

Measurements of aerosol absorption and scattering in the Mexico City Metropolitan Area during the MILAGRO field campaign: a comparison of results from the T0 and T1 sites

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Abstract. In March 2006, a multiagency field campaign was undertaken in Mexico City called the Megacities Initiative: Local and Global Research Observations (MILAGRO). Two of the five field components of the MILAGRO study focused a major part of their efforts on atmospheric particulate emissions from the Mexico City basin and their effects on radiative balance as a function of time, location and processing conditions. As part of these two MILAGRO components, measurements of aerosol optical properties were obtained at a site located in the northern part of Mexico City (T0) and also at a site located 29 km northwest (T1) to estimate the regional effects of aerosol emissions from the basin.

Measurements of aerosol absorption and scattering for fine mode aerosols were obtained at both sites. Aerosol absorption at 550 nm was similar at both sites, ranging from 7–107 Mm⁻¹ at T0 and from 3–147 Mm⁻¹ at T1. Aerosol scattering measured at 550 nm at T0 ranged from 16–344 Mm⁻¹ while the aerosol scattering values at T1 were much lower than at T0 ranging from 2–136 Mm⁻¹. Aerosol single scattering albedos (SSAs) were calculated at 550 nm for the fine mode aerosols at both sites using these data. The SSAs at T0 ranged from 0.47–0.92 while SSAs at T1 ranged from 0.35–

0.86. The presence of these highly absorbing fine aerosols in the lower atmosphere of the Mexico City area will result in a positive climate forcing and a local warming of the boundary layer in the region.

Broadband UVB intensity was found to be higher at site T0, with an average of 64 μW/cm² at solar noon, than at site T1, which had an average of 54 μW/cm² at solar noon. Comparisons of clear-sky modeled UVB intensities with the simultaneous UVB measurements obtained at sites T0 and T1 for cloudless days indicate a larger diffuse radiation field at site T0 than at site T1. The determination of aerosol Ångström scattering coefficients at T0 suggests that this is due to the predominance of aerosols in the size range of 0.3 micron, which leads to scattering of UVB radiation peaked in the forward direction and to an enhanced UVB radiation observed at ground level. This enhancement of the UVB diffuse radiation field would explain the enhanced photochemistry observed in the Mexico City area despite the reduction in UVB anticipated from light absorbing species.

1 Introduction

Megacities, large urban and suburban centers whose populations exceed ten million inhabitants, are steadily increasing worldwide with the most rapid growth in the tropical



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areas of South America and Asia. In 1800 only 3% of the world's population lived in urban areas. This increased to 47% by the end of the 20th century. In 1950 there were 83 cities with populations exceeding one million and New York City was the only megacity (UNEP/WHO, 1992). By 2007 there were 468 urban centers of more than one million and of these 14 are classified as megacities with the largest metropolitan complexes centered at Tokyo, Japan, and Mexico City, Mexico (Molina and Molina, 2002). If this trend continues, the world's urban populations will double every 38 years and within the next 10 to 15 years it is predicted that there will be more than 30 megacities worldwide.

The Mexico City metropolitan area (MCMA) is the largest urban center in North America and the second largest megacity worldwide. It occupies $\sim 3540 \text{ km}^2$ with a population of ~ 19 million (CAM, 2002). In general, megacities suffer from poor air quality due to the cumulative effects of rapid population growth and industrialization accompanied with increased traffic densities and total energy consumption. However, the topography of the MCMA also acts to exacerbate the poor air quality (Fast et al., 2007; Fast and Zhong, 1998; Doran et al., 1998) as Mexico City is located in a basin on the central Mexican plateau at an altitude of 2240 m and latitude of 19° N . The basin is surrounded on the west, south, and east by mountain ranges that rise up to 1000–3000 m above the basin floor. This topography serves to inhibit dispersion of emissions within the basin during the early morning hours and the high levels of incoming solar radiation at this latitude and elevation promotes atmospheric photochemical reactions that rapidly form secondary pollutants (Whiteman et al., 2000).

Due to the elevation and topography of Mexico City, the height of the boundary layer may reach up to 2–4 km above the surface (Raga et al., 2001a; de Foy et al., 2007). Therefore, pollutants are emitted from the basin at altitudes that are considered to be free troposphere elsewhere and are expected to travel long distances affecting the surrounding regions (Gaffney and Marley, 1998; Williams et al., 2002). Modeling results have indicated that the effects of this exported pollution can impact background levels 300 km or more from the urban area (Barth and Church, 1999; Whiteman et al., 2000). Indeed, past studies have found that the Mexico City air pollutants are typically vented during the late afternoon on a daily basis (Gaffney and Marley, 1998; Whiteman et al., 2000)

Past studies in the Mexico City area have estimated that emissions from the basin contribute 15 megatons of fine aerosol ($\text{PM}_{2.5}$) per year to the surrounding regions (Gaffney et al., 1999). This fine aerosol was found to be composed of approximately 32% organic carbon (OC), 15% elemental carbon (EC), 10% ammonium nitrate and 20% ammonium sulfate by elemental and thermal/optical methods (Chow et al., 1993, 2001, 2002; Vega et al., 2004). More recently, in 2003 the composition of fine aerosols was found to be 11% black carbon (BC), 32% OC, 13% ammonium nitrate, and

14% ammonium sulfate by aerosol mass spectrometry and optical attenuation methods (Salcedo et al., 2006; Aiken et al., 2008). This is an indication that although the emissions of reactive hydrocarbon have been reduced in the city due to the significant number of newer vehicles with catalytic converters that have replaced older higher emission vehicles, the aerosol composition has not changed significantly likely due to the lack of controls on diesel vehicles and biomass burning in the region (Marley et al., 2007). Thus, while air quality and ozone production has improved, Mexico City and 25 other megacities continue to be a major source of black carbon aerosols, which can be an important species in determining regional radiative balance and climate.

While sulfate is well known as an important light scattering aerosol species contributing to atmospheric cooling (Charlson et al., 1992), BC and associated OC (including secondary organic aerosol, SOA) have more recently gained attention as major light absorbing aerosol species exerting a positive radiative forcing and reinforcing the atmospheric warming due to increases in the greenhouse gases (Jacobson, 2002; Ramanathan et al., 2005). Some model calculations suggest that the contribution of carbon soot aerosols to global warming may be as much as $0.3\text{--}0.4^\circ \text{ C}$, rivaling the contributions from atmospheric methane (Jacobson, 2004; Chung and Seinfeld, 2005). The ultimate climate effects from carbon aerosols will depend on their physical and chemical properties, as well as their residence times and distributions in the atmosphere (Jacobson, 2001).

The presence of the highly absorbing BC aerosols in Mexico City leads to a reduction in overall solar flux of 17.6% locally (Raga et al., 2001b). The mass of these absorbing aerosols exported from this megacity into the surrounding region is estimated to be 6,000 metric tons per day or 2 megatons per year of BC (Gaffney et al., 1999). Since freshly emitted BC 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 the aerosols emitted from the Mexico City basin are introduced into the atmosphere at higher altitudes, they are assumed to have longer lifetimes than similar aerosols released at lower altitudes (Raga et al., 2001b). The MCMA is therefore a major source of BC aerosols to the surrounding regions and the release of these highly absorbing aerosols will have an impact on the radiative balance and climate on a regional scale.

The influences of aerosols on climate are much more complex than those of the greenhouse gasses (Schwartz and Buseck, 2000). Aerosol composition is highly variable, with different species present within the same particle, due to the different sources, production mechanisms and atmospheric transformations (Pósfai et al., 1999). In addition, these different aerosol species can be either internally or externally mixed within the particle yielding different optical and microphysical properties and different radiative effects (Pósfai

et al., 1999; Schnaiter et al., 2005). Aerosol distributions are also variable both spatially and temporally and although aerosol lifetimes are much shorter than those of the greenhouse gases, estimates of their atmospheric residence times range from less than a day to more than a month resulting in transport distances from a few miles to hemispheric scales (Marley et al., 2000; Williams et al., 2002). This variability in composition and distributions makes it difficult to quantify the aerosol impacts on climate and to represent these effects in climate models.

