

Nancy A. Marley and Jeffrey S. Gaffney
Environmental Science Division, Argonne National Laboratory, Argonne, IL 60439-4843

1. INTRODUCTION

Atmospheric aerosols play an important role in global climate because of their ability to both scatter and absorb solar radiation, depending on their chemical composition. The dominant light-absorbing aerosol is thought to be black carbon (BC) produced from combustion. Atmospheric aerosols containing BC can absorb as much as 20-25% of the incoming solar radiation leading to heating of the particles and local warming of the boundary layer (1). The absorption of solar light by BC particles is broad band and exhibits a $1/\lambda$ dependence over the entire spectral region from UV to the near IR, with a commonly accepted mass specific absorption coefficient of $10 \text{ m}^2/\text{g}$ at 550 nm (2).

Other light absorbing species have also been found in atmospheric aerosols. These usually include dicyclic and heterocyclic aromatics, including the amino acid tryptophan in biological particles (3), and polycarboxylic acids known as "humic-like" substances (HULIS) (4). These species have an enhanced absorption in the UV ($<400 \text{ nm}$) over that attributed to BC aerosols alone (5).

Due to the accelerated growth and high population densities of large megacities, they can suffer from a rapid deterioration of air quality with high loadings of both fine primary aerosols and trace gases that can lead to the formation of secondary aerosols. The use of heavy diesel engines in megacities has been identified as a significant source of diesel soot, an important contributor to BC levels in urban centers, and to primary BC emissions into the atmosphere on regional and global scales. We previously presented a paper on the significance of megacities as major sources of BC and the roles that BC can play in radiative forcing through both direct and indirect effects (6). Megacities can therefore function as large sources of atmospheric aerosols as the particulates are transported out of the urban area and can influence air quality, visibility and radiative balance of the atmosphere on urban, regional, and global scales.

The Mexico City metropolitan area (MCMA), which occupies $\sim 1300 \text{ km}^2$ with a population of $\sim 18 \text{ M}$, is one of the largest megacities in the world and is well known for its high levels of air pollution due to its large number of emission sources and its topography, which tends to

trap the emissions within the basin. It has been estimated that emissions from the Mexico City basin contribute around 15 Mega-tons of fine aerosol (PM-2.5) per year to the surrounding regions (7). This fine aerosol is composed of about 32% organic carbon, 15% elemental carbon, 10% ammonium nitrate and 20% ammonium sulfate (8). The emissions of sulfate aerosols alone from the MCMA are estimated to amount to about 1% of the total global burden (9).

In April of 2003, as part of the Department of Energy's Atmospheric Science Program, the Mexico City 2003 field study was conducted in collaboration with the Mexico City Metropolitan Area (MCMA) 2003 air quality study. Measurements of aerosol absorption were obtained at the National Center for Environmental Research and Training (Centro Nacional de Investigación y Capacitación Ambiental, or CENICA), on the Iztapalapa campus of the Universidad Autónoma Metropolitana (UAM) by using a seven-wavelength aethalometer (Thermo-Anderson). Here we present the results obtained for aerosol absorption as a function of wavelength in Mexico City as part of this study. Data were collected before and during the Easter holiday to assess the impacts of changes in aerosol loadings as a function of vehicle traffic levels. Also, during the latter part of April, there was evidence that the site was impacted by biomass burning aerosols from fires in the Yucatan.

2. METHODOLOGY

Measurements of aerosol absorption were made in Mexico City in April 2003 at a rooftop laboratory at the Centro Nacional de Investigación y Capacitación Ambiental (CENICA) in Iztapalapa, during a collaborative field project between the Department of Energy's Mexico City Megacity 2003 field study and the MCMA 2003 project. The field measurements were coordinated by Drs. Mario and Luisa Molina of the Massachusetts Institute of Technology and our research group.

The absorption of fine aerosols was measured by using a seven-wavelength aethalometer (Thermo-Anderson) with a sample inlet designed to collect aerosols in the size range $0.1\text{--}2 \mu\text{m}$. The aerosols in the air sample were 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.

*Corresponding author address: Jeffrey S. Gaffney, Environmental Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4843; e-mail: gaffney@anl.gov.

