0.6) was generally lower than that measured in Mexico City in 2003 (average of 0.7) and this also correlates well with the higher AAEs obtained for 2003. This is likely due to the larger impact of biomass burning in 2003 from the widespread Yucatan fires. In addition, the evening values of the fM values were consistently higher by about 0.1 (10%) than the morning values. This is consistent with the formation of SOA in the afternoon and is also correlated with the higher AAEs observed in the afternoon.

The fM value measured at site T1 in 2006 (average of 0.76) was generally higher than that measured at either site T0 in 2006 or at CENICA in 2003. Site T1 was heavily impacted by local grass fires during most of the study period and this resulted in higher measured fM values in the aerosol samples. While multi-wavelength aethalometer measurements were not available at site T1, an estimate of the AAEs at site T1 have been reported elsewhere (Marley et al., 2008). A comparison of the daily absorbance

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maxima reported at 880 nm for days 74 through 85 (Doran et al., 2007) with those recorded by a particle soot absorption spectrometer (PSAP) at 560 nm (Marley et al., 2008) yielded an average AAE of 2.1 at site T1. This is consistent with the previous results reported for aerosols impacted by biomass burning (Hoffer et al., 2006; Kirchstetter et al., 2004). The fM values measured at site T1 during the last few days of 2006 were lower than those during the rest of the study period due to heavy rains that extinguished the local fires thus reducing the biomass input to the aerosol carbon

The AAEs averaged over the same time periods used to collect the aerosol samples for radiocarbon analysis were compared to the fM value on each sample. The correlation between the fM values and the AAEs of the Mexico City aerosols is shown in Fig. 5. Estimates of the corresponding AAEs for site T1 have been calculated from data reported elsewhere (Doran et al., 2007; Marley et al., 2008). In general, those samples that have high fM values also show higher AAEs. The results obtained at site T0 in 2006 are most consistent with fresh carbon emissions. Those for 2003 are somewhat higher and consistent with a mixture of fresh urban emissions and aged biomass emissions. The two highest points shown in Fig. 5 for 2003 were obtained during the last week of the study period when Mexico City was impacted the most by aged biomass burning aerosols from the fires in the Yucatan. The results for site T1 in 2006 are highest and more typical of a larger impact of the low temperature grass fires in the area.

3.3 $^{13}C/^{12}C$ ratios

The $\delta^{13}C$ values of the aerosol samples collected in Mexico City in 2003 ranged from −22 to −30‰ with an average of −26‰; while those measured at site T0 in 2006 were similar, ranging from −23 to −28‰ with an average of −25‰ (see Fig. 6). These values are in the range of biogenic material from trees, shrubs and other C-3 plants. The $\delta^{13}C$ of the fine aerosol samples collected at T1 in 2006 were somewhat higher, ranging from −15 to −27‰ with an average of −23‰ indicating a mixture of biogenic materials from C-3 trees and shrubs with significant input from the C-4 grass fires in the area.

The relationship between the δ^{13}C and fM values of the aerosol samples is shown in Fig. 7. The samples from site T1 are generally higher in both δ^{13}C and fM than the samples collected at site T0 in 2006 again indicating the influence of local grass fires in the vicinity of site T1. While the fM values of the aerosol samples collected in 2003 are closer to those from site T0 than those from site T1 in 2006, the δ^{13}C values were lower at T0 in 2006. This is another indication of input from the Yucatan fires in 2003, which were C-3 forest fires that would result in lower δ^{13}C values.

4 Conclusions

The results of this study clearly indicate that there can be substantial differences in the AAEs of atmospheric carbonaceous aerosols and that these differences can be correlated to the sources of the carbon. While carbonaceous aerosols produced from the combustion of fossil fuels have Ångstrom coefficients near 1 (Bergstrom et al., 2002), this work clearly demonstrates significant variations in the absorption of UVB-Visible radiation for carbonaceous aerosols derived from both secondary photochemical processes and from biomass burning events. This is consistent with the fact that the organic aerosol components derived from these sources have significant amounts of partially oxidized functional groups present in the molecules. These include chromophores such as conjugated carbonyls, oxidized and nitrated PAH derivatives, and other molecular structures that serve to enhance absorption in the UVB-visible region leading to changes in the observed Ångstrom coefficients from a value of about 1 to values ranging from 0.75 to 2.8. This variation has been found to correlate with biomass burning as indicated from stable carbon isotope ratios and radiocarbon activities.