In order to better understand the evolution and transport of pollutant aerosols and gases from emissions in the Mexico City basin and their resulting impacts on regional climate, a multiagency field campaign was undertaken called the Megacities Initiative: Local and Global Research Observations (MILAGRO). The MILAGRO study was composed of five collaborative field experiments. Two of the components of the MILAGRO study focused a major part of their efforts on aerosol emissions. The Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex) was sponsored by the US Department of Energy (DOE) to investigate the direct radiative effect of aerosols in the Mexico City plume as a function of time, location and processing conditions. The MCMA-2006 study, supported by various Mexican institutions, the US National Science Foundation (NSF) and the DOE, deployed ground based instrumentation to examine fine particles and secondary aerosol precursor gas emissions within the Mexico City Basin. As part of these two MILAGRO components, aerosol scattering and absorption measurements were obtained at a site located at the Instituto Mexicano del Petróleo (IMP- Mexican Petroleum Institute), in the northwestern part of the Mexico City center. This site, known as T0, was chosen to represent the fresh emissions within the MCMA. Measurements were also obtained at the Universidad Tecnológica de Tecamac (Technological University of Tecamac), located approximately 29 km northwest of T0. This site, known as T1, was expected to represent a mixture of both fresh and aged pollutants as they exit the basin.

The evolution of absorbing aerosols downwind of Mexico City has been described previously in a comparison of measurements obtained at site T1 with those obtained at site T2 (Rancho La Bisnaga), located approximately 35 km north-northeast of T1 (Doran et al., 2007, 2008; Doran, 2007). This study focused primarily on the changes in the carbonaceous aerosol composition and the resulting effects on the aerosol mass specific absorption coefficients. It was concluded from this work that emission sources outside the MCMA, including biomass-burning sources, are important contributors to the regional aerosol burden. Other aerosol studies conducted in the Mexico City area have reported similar conclusions (Kleinman et al., 2008; Molina et al., 2007; Stone et al., 2008; Yokelson et al., 2007; DeCarlo et al., 2008; Salcedo et al., 2006).

Presented here is a comparison of measurements of aerosol absorption and aerosol scattering at 550 nm obtained at sites T0 and T1 during the MILAGRO campaign. In addition, the mass specific aerosol absorption coefficients were calculated at 550 nm by using total carbon (TC) measurements taken from high-volume quartz filters. These results are compared with absorption coefficients reported previously by Doran et al. (2007). Also reported here is a comparison of UVB radiation measurements obtained simultaneously at sites T0 and T1, under cloudless conditions, with clear sky modeled UVB values. These data are discussed with regard to the light scattering and absorption measurements obtained at both sites.

2 Experimental methods

2.1 Sample Sites

2.1.1 Site T0

Measurements were obtained from 10 March (day 69) to 29 March (day 88) 2006 at the Instituto Mexicano del Petróleo (IMP) laboratories [Mexico, D. F.]. This site, known as T0, is located in the north central part of Mexico City at latitude 19°29' N, longitude 99°09' W, and at an altitude of 2240 m above sea level. The IMP complex is a 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 buses. The nearest major roads are approximately 300 m away from the measurement site.

Relative humidity and rain intensity at site T0 during the study are shown in Fig. 1 (top). Rain events occurred during the last week of the study period, 23–28 March (days 82–87). Daily maximum relative humidity ranged from a low of 35% during the first week to a high of 89% during the last week of March 2006. Winds ranged from 0.1 to 9 m/s with an average of 2 m/s from the south, southwest.

2.1.2 Site T1

Measurements were also obtained from 1 March (day 60) to 29 March (day 88) 2006 at the Technological University of Tecamac, State of Mexico, 30 km north of Mexico City. This site, known as T1, is at latitude 19°43' N and longitude 98°58' W at an altitude of 2340 m a.s.l. Tecamac has a recorded population of 172 410, as of the 2000 census, and is primarily commercial with a total of 3070 small businesses, of which 1923 are food related. The principal mode of transportation in the area consists of light duty vehicles, and small diesel buses. The main transportation route is public road # 85, which runs south to north from Mexico City to Pachuca. The municipality of Pachuca, which is located 94 km north-east of Mexico City and 64 km northeast of Tecamac, is the capital of the state of Hidalgo with a recorded population of 267 751 in 2005.

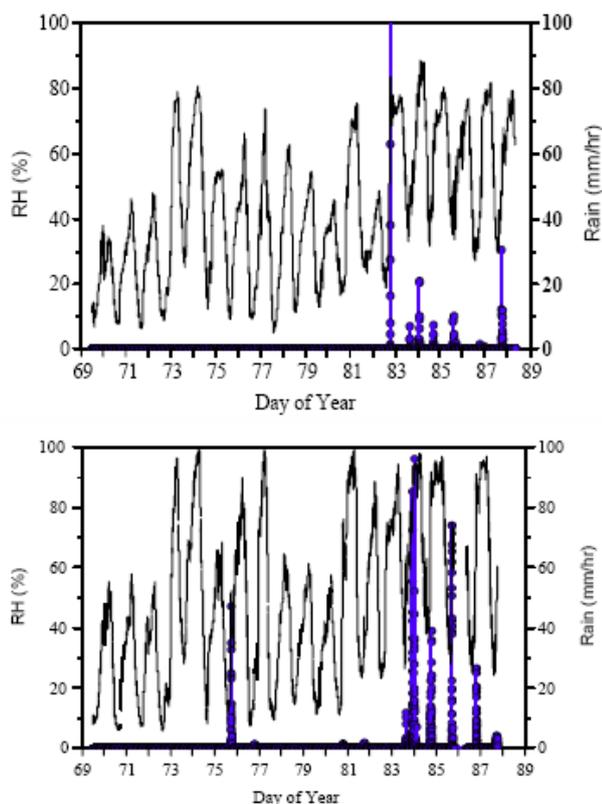


Fig. 1. Relative humidity and rain intensity (blue) measured at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

Relative humidity and rain intensity at site T0 during the study are shown in Fig. 1 (bottom). Rains events occurred at site T1 on 16, 17, 21, 22, and 24–28 March (days 75, 76, 80, 81, 83–87). Relative humidity ranged from a mid-day low of 40% during the first week to a high of 99% during the last week of March 2006. Winds ranged from 0.1 to 10 m/s with an average of 2 m/s from the south, southwest.

Aerosol Optical Properties

2.1.3 Site T0

The aerosol instrumentation at site T0 was located on the rooftop of Building No. 32 (Héctor Lara Sosa Building, IMP) 15 m above ground level. The sample inlets were designed to collect aerosols in the size range of 0.1 to 2 micron aerodynamic diameter (Hermann et al., 2001). Aerosol scattering was measured with a three wavelength integrating nephelometer (TSI Model 3563) operating at 450, 550, and 700 nm (Anderson and Ogren, 1998). Results obtained at 550 nm are reported here.

The instrument was calibrated by using CO₂ according to the manufacturer's specifications. An internal high efficiency particulate filter (HEPA) is used to provide a clean air measurement periodically for background subtraction. The TSI nephelometer was operated at ambient relative humidity. However, two single wavelength (550 nm) nephelometers (Meteorology Research Incorporated) were operated at low (20%) and high (80%) relative humidity for comparison.

Aerosol absorption was measured with a multi-angle absorption photometer, or MAAP (Thermo Electron Model 5012). The aerosols in the air sample are collected within the instrument by continuous filtration through a glass fiber tape strip and the aerosol absorption is determined by measuring the attenuation of 670 nm light as it passes through the particle laden filter. As the sample is deposited on the filter tape, the light attenuation steadily increases. At high sample loadings the high absorption can cause detection limits to increase. To prevent this, the instrument automatically advances the tape to a new sample spot when light attenuation reaches 25% of its initial value. After the tape advance, a background measurement is taken to correct for variations in filter surfaces and source light intensities.

The use of the filter based aerosol absorption methods have been met with some controversy due to artifacts introduced by depositing the aerosol particles on a filter substrate prior to measurement (Schmid et al., 2005; Arnott et al., 2005). Since these instruments rely on the measurement of light transmitted through a particle laden quartz fiber filter, 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. The MAAP represents a significant improvement over other filter-based methods in that it uses multiple detectors to simultaneously measure the light intensity both transmitted through and scattered from the filter tape. The instrument then uses a two-stream-approximation radiative transfer scheme to determine the aerosol absorption. This explicit treatment of light scattering effects caused by the aerosol and filter matrix in the radiative transfer scheme improves the determination of aerosol absorption considerably over methods that rely on the measurement of transmission alone (Petzold et al., 2005).

The MAAP automatically calculates the BC content in the aerosol samples from the aerosol absorption measurements by assuming BC to be the main absorbing aerosol species in the samples with a mass specific absorption coefficient of 6.6 m²/g at 670 nm. However, these results are easily reconverted to the initial aerosol absorption measurement using the manufacturer's absorption coefficient.

