Short communication

Optical properties of aerosols: southern México City

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RESUMEN

Se obtuvieron medidas de absorción (σ_a) a 500 nm, esparcimiento (σ_s) a 530 nm y concentración de partículas (0.01 a 3 µm) en el Sur de la Cd. de México durante las temporadas de secas (febrero-mayo) y lluvias (junio-agosto) del 2005. Los promedios mensuales de σ_a en los días de muestreo presentaron pequeñas variaciones de 20 a 29.4 Mm⁻¹ y 12 a 14.7 Mm⁻¹ en secas y lluvias, respectivamente. Sin embargo, σ_s varía notablemente en la temporada seca de 78.1 a 93.3 Mm⁻¹ y en la temporada de lluvias de 20.6 a 35.5 Mm⁻¹. El promedio del albedo de dispersión simple (SSA) fue de 0.82 durante la temporada seca mientras que en la de lluvias fue un poco menor 0.68. Estos datos son útiles en estudios de fotoquímica atmosférica que consideren los efectos de los aerosoles.

ABSTRACT

Measurements of aerosol absorption (σ_a) and scattering (σ_s) at wavelengths of 550 nm and 530 nm, respectively, and particle (0.01 to 3 µm) concentration were obtained in south of México City (19° 21' 00'' N, 99° 09' 42'' W and 2276 masl) during dry (February-May) and rainy (June-August) seasons of 2005. The averages over the sampling days of each month for σ_a presented small variations on each season, ranging from 20 to 29.4 Mm⁻¹ and from 12 to 14.7 Mm⁻¹ in dry and rainy seasons, respectively. However, σ_s values varied notoriously, from 78.1 to 93.3 Mm⁻¹ in dry season, compared with 20.6 to 35.5 Mm⁻¹ during rainy season. The single scattering albedo (SSA) average was 0.82 during dry season while in the rainy season it was slightly lower, that is 0.68. These data are useful in atmospheric photochemistry studies where aerosol effects are considered.

Keywords: Aerosols absorption and scattering coefficients, single scattering albedo, México City.

1. Introduction

The impact of atmospheric aerosols on global climate is now a major environmental issue (Charlson *et al.*, 1992; Chung and Seinfeld, 2005). In urban areas atmospheric aerosols are also a major issue with respect to their impact on public health and damage to environment (Pope III and Dockery, 2006). Anthropogenic aerosols can perturb the Earth's radiative budget directly by scattering and

absorption of solar and terrestrial radiation and indirectly by their ability to nucleate cloud droplets (Ramanathan *et al.*, 2001).

The radiative effects of aerosols can be studied in terms of its optical properties: σ_s , σ_a and single scattering albedo (SSA= σ_s/σ_{ext}) where σ_{ext} is the aerosol extinction coefficient of particles ($\sigma_{ext} = \sigma_s + \sigma_a$). Light scattering is one of the two attenuation effects of aerosols on solar radiation (the other being absorption) and can be quantified directly by means of scattering coefficient (σ_s). Visibility (V) reflects the contribution of aerosols and gases to total light extinction $\sigma_t(\sigma_t = \sigma_g + \sigma_{ext})$ where σ_g is the gas extinction coefficient (Jacobson, 2002). For this study we calculate visibility taking into account only the aerosol contribution to light extinction in Koschmieder's equation (V=3.912/ σ_t).

México City Metropolitan Area (MCMA) occupies ~3540 km² and has a population of ~19 M, this classifies the zone as the second largest urban megacity worldwide (INEGI, 2005; CAM, 2002). México City as well as other megacities produces significant amounts of highly absorbing carbonaceous aerosols; according with the last Emission Inventories for MCMA (SMA, 2006), 23 053 ton/year of PM₁₀ and 6191 ton/year of PM_{2.5} are released to the atmosphere. These aerosols lead to a significant reduction in actinic flux and photochemistry may be affected (Castro *et al.*, 2001). An important variable needed for modeling the influence of global warming on photochemical reactivity is the photolysis constant of nitrogen dioxide, that can be calculated through the optical properties of aerosols (Ruiz-Suárez *et al.*, 2008). The reduction in photolysis constants of nitrogen dioxide, J_{NO2} (and in the values of J for other photochemical reactions) has great impact on air quality, radiative balance and local climate (Raga *et al.*, 2001; Madronich, 2006).