As the sample is deposited on the paper tape strip, light attenuation increases steadily. At high sample loadings, the high absorptions cause instrument sensitivity to decrease. To prevent this, the instrument automatically advances the tape to a new sample spot when light attenuation becomes severe. After the tape advance, a background measurement is taken at each of the seven wavelengths to correct for variations in filter surfaces and source light intensities. The instrument also collects some sample on the filter before taking sample measurements to minimize artifacts due to light scattering from the clean filter surface.

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

$$ATN(\lambda) = \sigma(1/\lambda) * [BC]$$

where [BC] is the mass of black carbon in the sample and $\sigma(1/\lambda)$ is the wavelength dependent optical absorption coefficient. Under normal operating conditions, the instrument automatically calculates the BC content from the transmission measurements assuming that BC is the main absorbing aerosol species in the samples (2,10).

The aethalometer is operated by an embedded computer that controls all the instrumental functions. Data are automatically recorded to a built-in 3.5-inch floppy diskette. For routine calculation of BC concentrations, the instrument software uses values of $\sigma(1/\lambda)$ determined previously by comparison of laser transmission measurements with thermal evolution methods (11). The values of σ for other wavelengths are calculated assuming a $1/\lambda$ dependency. These values for σ are given in Table 1 for the source wavelengths used in the aethalometer. Thus, the aethalometer results of BC aerosol concentrations ($\mu\text{g}/\text{m}^2$) can easily be converted to aerosol optical absorption (m^{-1}) at each wavelength by using the values for $\sigma(1/\lambda)$ given in Table 1.

Table 1. Values of $\sigma(1/\lambda)$ used by the aethalometer software to calculate BC concentration from optical attenuation measurements made at each wavelength.

Lamp	Wavelength (nm)	σ
UV	370	39.5
Blue	470	31.1
Green	520	28.1
Yellow	590	24.8
Red	660	22.2
IR-1	880	16.6
IR-2	950	15.4

3. RESULTS

Measurements of fine aerosol absorption in Mexico City during the month of April, 2003 are shown in Figure 1 for 370 nm and 880 nm. The lowest absorption values were observed on Good Friday, April 18 (Julian Day 108), due to the lower BC emissions consistent with a reduction in heavy-duty diesel traffic on the holiday. The average aerosol absorption on Good Friday was approximately a two to threefold reduction compared to the other Fridays. Low aerosol absorption levels continued for the next 5 days throughout the extended holiday period and began to return to more normal levels by Julian Day 113.

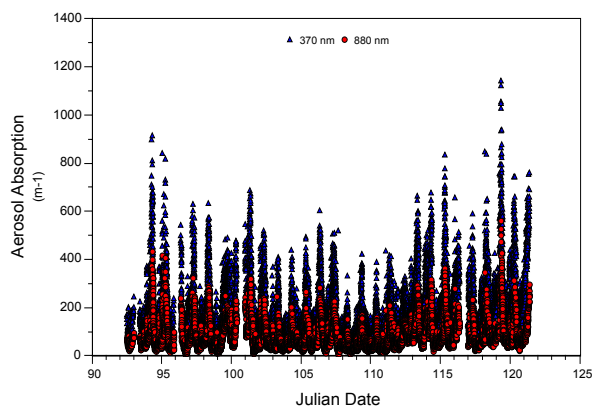


Figure 1. Fine aerosol absorption in Mexico City, from April 2, 2003 (Julian Day 92) to May 1, 2003 (Julian Day 121), at 370 nm and 880 nm.

Since the absorbance of fine particulates with a broadband absorption profile will exhibit an inverse wavelength dependence, the UV absorption is expected to be greater than that in the near infrared. The variation of the ratio of absorption at 370nm to that at 880 nm gives a better indication of aerosol components with enhanced UV absorption over that expected from BC content alone. The ratio of aerosol absorption at 370 nm to the absorption at 880 nm is shown in Figure 2. For particles with a purely $1/\lambda$ absorption dependence, the ratio shown in Figure 2 would be expected to be 2.38. The aerosol absorption observed in Mexico City during April 2003 gave ratios from 2.03 to 3.21 with the largest values occurring later in the study period.