The aerosol absorption measurements obtained by the MAAP at 670 nm were corrected to 550 nm for direct comparison of the aerosol scattering measurements. The wavelength dependence of the extinction of light by fine aerosol particles (τ) is defined by Ångström's turbidity formula as $\tau = \beta\lambda^{-\alpha}$; where β , known as the Ångström turbidity coefficient, is the value of τ at a wavelength of 1 μ m and α is

the Ångström exponent. The total aerosol extinction is the sum of aerosol scattering and absorption as described in the expanded turbidity formula,

$$\tau = \beta_s \lambda^{-\alpha_s} + \beta_a \lambda^{-\alpha_a} \quad (1)$$

where α_s is the Ångström exponent for aerosol scattering, α_a is the Ångström exponent for aerosol absorption, and β_s and β_a are the corresponding values of aerosol scattering and absorption at a wavelength of $1 \mu\text{m}$. The wavelength dependence of aerosol absorption can be determined independently by

$$A = \beta \lambda^{-\alpha_a} \quad \text{and} \quad (2)$$

$$\ln(A) = -\alpha_a^* \ln(\lambda) \quad (3)$$

Once determined, α_a can then be used to convert absorption measurements made at one wavelength to values at another wavelength.

The aerosol absorption Ångström coefficients were calculated from Eq. (2) by using aerosol absorption measurements at 7 wavelengths (370, 450, 520, 590, 660, 880, and 950 nm) made with a 7-channel aethalometer (Hansen et al., 1982). The 7-channel aethalometer is currently the best method available for the determination of α_a in the field. The aethalometer is the only instrument available that allows for the measurement of aerosol absorption at more than 2 wavelengths and includes the UVB spectral range. It is important to include the UV measurement in the determination of α_a since most enhanced absorption occurs in this range (Bergstrom et al., 2002; Kirchstetter et al., 2004; Andreae and Gelencser, 2006; Barnard et al., 2008). Therefore, instruments that use only visible wavelengths to determine α_a will greatly underestimate the wavelength dependence of aerosol absorption.

For small spherical particles with a constant refractive index across the wavelength range of interest, $\alpha_a=1$ (Bergstrom, 1973). This has been determined to be a good approximation for aerosols composed mostly of BC or for particles containing a significant fraction of OC over a narrow wavelength range <600 nm (Bergstrom et al., 2002; Kirchstetter et al., 2004). However, the aerosol absorption Ångström coefficients of mixed carbon aerosols containing BC, secondary OC, and primary OC from biomass burning has been found to be closer to 1.5 (Schmid et al. 2006). In areas impacted heavily by biomass burning, α_a can be closer to 2 to 2.5 (Dubovik et al., 1998; Kirchstetter et al., 2004; Swap et al., 2003). It is therefore important to determine α_a at the same time resolution as the absorption measurements to reduce errors in calculating aerosol absorption at different wavelengths. The aerosol absorption Ångström coefficients were calculated simultaneously with the aerosol absorption measurements obtained at 670 nm by the MAAP and these values were used to calculate aerosol absorption at 550 nm. The results obtained for α_a at site T0 varied from 0.54 to 1.52 with an overall average of 0.93 (Marley et al., 2008).

The analog outputs of the MAAP absorption photometer and the nephelometers were monitored continuously and one-minute averages of aerosol absorption and scattering were recorded by a laptop computer operating with LabVIEW software. The data reported here are an hourly running average of the one-minute values for aerosol scattering at 550 nm and aerosol absorption corrected to 550 nm by Eq. (2).

The aerosol scattering measurements made at 550 nm and the aerosol absorption measurements corrected to 550 nm were used to calculate the fine mode aerosol single scattering albedo (SSA). The SSA is defined as the ratio of aerosol scattering to total light extinction (absorption + scattering) as

$$\text{SSA} = \sigma_s / (\sigma_s + \sigma_a) \quad (4)$$

where σ_s is the aerosol scattering coefficient and σ_a is aerosol absorption coefficient. The SSA is therefore the fraction of total light extinction that is due to scattering by aerosols. The results reported here for aerosol SSAs are for the fine mode aerosols only. These are expected to be lower than that for the total aerosol burden due to the fact that the highly absorbing carbonaceous aerosols exist principally in the fine mode. However, the more highly scattering coarse mode aerosols in the size range of 2–10 micron aerodynamic diameter have settling velocities from 60–1000 cm/h and will not be transported as far into the surrounding region unless they are accompanied by high winds and/or are lofted to significant altitude (Finlayson-Pitts and Pitts, 2000).

2.1.4 Site T1

The sample inlet at site T1 was located at a height of 10 m above ground level and collected aerosols in the size range of 0.1 to 2 micron aerodynamic diameter at a flow rate of 16.7 l/min at ambient temperature and pressure. Aerosol scattering was measured at site T1 with a portable integrating nephelometer (Radiance Research Model 903) operating at 530 nm, which was calibrated by comparison to a second nephelometer (Radiance Research Model 903) located at the Universidad Nacional Autónoma de México (UNAM). The scattering measurements were recorded by internal data loggers at 1 min intervals. The stored data was retrieved using a personal computer through an RS232 port. These data are reported here as an hourly running average of these one minute values.

Aerosol absorption was obtained by a particle soot absorption photometer, or PSAP (Radiance Research), which is also a filter based measurement technique. The particle laden air stream is first passed through a primary filter and the aerosol absorption is determined by measuring the light attenuation at 550 nm. The clean air stream is then passed through a second filter adjacent to the primary filter, which is used as a reference in order to ensure that the observed change in primary filter transmittance is not due to changes in the intensity of the light source.

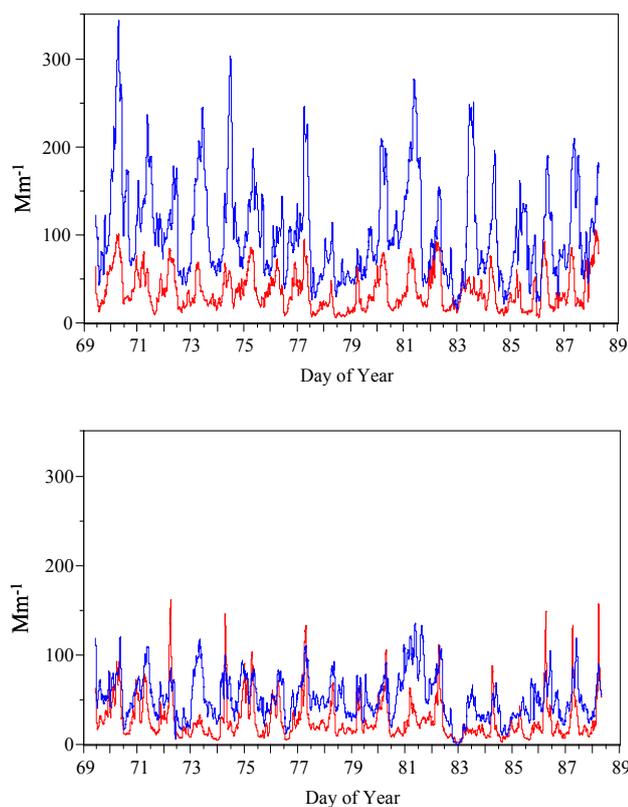


Fig. 2. Measurements of fine (0.1–2 micron) aerosol absorption (red) and scattering (blue) obtained at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

The PSAP is also susceptible to errors associated with measuring light transmission through a particle laden filter substrate. Light scattering from the filter surface as well as multiple scattering within the filter medium results in an enhancement of the absorption measurements (Arnott et al., 2005). The instrument manufacturer has empirically determined calibration factors to correct for both the magnification of the absorption by the filter medium as well as for nonlinearities in the instrument response as the filter is loaded with particulates. The aerosol absorbances (σ_a) reported here for 550 nm were calculated from the measured aerosol absorbances (σ_{meas}) by Eq. (5);

$$\sigma_a = (\sigma_{\text{meas}} - K_1\sigma_s)/K_2 \quad (5)$$

where σ_s is the measured aerosol scattering, $K_1=0.02$, and $K_2=1.2$ (Bond et al., 1999). In addition, transmittance values below 0.5 have been omitted as invalid due to low particle loadings on the filter.

2.2 Meteorology and UV-B measurements

Broadband ultraviolet-B (UV-B) radiation measurements were taken at both site T0 and site T1 with Robertson-Berger (RB) radiometers (Solar Light Co. Model 501). These radiometers record continuous measurement of global (direct + diffuse) broadband ultraviolet radiation from 280–320 nm. Since the output of the detectors vary 1% per degree C, the internal temperatures of the radiometers are maintained at $25 \pm 1^\circ\text{C}$ with Peltier elements inside the housings and the internal temperature is monitored to assure stability. Both radiometers were factory calibrated with a 200 W quartz halogen lamp traceable to NIST. After calibration, stability of the detectors has been shown to be excellent over the life of the meter (Deluisi et al., 1992; Weatherhead et al., 1997; Xu and Huang, 2003). The detector has a spectral response that mirrors the erythemal action spectra (McKinlay and Diffy, 1987). They are calibrated in units of minimum erythemal dose per hour (MED/h) where one MED/h is defined as 0.0583 W/m^2 . Results reported here have been converted to $\mu\text{W/cm}^2$.