The radiocarbon results clearly indicate a significant impact from modern carbon aerosol sources even in the urban area, and these aerosols have absorption properties much different than those derived from fossil fuel combustion. These biomass sources could include both grass and forest fires as well as trash-burning in the megacity environment. Two types of biomass burning events that occurred during the 2003 and 2006 studies allowed for the impact of biomass burning on Ångstrom coefficients to be examined. These results indicate the low temperature grassfires that occurred near site T1 in 2006 resulted in aerosols with significantly higher AAEs than the higher temperature and more remote forest fires that impacted Mexico City in 2003.

The variance observed in the AAEs clearly needs to be taken into account in areas where significant photochemical production of SOA is occurring, such as in megacity environments and downwind of these sites, as well as in areas where significant biomass burning occurs. This is important not only for the determination of aerosol radiative impacts but also for the interpretation of remote sensing of absorbing aerosols by satellites such as TOMS or OMI as well as in reconciling the results of BC mass measurements obtained by different methods. As well, the variances in UV region absorption by carbonaceous aerosols from various sources will also need to be considered in modeling photochemical production of oxidants, particularly in biomass burning regions.

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Table 1. Fraction of modern carbon (fM) reported for some urban areas.

Site	Sample	Season	Year	fM average (range)	Reference
Los Angeles, Ca	PM_{10}	S	1982	0.31	Hildemann et al. (1994)
Los Angeles, Ca	PM_{10}	W	1982	0.41	Hildemann et al. (1994)
Long Beach, Ca	PM_{10}	S	1982	0.49	Hildemann et al. (1994)
Long Beach, Ca	PM_{10}	W	1982	0.47	Hildemann et al. (1994)
Denver, Co	$PM_{2.5}$	S	1996	0.44 (0.09–0.70)	Klinedinst and Currie (1999)
Denver, Co	$PM_{2.5}$	W	1996–1997	0.27 (0.13–0.72)	Klinedinst and Currie (1999)
Nashville, Tn	$PM_{2.5}$	S	1999	0.69 (0.56–0.80)	Lewis et al. (2004)
Houston, Tx	$PM_{2.5}$	S	2000	0.54 (0.27–0.77)	Allen (2001)
Tampa, Fl	$PM_{2.5}$	S	2002	0.75 (0.55–0.95)	Lewis and Stiles (2006)
Zurich, Ch	$PM_{2.5}$	S	2002	0.63 (0.60–0.67)	Szidat et al. (2004)
Launceston, Au	PM_{10}	W	2003–2004	0.95 (0.86–1.0)	Jordan et al. (2006)
Seattle, Wa	$PM_{2.5}$	S	2004	0.55 (0.38–0.64)	Bench et al. (2007)
Seattle, Wa	$PM_{2.5}$	W	2004–2005	0.58 (0.46–0.69)	Bench et al. (2007)
Tokyo, Jp	$PM_{2.1}$	S	2004	0.38 (0.31–0.50)	Takahashi et al. (2007)
Tokyo, Jp	$PM_{2.1}$	W	2004–2005	0.47 (0.41–0.54)	Takahashi et al. (2007)
Phoenix, Az	$PM_{2.5}$	S	2005	0.60 (0.49–0.75)	Bench et al. (2007)
Phoenix, Az	$PM_{2.5}$	W	2005–2006	0.53 (0.49–0.59)	Bench et al. (2007)

Note: $PM_{2.1}$ is particulate matter less than 2.1 microns, $PM_{2.5}$ is particulate matter less than 2.5 microns, PM_{10} is particulate matter less than 10 microns. S is summer, W is winter.