In general, the 370nm/880nm absorption ratio was higher in the afternoon than the morning hours, indicating an increase in secondary aerosol formation and photochemically generated UV absorbing species in the afternoon. The afternoon values of the absorption ratio were 0.25 to 0.62 higher than the corresponding morning values. In addition, some morning absorbance ratios fell below the expected ratio of 2.38 for a $1/\lambda$ dependence. This could be due to biogenic aerosols formed by oxidation of mono- and sesquiterpene compounds emitted from a nearby fruit drying facility resulting in visible and near IR absorbing products.

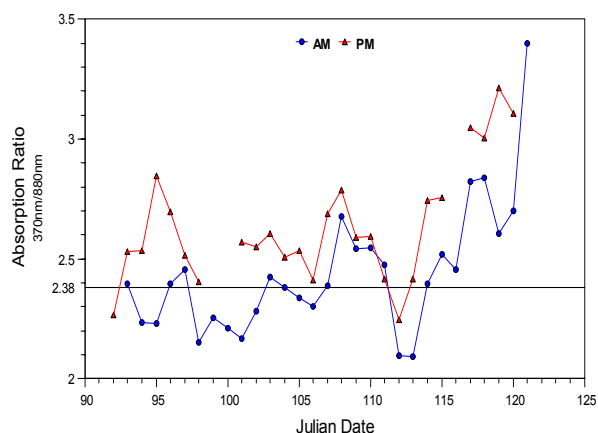


Figure 2. Morning (2400 – 1200) and afternoon (1200 – 2400) daily average ratios of aerosol absorption at 370nm to 880 nm in Mexico City, from April 25, 2003 (Julian Day 92) to May 1, 2003 (Julian Day 121).

The 370nm/880nm ratios were much higher during the last week of the study for both morning and evening hours. The aerosol absorbance profiles for the last week of the study are shown in Figure 3 after correction for the $1/\lambda$ dependence arising from broadband absorbers. The profiles show an increasing enhancement in absorbance at wavelengths below 550 nm with the most dramatic enhancement at 370nm, as indicated by the 370nm/880nm ratios shown in Figure 3

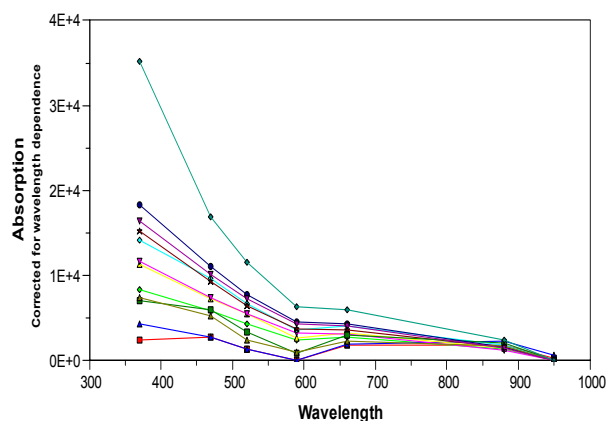


Figure 3. Aerosol absorption profiles, corrected for the $1/\lambda$ dependence from broadband absorbers, for April 25 to May 1, 2003 (Julian Day 115 – 121).

Aerosol samples collected by high volume impactors during this later period were analyzed for ^{14}C using accelerator mass spectrometry (12). Results of the biogenic to fossil carbon ratios in these aerosol samples were found to be 70% biogenic. In addition, analysis of satellite data indicated that the plumes from the biomass fires in the Yucatan 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 (13). Therefore, A substantial amount of the background carbonaceous aerosol affecting Mexico City during this later study period was due to long range transport from this biomass burning event which lasted throughout the month of April and directly impacted the city during the later part of the month. Carbonaceous aerosols generated from biomass burning have been shown to have a stronger wavelength dependence than that expected from BC alone (14, 15). The most abundant organic compounds detected in fine particulate matter from biomass burning events have been identified as the sugar anhydrides, galactosan and mannosan and levoglucosan, (16) as well as polycarboxylic acids (HULIS) which are well known UV absorbers (17).

5. ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Atmospheric Science Program, under contract W-31-109-Eng-38, and by The University of Chicago as part of its Center for Environmental Science.