Measurements of wind speed, wind direction, rain intensity, pressure, temperature, and relative humidity (RH) were obtained at both sites with weather multi-sensor packages (Vaisala, WXT150). Rain intensity measurements reported here were made by the RAINCAP sensor included in the weather package. The sensor detects the impact of individual raindrops by a piezoelectric sensor. The resulting voltage signal is proportional to the volume of the drop and is converted into total accumulated precipitation. All measurements were collected at a five-minute time resolution with a laptop computer operating with LabVIEW software.

2.3 Total Carbon Determinations

Samples of fine (<1.0 micron) aerosols were collected in Mexico City from 1–28 March 2006 (day 60–day 68) at site T0 and site T1. The Aerosol samples were collected on quartz fiber filters by using high volume samplers (Hi-Q Environmental, Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). The air samplers were equipped with brushless, three stage centrifugal fan blowers controlled by an electronic mass flow sensor that detects changes in 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 1.1 cubic m/min or 40 scfm. Three separate LCD's, display elapsed time, total volume of air sampled, and instantaneous flow rate.

The quartz filter 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 . The aerosol samples were analyzed for TC content by thermal combustion. Each sample was

sealed under vacuum in a quartz tube with copper oxide, metallic copper and silver and combusted at 900°C. The CO₂ produced from combustion was cryogenically isolated from other combustion products and its amount measured manometrically ($\pm 0.2\%$).

3 Results and discussion

The results of fine aerosol absorption and scattering at sites T0 and T1 are shown in Fig. 2. Aerosol absorption at site T0 ranged from 7–107 Mm⁻¹ with an overall average of 37 Mm⁻¹ and followed a diurnal pattern that reached a maximum at around 06:30 (range of 05:00 to 08:00) LST and a minimum at 13:00 (range of 12:00 to 14:00) LST. Previous measurements of aerosol absorption have been reported for the Centro de Ciencias de la Atmósfera inside the campus of UNAM in the southwest quadrant of the Mexico City basin (Baumgardner et al., 2007). Results averaged over 14 days between the years 2003 and 2005 were found to follow a similar diurnal pattern as observed at site T0 but results were much lower than reported here. Aerosol absorption ranged from a low of 7 Mm⁻¹ in the early morning (01:00) to a maximum of 33 Mm⁻¹ at 06:00 LST. A comparison of the aerosol absorption at T0 showed excellent agreement with data obtained from co-located aethalometer and photoacoustic spectrometer instrumentation (Paredes-Miranda et al., 2008).

The values obtained in this study can also be compared to aerosol absorption measurements reported for Santiago, Chile, which has a similar terrain but a lower altitude. The major sources of absorbing aerosols in both Mexico City and Santiago are motor vehicle traffic, especially diesel buses (Horvath et al., 1997; Molina and Molina, 2002). Aerosol absorption in Santiago was found to reach maximum values of 100–200 Mm⁻¹ at around 09:00 LST and correlated with peak traffic hours (Horvath et al., 1997).

Aerosol absorption measurements at site T1 ranged from 3–147 Mm⁻¹ with an overall average of 27 Mm⁻¹. The same diurnal pattern observed at T0 was also evident at site T1 (maximum at 06:30 and minimum at 13:00 LST). While the daily maximum absorption values at T1 exceeded those at T0 on 9 of the days studied, these high levels were of much shorter duration, lasting only about 1 to 2 h as compared to 7 to 9 h of peak levels at site T0. In addition, the minimum aerosol absorption observed at site T1 routinely fell below those observed at site T0.

Forty-six minute averages of aerosol absorption obtained from day 74 (15 March) through day 85 (26 March) with a photoacoustic spectrometer operating at 870 nm have been reported previously for site T1 (Doran et al., 2007). A comparison of the daily absorbance maxima reported at 870 nm (Doran et al., 2007) with those recorded by the PSAP at 550 nm, assuming an α_a of 1, yields a difference between the data sets of -0.1 to $+83$ Mm⁻¹ with an average difference of

31 Mm⁻¹. The major source of error in this comparison is probably due to the assumption of $\alpha_a=1$. During much of the MILAGRO study, site T1 was impacted by local grass fires (Gaffney et al., 2008; Yokelson et al., 2008), which could have contributed significantly to the overall aerosol loadings and to a larger α_a (Kirchstetter et al., 2004). Carbon-14 analysis of 12-h aerosol samples collected at site T1 found that 70% of the carbon in the aerosols was from modern sources (Gaffney et al., 2008), which confirms that much of the carbon aerosol burden in the area arises from biomass derived sources. Determinations of α_a in areas impacted by biomass burning have been shown to be closer to 2 (Dubovik et al., 1998; Kirchstetter et al., 2004; Swap et al., 2003). If $\alpha_a=2$ is used to convert the values reported at 870 nm to 550 nm, the difference in the two data sets becomes 1 Mm⁻¹ \pm 30 Mm⁻¹. The major source of error in this comparison is most likely due to the differences used in data averaging.

Aerosol scattering measurements obtained at site T0 ranged from 16–344 Mm⁻¹ with an overall average of 105 Mm⁻¹. Scattering values generally reached a maximum at 10:30 (range of 07:30 to 13:00) LST. Measurements of aerosol scattering species obtained in Mexico City in April 2003 found that both nitrate and ammonium concentrations showed a sharp diurnal pattern with a maximum of 10–20 $\mu\text{g}/\text{m}^3$ for nitrate and 4–8 $\mu\text{g}/\text{m}^3$ for ammonium occurring from 10:00–12:00 LST, while sulfate concentrations did not vary significantly, remaining at round 2–3 $\mu\text{g}/\text{m}^3$ most of the time (Salcedo et al., 2006). The sharp diurnal pattern of nitrate is due to the photochemical formation of nitric acid from the reaction of NO₂ and OH, and subsequent reaction with ammonia to form the highly scattering aerosol species ammonium nitrate.

Similar rapid photochemical production of secondary organic aerosols (SOA) has also been observed in the Mexico City area (Salcedo et al., 2006; Hennigan et al., 2008; Aiken et al., 2008; Volkamer et al., 2006). The formation of particulate nitrate and SOA were found to be highly correlated suggesting that reaction with OH was also the primary source of the morning rise in SOA (Salcedo et al., 2006; Hennigan et al., 2008). The photochemical SOA formation showed approximately the same enhancement as for ammonium nitrate and occurred between the hours of 08:00–12:45 (Hennigan et al., 2008; Salcedo et al., 2006). This late morning formation of both ammonium nitrate and SOA in Mexico City contributes to the aerosol scattering in the diurnal profile shown in Fig. 2.

Aerosol scattering measured in Denver during the winter reached a maximum of 60–140 Mm⁻¹ at approximately 14:00–19:00 LST, 6 h later than observed in Mexico City (Groblicki et al., 1981). The primary aerosol scattering species in Denver is ammonium sulfate formed from the atmospheric oxidation of SO₂, with significant contributions from ammonium nitrate, as well. The photochemical formation of these secondary aerosol species would be expected to be slower in Denver due to the lower actinic flux in the winter