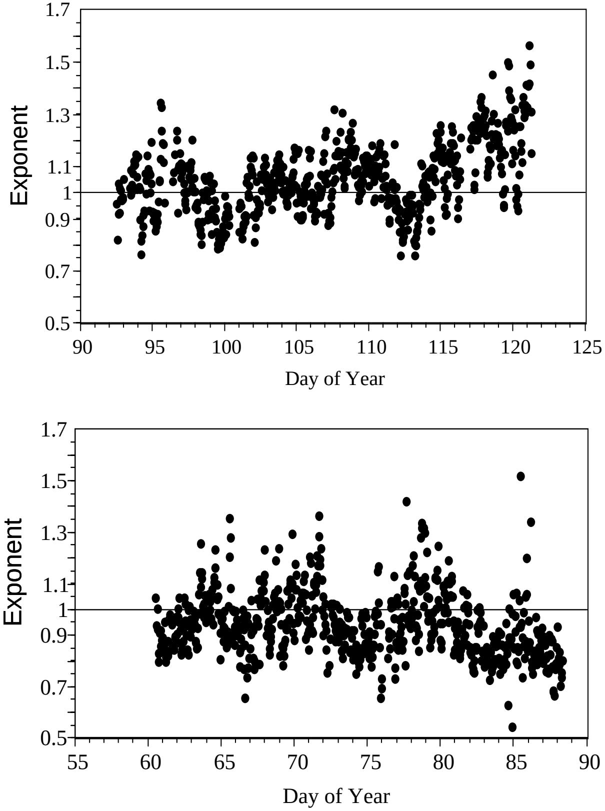

Fig. 1. Aerosol absorption Ångstrom exponents calculated from aerosol absorption measured at 7 wavelengths in Mexico City during April 2003 (top) and March 2006 (bottom).

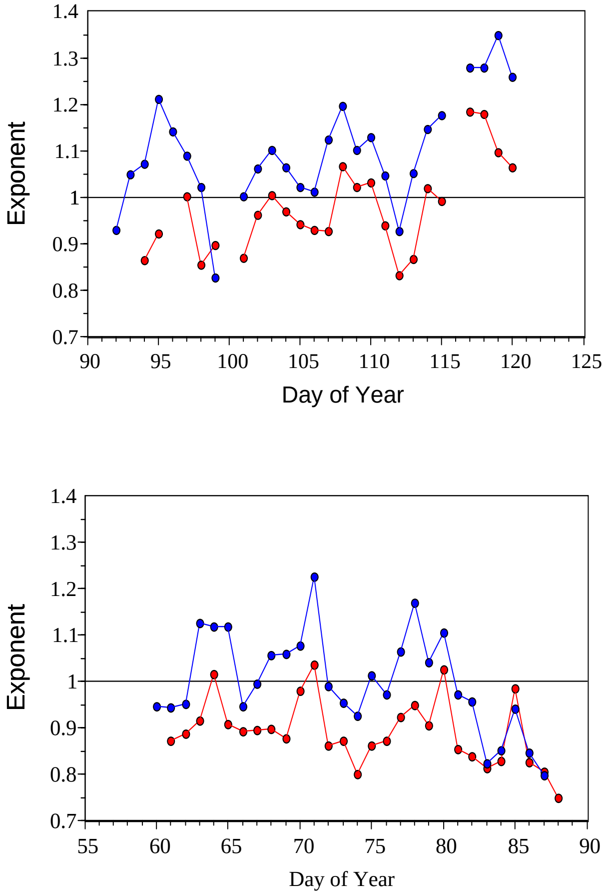

Fig. 2. Aerosol absorption Ångstrom exponents calculated for morning (red) and afternoon (blue) hours in Mexico City during April 2003 (top) and March 2006 (bottom).