In this study, variation during dry and rainy seasons for absorption and scattering coefficients and total number concentration of particles were measured at south of México City and results are shown here. Single scattering albedo and visibility are also reported. These parameters are very important to establish part of initial conditions for photochemical and air quality models.

2. Method

Sample site was the Centro de Ciencias de la Atmósfera (CCA) building, located at the Universidad Nacional Autónoma de México (19° 21' 00" N, 99° 09' 42" W and 2276 masl) in México City. An air flow passed through a sampler system for 24 hours, during 5 or 6 days per month. Sampling dates were: February 17 to 21, March 17 to 21, April 27 to May 2, May 25 to 30, June 22 to 27, July 20 to 25 and August 24 to 29, 2005.

The scattering coefficient σ_s was measured with a nephelometer (Radiance Research, Model 903) at a wavelength of 530 nm. The sample inlet was located at a height of 10 m above ground level and collected aerosols in the size range of 0.1 to 2 µm aerodynamic diameter at ambient temperature and pressure. Aerosol absorption σ_a was obtained by a particle soot absorption photometer (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. The PSAP measurements were corrected for light scattering and other effects that bias the absorption measurement using the empirical correction suggested by Bond *et al.* (1999) (Eq. 1) that accounts for the scattering of the aerosol on the collection filter.

$$\sigma_{a} = [\sigma_{a \text{ (measured)}} - 0.02 \sigma_{s \text{ (measured)}}]/1.2$$
(1)

Where: $\sigma_{a \text{ (measured)}}$ is the absorption coefficient measured with the PSAP and $\sigma_{s \text{ (measured)}}$ is the scattering coefficient measured with the nephelometer.

The total number concentrations of particles (CN) were obtained with a condensation particle (nucleus) counter (CPC), TSI Model 3010. The equipment measures aerosols as small as 10 nm with concentrations of up to 10^4 cm⁻³ using only the single-particle-counting mode.

The equipment was installed on the CCA building roof. The aerosol samples were taken from air brought through a chimney (10 m above ground level) with a fan that maintained a flow rate of $\sim 90 \text{ Lm}^{-1}$. Measurements were recorded with a personal computer at 1 minute intervals. The stored data was retrieved through a RS232 port. Data are reported here with an hourly running average of these one minute values.

3. Results

Table I shows the average for aerosols scattering and absorption coefficients, concentration of particles, single scattering albedo and visibility in dry (February-May) and rainy (June-August) seasons. Values of scattering and absorption coefficients are higher during dry months than in the rainy season (Fig. 1). The averages over the sampling days of each month for σ_a present small variations, ranging from 20 Mm⁻¹ to 29.4 Mm⁻¹ and 12 to 14.7 Mm⁻¹ in dry and rainy seasons, respectively. However, the values for σ_s varied notably, 78.1 Mm⁻¹ to 93.3 Mm⁻¹ in dry season, compared with 20.6 Mm⁻¹ to 35.5 Mm⁻¹ during the rainy season. Fresh particulate emissions due to traffic in México City are mostly carbonaceous with very low sulfur content (Molina and Molina, 2002) therefore the absorption coefficients show small variations on both seasons.

The aerosol single scattering albedo average for fine mode aerosols is shown in Table I.

Dry season						
Month	CN particles/cm ³	$\sigma_{s} \left(Mm^{-1} \right)$	$\sigma_{a} \left(Mm^{-1} \right)$	$\sigma_{e} \left(Mm^{-1} \right)$	V (Km)	SSA
February	5828 7224	93.3	20.4	114	34.42	0.82
April	5080	86.4	29.4	100.7	42.03	0.83
May Average	2966 5274	78.1 54.8	20.0 23.2	98.1 104.3	39.86 38.8	0.80 0.82
			Rainy season	n		
Month	CN particles/cm ³	$\sigma_{s} \left(Mm^{-1} \right)$	$\sigma_{a} \left(Mm^{-1} \right)$	$\sigma_{e} \left(Mm^{-1} \right)$	V (Km)	SSA
June	3098	20.6	14.1	34.7	112.74	0.59
July	2662	34.9	12.0	46.9	83.49	0.74
August Average	2088 2616	35.5 30.3	14.7 13.6	50.2 43.9	77.87 91.36	0.71 0.68

Table I. Aerosol physical properties at the south of México City, for 2005.