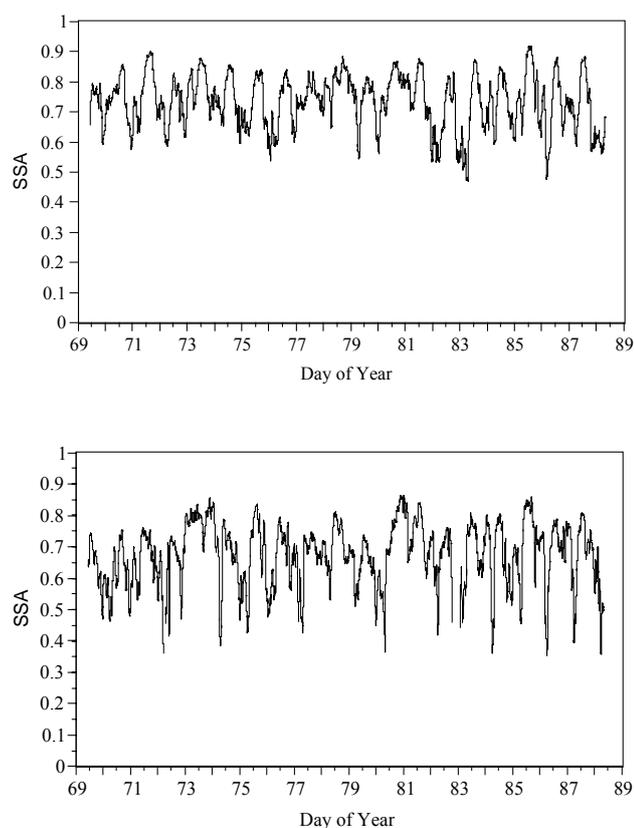


Fig. 3. Aerosol single scattering albedo (SSA) determined at site T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

at these higher latitudes, resulting in the later scattering maxima than observed in Mexico City. Aerosol scattering values at T1 were in general much lower than at T0, ranging from $2\text{--}136\text{ Mm}^{-1}$ with an overall average of 53 Mm^{-1} , and reached a maximum at 08:30 (range of 06:00 to 13:30) LST. On clear days the boundary layer in Mexico City during March–April grows slowly after sunrise at 06:40 to a height of approximately 1000 m by 11:00 LST (Doran et al., 1998, 2007; de Foy et al., 2008; Fast and Zhong, 1998; Fast et al., 2007). This serves to dilute the pollutants already present in the boundary layer. After 12:00 LST the boundary layer grows rapidly to 3000 m or greater. The maximum scattering values at site T0 occurred 2 h later than the maximum scattering values seen at T1 and 4 h later than the peak aerosol absorption values. This suggests that the high aerosol scattering values measured at T0 were primarily due to rapid SOA formation in the city. Although the overall SOA levels at T1 were found to be similar to those at T0 (Hennigan et al., 2008; Stone et al., 2008), the diurnal pattern of aerosol scattering at site T1 appeared to be controlled primarily by changes in the boundary layer height in the early morning, and by the presence of photochemically aged aerosols in the afternoon (Carabali, 2008; Stone et al., 2008; Aiken, et al., 2008).

The fine mode aerosol SSAs calculated from the ground level absorption and scattering measurements at 550 nm are shown in Fig. 3. The lower aerosol scattering observed at site T1 translates into lower values for fine aerosol SSAs at T1 with a range of 0.35–0.86 and an overall average of 0.68. The very low values for SSAs at site T1 are of very short duration, indicating a local source of absorbing BC aerosol. The fine aerosol SSAs calculated for site T0 ranged from 0.47–0.92 with an overall average of 0.73. While the total aerosol SSAs recorded over most of the Northern Hemisphere are usually about 0.85–0.95 (Jacobson, 2001), values as low as 0.68 have been reported over the southern Atlantic Ocean (Clarke, 1989). The occurrence of lower total aerosol SSAs is an indication of higher levels of more absorbing fine mode aerosols.

The SSA is a function of aerosol chemical composition and morphology. For a completely scattering aerosol, such as sulfate, the $\text{SSA} \sim 1$ and for a highly absorbing aerosol, such as freshly emitted BC, the SSA theoretically would approach zero. The SSA of freshly emitted diesel soot has been reported at 0.2 (Ramanathan et al., 2001; Ban-Weiss et al., 2008). Therefore, aerosols with an $\text{SSA} > 0.95$ will have a negative climate forcing and an overall cooling effect on the atmosphere, while an $\text{SSA} < 0.85$ will result in a positive climate forcing and an overall warming effect due to the enhanced aerosol absorption (Ramanathan et al., 2001). In addition, the presence of highly absorbing fine mode aerosols in the lower atmosphere will result in heating of the particles and significant local warming of the boundary layer (Hermann and Hanel, 1997; Ramanathan and Carmichael, 2008). This can result in an increase in the convective available potential energy of the boundary layer and a large scale rising motion over time (Chung and Zhang, 2004). This may help to explain the rapid increase in the boundary layer height observed in this area (Shaw et al., 2008; Fast and Zhong, 1998; Whiteman et al., 2000).

Doran et al. (2007) have calculated forward and back trajectories of air masses at 1000 m above ground level (a.g.l.) over site T1 during daylight hours (06:00–18:00 LST) for a 20-day period during the month of March 2006. The most favorable conditions for transport from site T0 to site T1 were seen to occur on days 69, 70, 77, 78, 79, 81, 83, 86 and 87 (10–11, 18–20, 22, 24, 27–28 March). On days 71–76 (12–17 March) and day 82 (23 March) the back trajectories indicate that transport would have likely been from site T1 towards Mexico City and site T0.

The aerosol absorption, scattering, and SSAs obtained at site T0 and T1 have been averaged over the same daylight hours reported by Doran et al. (2007) for direct comparison to their calculated back trajectories. The daily average aerosol absorption at sites T0 and T1 is shown in Fig. 4 along with the measurement ranges observed during each day. The daily average absorption values are similar at both sites ranging from $16\text{--}50\text{ Mm}^{-1}$ with an overall average value of 35 Mm^{-1} at T0 and a range of $15\text{--}41\text{ Mm}^{-1}$

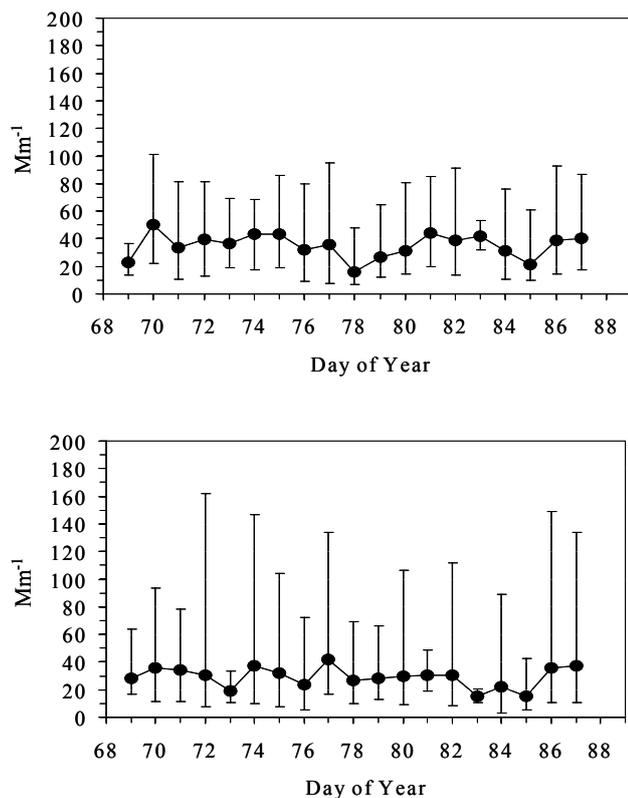


Fig. 4. Daily aerosol absorption averaged from 06:00–18:00 LST and absorption ranges measured at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

with an overall average of 29 Mm^{-1} at site T1. The two sites differ primarily in the range of aerosol absorption values observed during the day. While the lower limits on the ranges are similar at both sites, indicating a regional background of around 5 Mm^{-1} , the upper limits of the aerosol absorption measurements are more variable at site T1 with a range of $21\text{--}162 \text{ Mm}^{-1}$ as compared to site T0 with a range of $36\text{--}101 \text{ Mm}^{-1}$. There also appears to be no clear correlation of absorption values with transport from the Mexico City area, again indicating a local source of absorbing aerosols at site T1. Days 77, 86 and 87 (18, 27, 28 March), which were identified as likely transport days from site T0 to site T1, show high maximum aerosol absorbance. However, high maxima were also observed on days 72 and 74 (13 and 14 March) when transport has been identified as from the north. This suggests an impact at site T1 from Pachuca and/or Tizayuca (an important industrial center), which are located 10 and 64 km northeast of T1. Concentrations of TC obtained on fine mode aerosol samples collected over the daylight hours at sites T0 and T1 are shown in Fig. 5. The overall profile of the daily carbon concentrations during the study period is similar at both sites with the highest values ($25\text{--}35 \mu\text{g}/\text{m}^3$)