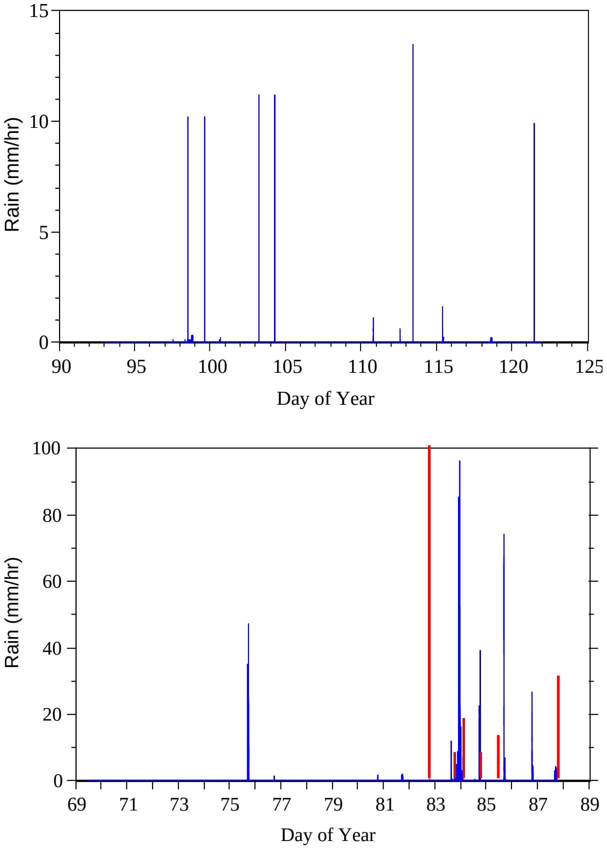

Fig. 3. Rain intensity measured at CENICA in April 2003 (top) and T0 (red) and T1 (blue) in March 2006 (bottom).

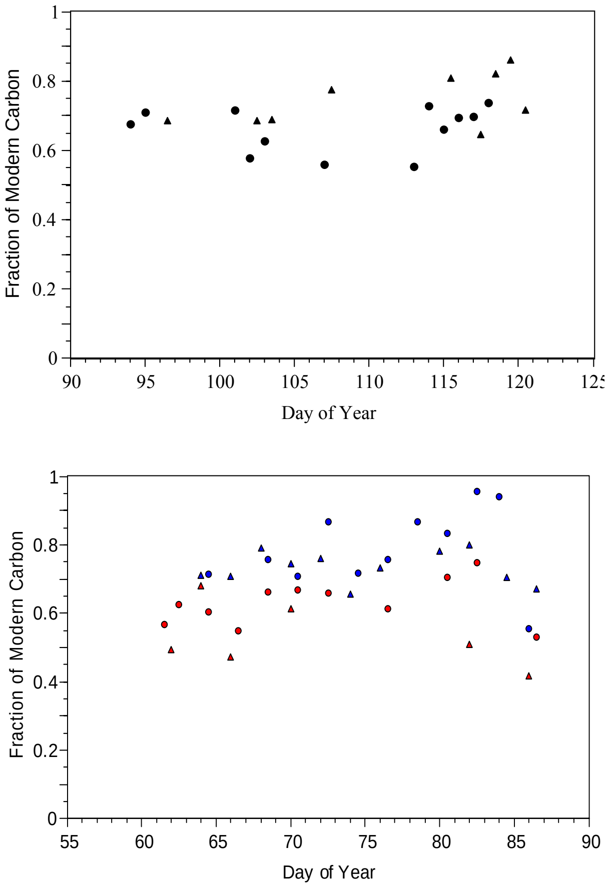

Fig. 4. Fraction of modern carbon in daytime (•) and nighttime (▲) fine aerosol samples collected at CENICA in Mexico City in April 2003 (top) and at sites T0 (red) and T1 in (blue) March 2001 (bottom).