6. REFERENCES

1. P. Hermann and G. Hanel, 1997: "Wintertime optical properties of atmospheric particles and weather." *Atmos. Environ.* **24**, 4053.
2. N. A. Marley, J. S. Gaffney, J. C. Baird, C. A. Blazer, P. J. Drayton, and J. E. Frederick, 2001: "The determination of scattering and absorption coefficients of size-fractionated aerosols for radiative transfer calculations." *Aerosol Sci. Technol.* **34**, 535–549.
3. R.C. Pinnick, S.C. Hill, Y.-L. Pan, and R.K. Chang 2004: "Fluorescence spectra of atmospheric aerosol at Adelphi, Maryland, USA: measurement and classification of single particles containing organic carbon." *Atmos. Environ.* **38**, 1657.
4. A. Cappiello, E. De Simoni, C. Fiorucci, F. Mangani, P. Palma, H. Truffelli, S. Decesari, M.C. Facchini, and S. Fuzzi, 2003: "Molecular characterization of the water-soluble organic compounds in fogwater by ESIMS/MS." *Environ. Sci. Technol.* **37**, 1229.
5. A. Gelencser, A. Hoffer, G. Kiss, E. Tombacz, R. Kurdi, and L. Bencze, 2003: "In-situ formation of light absorbing organic matter in cloud water." *J. Atmos. Chem.* **45**, 25.
6. J. S. Gaffney and N. A. Marley, 2004: "Megacities as sources of black carbon." *Combined Preprints, Sixth Conference on Atmospheric Chemistry: Air Quality in Megacities*, Amer. Meteor. Soc., Paper J2.3, on CD-ROM, and references therein.

7. Gaffney, J.S., N.A. Marley, M.M. Cunningham, and P.V. Doskey, "Measurements of peroxyacyl nitrates (PANS) in Mexico City: implications for megacity air quality impacts on regional scales" *Atmos. Environ.*, **33**, 5003-5012 (1999).
8. J.G. Chow, J.G. Watson, S.A. Egerton, and E. Vega, 2002: "Chemical composition of PM_{2.5} and PM₁₀ in Mexico City during winter 1997." *Sci. Tot. Environ.* **287**, 1221.
9. Barth, M.C. and A.T. Church, 1999: "Regional and global distributions and lifetimes of sulfate aerosols from Mexico City and southeast China." *J. Geophys. Res.*, **104**, 30,231.
10. A..D.A. Hansen, H. Rosen, and T. Novakov, 1982: "Real-time measurement of the absorption coefficient of aerosol particles," *Appl. Opt.* **21**, 3060.
11. Gundel, L.A., Dod, R.L., Rosen, H., Novakov, T. 1984: "The relationship between optical attenuation and black carbon concentration for ambient and source particles." *Sci. Tot. Environ.* **36**, 197.
12. J.S. Gaffney, N.A. Marley, N.C. Sturchio, T. Guilderson, M. Rowe and K. L. Steelman, 2005: "Measurements of Black Carbon and Ammonia in Mexico City Aerosol: Evidence for Biomass and Regional Source Contributions" V Simposio Contaminación Atmosférica, July 19- 21 2005, El Colegio Nacional, México D.F.
13. S. T Massie, J. Gille, and D. Edwards, 2004: "Satellite observations of aerosol and CO over Mexico City." Presented in MIRAGE Special Session, Transportation and Polluti
14. E.M. Paterson, C.K. McMahon, 1984: "Absorption characteristics of forest fire particulate matter" *Atmos. Environ.* **18**, 2541.
15. T.W. Kirchstetter and T. Novakov, 2004: "Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon" *J. Geophys Res.* **109**, D21208.
16. C.G. Nolte, J.J. Schauer, G.R. Cass, and B.R.T. Simonet, 2001: "Highly polar organic compounds present in wood smoke and in the ambient atmosphere" *Environ. Sci. Technol.* **35**, 1912.
17. O.L. Mayol-Bracero, P.Guyon, B. Graham, M.O. Andreae, S. Decesari, M.C. Facchini, S. Fuzzi, and P. Araxo, 2002: "Water-soluble organic compounds in biomass burning aerosols over Amazonia, 2. Apportionment of the chemical composition and importance of the polyacidic fraction" *J. Grophys. Res.* **107**, D20,8091.