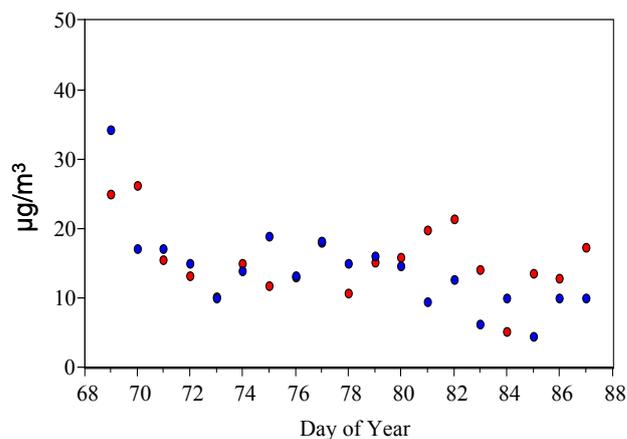


Fig. 5. Total carbon concentrations measured on fine (0.1–1 micron) aerosol samples collected from 05:30–17:30 at site T0 (red) and T1 (blue) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

observed on the first two days of the study period and lower values ($5\text{--}15 \mu\text{g}/\text{m}^3$) during the rest of the study. The mass absorption coefficients for BC at 550 nm were estimated assuming that the TC content of the <1 micron aerosols was 30% BC. This is in good agreement with past measurements made in the Mexico City area (Chow et al., 2002; Vega et al., 2004) as well as for measurements made in other urban areas (Tanner et al., 1982; Gaffney et al., 1984). The adjusted values reported for OC/EC ratios measured at site T1 are also in this range (Doran, 2007) as well as estimates made from aerosol mass spectrometry measurements (Aiken et al., 2008; Salcedo et al., 2006). The BC mass absorption coefficients shown in Fig. 6 range from $3.0\text{--}12.2 \text{ m}^2/\text{g}$ with an average of $7.7 \text{ m}^2/\text{g}$ at T0 and from $2.7\text{--}12.3 \text{ m}^2/\text{g}$ with an average of $7.7 \text{ m}^2/\text{g}$ at T1.

The mass absorption for EC reported for T1 by continuous OC/EC analysis was $5.6 \text{ m}^2/\text{g}$ with a range of $1\text{--}18 \text{ m}^2/\text{g}$ at 870 nm and $8.9 \text{ m}^2/\text{g}$ at 550 nm assuming an α_a of 1 (Doran, 2007). Other reported estimates of BC mass absorption in Mexico City vary from $4.8 \text{ m}^2/\text{g}$ (Baumgardner et al., 2007) to $9.5 \text{ m}^2/\text{g}$ (Schuster et al., 2005) at 550 nm. The mass absorption coefficient for BC calculated from a multi-filter rotating shadow-band radiometer (MFRSR) measurements in Mexico City was reported to be $8.2\text{--}8.9 \text{ m}^2/\text{g}$ at 550 nm as (Barnard et al., 2007, 2008). However, these estimations are based on assumptions of BC density, BC refractive index, and aerosol mixing state and may have a “worst case” uncertainty of about 70% (Barnard et al., 2008).

While the mass absorption coefficient of freshly emitted BC aerosols is estimated to be in the range of $6.3\text{--}8.7 \text{ m}^2/\text{g}$ at 550 nm (Bond and Bergstrom, 2006), OC aerosol species such as humic-like substances (HULIS) derived from biomass burning or secondary organic aerosols generated photochemically have mass absorption coefficients $<1 \text{ m}^2/\text{g}$

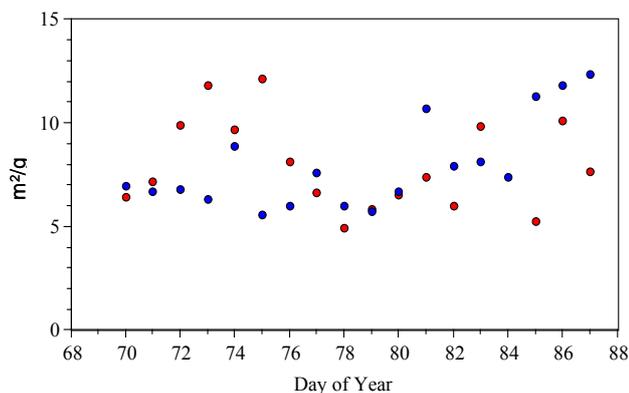


Fig. 6. Daily average mass absorption coefficient calculated for black carbon at site T0 (red) and T1 (blue) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

at 550 nm (Hoffer et al., 2006; Patterson and McMahon, 1984). The overall mass absorption coefficients measured for total carbon (BC+OC) will be dependent on the relative concentrations of BC and OC as well as their mixing state (Hitzenberger and Pauxbaum, 1993; Bond et al., 2006). The similarity of the mass absorption for both sites T0 and T1 suggests that the aerosol carbon composition was similar at both sites. The fine mode aerosol scattering averaged over the daylight hours is shown in Fig. 7 for sites T0 and T1 along with the measurement ranges for each day. The daily averages vary from 60–187 Mm^{-1} with an overall average of 123 Mm^{-1} at T0. The daily average aerosol scattering was lower and more consistent at site T1 with a range of 38–105 Mm^{-1} and an overall average of 57 Mm^{-1} . There also does not seem to be a general trend of major impacts on aerosol scattering at T1 due to transport from Mexico City except for possibly day 81 (22 March). Day 81 was identified as having favorable conditions for transport from site T0 to site T1 (Doran et al., 2007) and that day showed high scattering values for both sites.

The period from day 82 (23 March) to day 87 (24 March) was dominated by heavy regional rains and an overall increase in relative humidity (see Fig. 1). Rain totals before day 82 were 0 mm at site T0 and 6.7 mm at site T1. After day 82 rain totals were 19.2 mm at T0 and 59.5 mm at T1. This was accompanied by an increase in the average daily maximum RH from 59% to 76% at T0 and from 73% to 89% at T1. The increased rains resulted in a decrease in aerosol scattering at both sites by approximately the same amount. The average aerosol scattering at site T0 before the rainy period was 128 Mm^{-1} (range of 62–197 Mm^{-1}) and during the rainy period the aerosol scattering dropped to 118 Mm^{-1} (range of 85–157 Mm^{-1}). The same values for site T1 were 61 Mm^{-1} (range of 39–105 Mm^{-1}) before day 82 and 50 Mm^{-1} (range of 38–66 Mm^{-1}) after day 82. However, the aerosol absorption remained the same at site

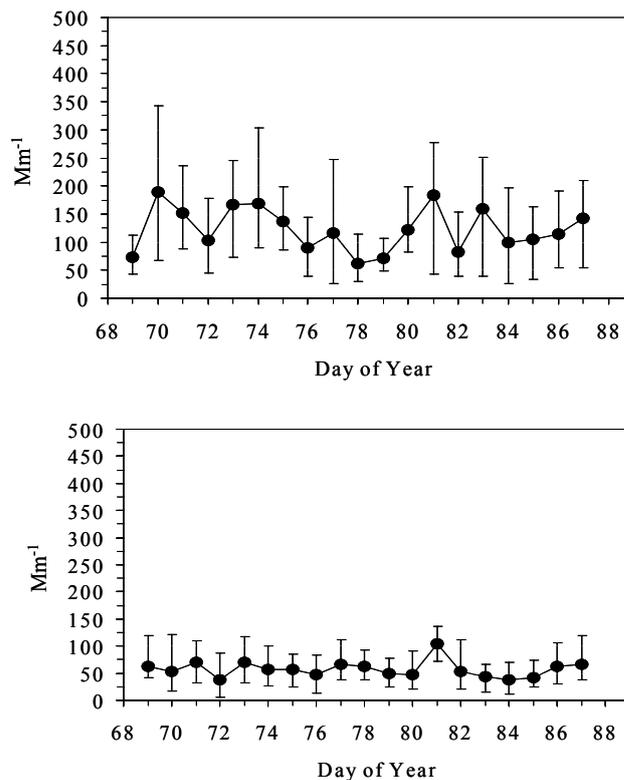


Fig. 7. Daily aerosol scattering averaged from 06:00–18:00 LST and scattering ranges measured at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

T0 with a value before day 82 of 35 Mm^{-1} (range of 16–50 Mm^{-1}) and a value of 35 Mm^{-1} (range of 21–42 Mm^{-1}) after day 82. The aerosol absorption at T1 decreased slightly from 30 Mm^{-1} (range of 19–41 Mm^{-1}) before the rainy period to 26 Mm^{-1} (range of 15–37 Mm^{-1}) during the rainy period. Since a significant fraction of highly scattering non-absorbing aerosols are primarily inorganic and hydrophilic, it is expected that they will wash out more readily during rain events than the freshly emitted absorbing BC aerosols that are more hydrophobic in nature (Marley et al., 2000; Gaffney and Marley, 2005; Marley and Gaffney, 2007). However, as the BC aerosols become coated with SOA, they will become more hydrophilic in nature and their washout rates would be expected to increase.