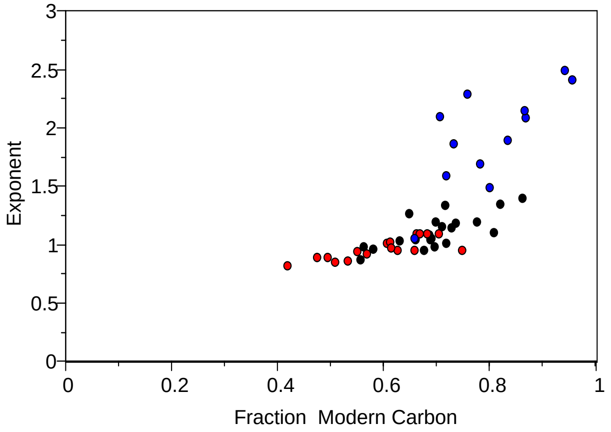

Fig. 5. Aerosol absorption Ångstrom exponents as a function of the fraction of modern carbon determined in Mexico City during April 2003 (black) and March 2006 at site T0 (red) and site T1 (blue).

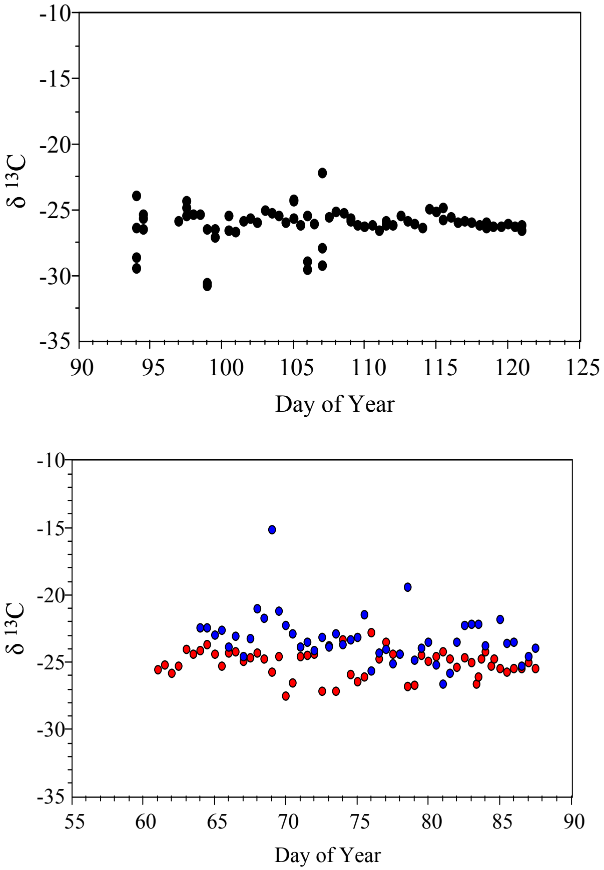

Fig. 6. Carbon-13 content in fine aerosol samples collected at CENICA in Mexico City in April 2003 (top) and at sites T0 (red) and T1 (blue) in March 2001 (bottom) expressed as δ^{13}C, the ratio of ^{13}C/^{12}C in units of per mil (‰) deviation relative to the standard reference VPDB.

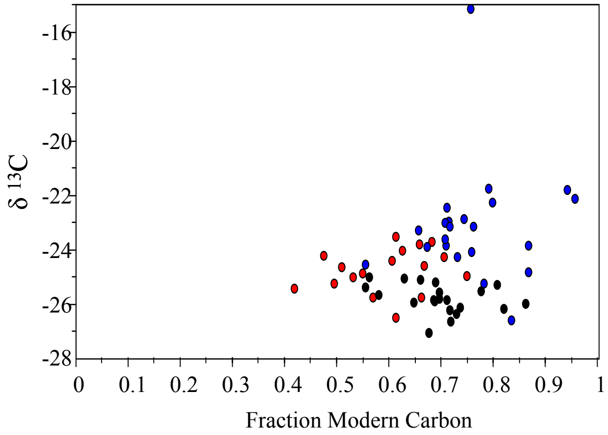

Fig. 7. Carbon-13 content (δ^{13}C) in fine aerosol samples as a function of the fraction of modern carbon (fM). Samples were collected at CENICA in Mexico City in April 2003 (black) and at sites T0 (red) and T1 (blue) in March 2001.