The fine mode aerosol SSAs averaged over the daylight hours at site T0 and T1 are shown in Fig. 8. The average fine aerosol SSA at site T0 ranged from 0.72–0.83 with an overall average of 0.78 while the average fine aerosol SSA at T1 was slightly lower and ranged from 0.63–0.78 with an overall average of 0.70. Doran et al. (2007) reported daily average total column aerosol SSAs at T1 at 500 nm determined by using a MFRSR. These results were reported for days 71, 78 and 86 as 0.84, 0.85 and 0.89 (12, 19, and 27 March) (Doran et

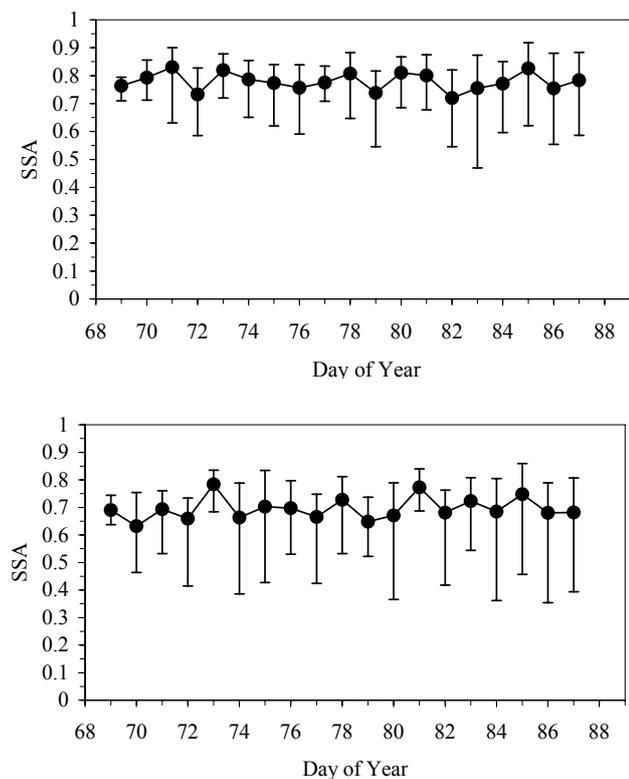


Fig. 8. Daily aerosol single scattering albedo (SSA) averaged from 06:00–18:00 LST and SSA ranges measured at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

al., 2007). The corresponding average fine aerosol SSAs reported here from ground-based aerosol absorbance and scattering measurements at 550 are 0.69, 0.73, and 0.68. The MFRSR SSA values are for the total aerosol burden while the values calculated in this work represent a surface measurement of fine mode aerosols only. The fine aerosol fraction measured here (0.1 to 2 micron diameter) contains the more highly absorbing carbonaceous aerosols. The much larger mechanically generated coarse mode aerosols (>2 micron), which are included in the MFRSR measurements are very highly scattering species. The total aerosol SSAs are therefore generally expected to be higher than the SSAs measured for the fine aerosol fraction alone.

Daily average fine mode aerosol SSAs have also been reported for La Merced, located in central Mexico City, and Pedregal, a suburban neighborhood in the southwest portion of Mexico City during March of 1997 (Eidels-Dubovoi, 2002). These SSA values were calculated from ground level aerosol absorption measurements obtained with a single channel aethalometer and aerosol scattering measurements obtained by an open air integrating nephelometer at 530 nm. The SSA values reported at La Merced varied from 0.63–0.86 with an

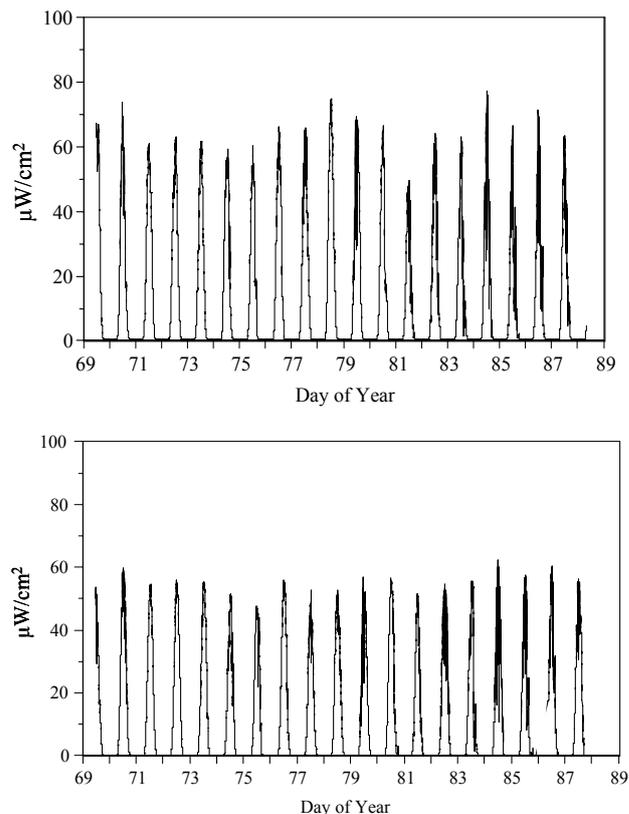


Fig. 9. Broadband UVB measured at sites T0 (top) and T1 (bottom) from 10 March (day 69) to 29 March (day 88) 2006 during the MILAGRO field campaign.

average of 0.72 and those reported at Pedregal ranged from 0.60–0.84 with an average of 0.68. These results compare well with the fine mode aerosol SSAs reported here.

Broadband UVB measurements obtained at sites T0 and T1 are shown in Fig. 9. The UVB intensity was higher at site T0, with an average of $64 \mu\text{W}/\text{cm}^2$ and a range of $50\text{--}70 \mu\text{W}/\text{cm}^2$ at solar noon, than at site T1, which had an average of $54 \mu\text{W}/\text{cm}^2$ and a range of $48\text{--}58 \mu\text{W}/\text{cm}^2$ at solar noon. In general, UVB reached a maximum at both sites at 12:30 LST. However, the variability of the daily maximum was larger at site T0 (11:30–14:00 LST) than at site T1 (12:00–13:00 LST). A comparison of simultaneous measurements from site T0 and T1 for cloudless days gave a correlation coefficient of 0.931 (slope of 1.18, intercept of 1.01). The measured UVB irradiances have been compared to that expected for clear sky conditions as determined by a radiative transfer model developed at The University of Chicago (Frederick and Lubin, 1988). The input to this model includes column ozone, determined from the Total Ozone Mapping Spectrometer (TOMS) satellite data, atmospheric optical thickness, UVB surface albedo, site location, day of year and time of day. The results of this comparison

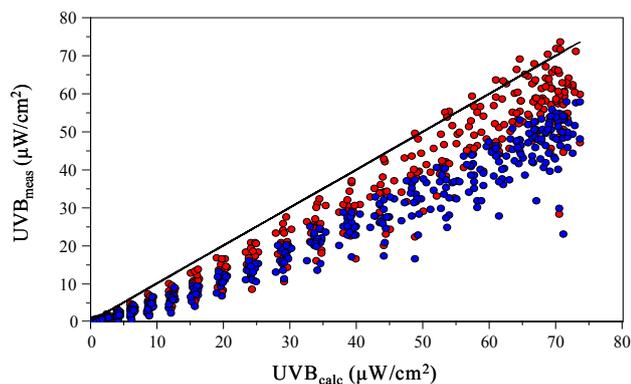


Fig. 10. Broadband UVB measured at sites T0 (red) and T1 (blue) compared to calculated clear sky UVB on days without rain events during the MILAGRO field campaign.

are shown in Fig. 10 for days without rain events. Both sites show reduced UVB radiation when compared to the clear sky modeled values, as expected for sites with significant UVB absorbing gases and aerosols (Castro et al., 2001; Gaffney et al., 2002; Barnard et al., 2008). However, the UVB radiation field observed at site T1 is reduced further than that observed at site T0. The measured UVB at both sites showed good correlation with the modeled UVB values ($r^2=0.95, 0.96$). However, the slope for site T0 was 0.87 while that for site T1 was 0.72. It should be noted that ozone, an important UVB absorbing gas was at similar or higher levels at T0 than T1, and the difference in observed UVB at the sites was not due to higher ozone at T1 for the clear days examined.

The ratio of UVB measurements obtained simultaneously at site T0 and site T1 for cloudless days are shown in Fig. 11 as a function of solar zenith angle (SZA). This ratio of measured UVB at T0 to UVB at T1 increases dramatically at high SZAs. At high SZAs, when the sun is close to the horizon, the optical path is sufficiently long that the majority of radiation measured by the RB meters is from the diffuse radiation field. The ratio of direct to diffuse insolation measured by the RB meter is 1.3 at a SZA of 20 deg. and reaches 0.1 at an SZA of 70 deg. (Granger et al., 1993). Therefore, since magnitude of the ratio of the UVB radiation at both sites is so strongly tied to the SZA, the data shown in Fig. 11 suggests that the diffuse radiation field at site T0 is much larger than that at site T1.

The aerosol scattering values measured by the three-wavelength nephelometer located at site T0 were used to calculate the average aerosol scattering Ångström coefficient (α_s). The Ångström coefficient for aerosol scattering is dependent on the particle size distribution with higher values ($\alpha_s > 1$) typically observed for accumulation mode particles (0.1–2 micron diameter) and lower values ($\alpha_s \approx 0$) for coarse mode particles (>2 micron) (Hand et al., 2004). The values calculated for the fine mode particles at site T0 ranged from

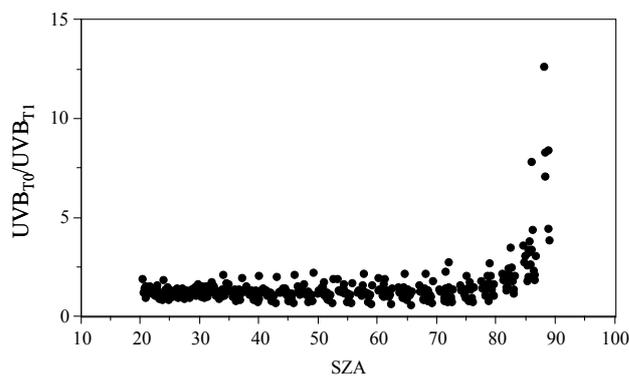


Fig. 11. Ratio of broadband UVB measured at sites T0 and T1 on days without rain events as a function of solar zenith angle (SZA) during the MILAGRO field campaign.

0.93 to 1.30 with an average of 1.11 over the entire study period. This corresponds to an average effective particle radius of 0.3 micron. (O’Niell and Royer, 1993; Lenoble and Brogniez, 1985). The direction of light scattered by particles is also dependent on the size of the particle. This is described by the particle scattering asymmetry factor (g). Mie scattering theory predicts that particles that approach the same size as that of the wavelength of the incoming radiation will scatter the radiation most favorably toward the forward direction. The dominant particle size of the fine mode particles at site T0, as determined by the Ångström coefficient for scattering, is 0.3 micron (300 nm), which is of a similar size as the incoming UVB radiation. Therefore the UVB spectral range will be scattered most efficiently toward this forward direction by these fine mode particles. In addition, the Ångström scattering exponent of 1.1 corresponds to a g of 0.7 (Lenoble and Brogniez, 1985), which implies that the aerosol scattering intensity will be peaked 45 deg. toward the forward direction. Therefore, the predominance of highly scattering submicron aerosols at T0 results in a larger amount of diffusely scattered UVB radiation and a higher UVB intensity at ground level than was observed at site T1.

The presence of highly absorbing fine mode aerosols in the Mexico City area, as indicated by the low SSAs, are expected to reduce the UV flux at ground level and therefore to reduce the photochemical production of oxidants such as ozone (Dickerson et al., 1997; Castro et al., 2001). However, as seen in Figs. 10 and 11, the presence of fine mode scattering aerosols in the boundary layer that approach the same size as the wavelength of the incoming UV radiation may also increase the UV flux at ground level due to their ability to strongly scatter light towards the forward direction and this increase in UVB flux also leads to an increase in photochemical oxidant production (Dickerson et al., 1997). Therefore, the larger UVB radiation measured at site T0 than at site T1 helps to explain the high levels of photochemical

activity observed in the Mexico City area during MILAGRO, despite the reduction in UVB anticipated from the presence of light absorbing species (Thompson et al., 2008; Stephens et al., 2008; Shim et al., 2008; Shon et al., 2008; Dusanter et al., 2008; Wood et al., 2008).

4 Conclusions

Measurements of fine mode aerosol absorption and scattering were obtained in Mexico City at site T0 located in the northern part of Mexico City at the IMP (Instituto Mexicano del Petróleo) laboratories and for site T1 located at the Technical University of Tecamac, 29 km northwest of T0. Hourly averages of aerosol absorption at 550 nm was similar at both sites, ranging from 7–107 Mm^{-1} with an average of 37 Mm^{-1} at T0; and from 3–147 Mm^{-1} with an average of 27 Mm^{-1} at T1. Aerosol scattering measured at 550 nm at T0 ranged from 16–344 Mm^{-1} with an average of 105 Mm^{-1} ; while the aerosol scattering values at T1 were much lower than at T0 ranging from 2–136 Mm^{-1} with an average of 53 Mm^{-1} . The maximum scattering values at site T0 occurred 2 h later than the maximum scattering values seen at T1 and 4 h later than the peak aerosol absorption values at either site. This suggests that the high aerosol scattering values measured at T0 were primarily due to rapid secondary aerosol formation in the city, while the lower aerosol scattering values at T1 were controlled primarily by changes in the boundary layer height in the early morning.

Fine mode aerosol SSAs were calculated at 550 nm for both sites using these data. The lower aerosol scattering values result in lower values for aerosol SSA at T1. The SSAs at T0 ranged from 0.47–0.92 with an average of 0.73 while SSAs at T1 ranged from 0.35–0.86 with an average 0.68. The low SSA determined for the fine mode aerosols indicate the presence of highly absorbing fine mode aerosols in the lower atmosphere. These fine mode aerosols will have a much slower settling velocity (0.3–60 cm/h) than the more highly scattering coarse mode aerosols (60–1000 cm/h) and will be transported more readily from the Mexico City basin into the surrounding regions (Finlayson-Pitts and Pitts, 2000). The absorption of solar radiation by these highly absorbing fine mode aerosols in the lower atmosphere will result in a heating of the particles and a significant local warming of the boundary layer (Hermann and Hanel, 1997; Ramanathan and Carmichael, 2008). This can result in an increase in the convective available potential energy of the boundary layer and a large scale rising motion over time (Chung and Zhang, 2004) and may help to explain the rapid increase in the boundary layer height observed in past studies in this area (Fast and Zhong, 1998; Whiteman et al., 2000; Shaw et al., 2008). Therefore, studies of boundary layer meteorology processes need to consider absorbing aerosol species when calculating heating rates (Fast and Zhong, 1998; Whiteman et al., 2000).

Comparisons of aerosol absorption averaged over the daylight hours with back trajectories reported by Doran et al. (2007) showed no clear correlation with transport from the Mexico City area, indicating a local source of absorbing aerosols at site T1, as suggested earlier (Doran et al., 2007). Similar comparisons of scattering measurements averaged over the daylight hours also do not seem to show a general trend of major effects on aerosol scattering at T1 due to transport from Mexico City except for possibly day 81 (22 March). Day 81 was identified as having favorable conditions for transport from site T0 to site T1 (Doran et al., 2007) and that day showed high scattering values for both sites.

Broadband UVB intensity was higher at site T0, with an average of 64 $\mu\text{W}/\text{cm}^2$ and a range of 50–70 $\mu\text{W}/\text{cm}^2$ at solar noon, than at site T1, which had an average of 54 $\mu\text{W}/\text{cm}^2$ and a range of 48–58 $\mu\text{W}/\text{cm}^2$ at solar noon. Comparisons of modeled UVB intensities with the simultaneous UVB measurements obtained at site T0 and at site T1 for cloudless days imply a larger diffuse radiation field at site T0 than at site T1. The determination of aerosol scattering Ångström coefficients at T0 suggests the predominance of aerosols at T0 in the size range of 0.3 micron. This results in aerosol scattering peaked 45 deg. toward the forward direction leading to the enhanced diffuse radiation at T0. This enhanced diffuse UVB radiation would help to explain the significant photochemistry observed in the Mexico City area during MILAGRO, despite the reduction in UVB anticipated from the high levels of light absorbing aerosol species (Thompson et al., 2008; Stephens et al., 2008; Shim et al., 2008; Shon et al., 2008; Dusanter et al., 2008; Wood et al., 2008).

The results of this study confirm that the Mexico City megacity environment has significant levels of fine mode absorbing aerosols. The high loadings of BC aerosols from fossil fuel emissions in the urban environment along with biomass burning contributions contribute to significant aerosol absorption, which will lead to local warming in the boundary layer at both the urban and regional sites. The presence of these high concentrations of absorbing aerosols in the urban area will contribute to the urban heat island effects and the transport of these absorbing aerosols into the surrounding areas will result in a positive climate forcing and an overall warming effect in the region.

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