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coefficients at the south of México City, for 2005.

This average ranged from 0.80 to 0.83 with an overall average of 0.82 during dry season, while in the rainy season it was slightly lower and ranged from 0.59 to 0.74 with an overall average of 0.68. The monthly aerosol SSA shows a small change in the dry season while changes are outstanding when there is an increase in rain intensity. This can be due to the fact that in México City the major source of absorbing aerosols is motor vehicle traffic, especially diesel engines (Molina and Molina, 2002), that in the morning shows fresh particle emissions with a high BC content which along the day get covered by secondary organics (Salcedo *et al.*, 2006; Paredes-Miranda, 2009; Paredes-Miranda *et al.*, 2009). 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 the rainy season than the freshly emitted absorbing BC aerosols that are more hydrophobic in nature. However, as the BC aerosols become coated with secondary organic aerosols, they will become more hydrophilic in nature and their washout rates would be expected to increase (Marley *et al.*, 2009). The decrease in SSA during rainy season could then indicate that besides the highly scattering non absorbing aerosols, there are substantial amounts of fresh BC aerosols that are not readily washed out.

Dry season results are in agreement with Marley *et al.* (2009), who reported single scattering albedo ranged from 0.47–0.92 for a site located at the north of México City (T0 site, MILAGRO campaign, March, 2006). The occurrence of lower total aerosol SSA is an indication of higher levels of more absorbing fine mode aerosols.

During dry season the average of the total number concentration of particles (CN) was 5274 particles/cm³ and due to the atmospheric washout in the rainy season, the concentration obtained was 2616 particles/cm³. The CN concentrations (obtained on both seasons) depend on the sources and intensity of the emissions and on the meteorological conditions that affect the rate of mixing and dilution. We assume that the CN concentrations come from the same local sources.

4. Conclusions

The results indicate that in the atmosphere of México City, there are substantial amounts of fresh BC aerosols that are not readily washed out during rain events leading to a decrease in aerosol single scattering albedo during rainy season. According to measurements, the aerosols extinction coefficients are controlled mainly by the fine particle scattering. Results on optical properties of aerosols presented in this study are significant when they are used in photochemical models; also

for studies on interaction between radiation and aerosols in the search of understanding their impact on local or regional climates.

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References

- Bond T. C., T. L. Anderson and D. Campbell, 1999. Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols. *Aerosol Sci. Technol.* **30**, 582-6000.
- CAM, 2002. Programa para Mejorar la Calidad del aire de la Zona Metropolitana del Valle de México 2002–2010, Capitulo 2, La Zona Metropolitana del Valle de México, 25 pp. Online available at: http://www.paot.org.mx/centro/libros/proaire/cap02.pdf, last access: September 2009.
- Charlson R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr., J. E. Hansen and D. J. Hoffman, 1992. Climate forcing by anthropogenic aerosols. *Science*, **255**, 423-430.
- Castro T., S. Madronich, S. Rivale, A. Muhlia and B. Mar, 2001. The Influence of Aerosols on Photochemical Smog in México City. *Atmospheric Environment*, **35**, 1765-1772.
- Chung S. H. and J. H. Seinfeld, 2005. Climate response of direct radiative forcing of anthropogenic black carbon. *J. Geophys. Res.* **110**, D11102, doi:10.1029/2004JD005441
- INEGI, 2005. Censo de Población 2005. México. http://www.inegi.gob.mx, last access: December, 2009.
- Jacobson M. Z., 2002. *Atmospheric Pollution: History, Science, and Regulation*. Cambridge Press, 399 pp.
- Johnson K. S., B. Zuberi, L. T. Molina, M. J. Molina, M. J. Iedema, J. P. Cowin, D. J. Gaspar, C. Wang and A. Laski, 2005. Processing of soot in an urban environment: Case study from the México City Metropolitan Area. *Atmos. Chem. Phys.*, 5, 3033-3043.
- Marley N.A. and J. S. Gaffney, 2007. The Impact of Rain Events on Aerosol Optical Properties: México City 2003 and 2006. *EOS Trans. AGU*, **88**, (23), Jt. Assem. Suppl. Abstract A41E-03.
- Marley N. A., J. S. Gaffney, T. Castro, A. Salcido and J. Frederick, 2009. Measurements of aerosol absorption and scattering in the México City Metropolitan Area during the MILAGRO field campaign: a comparison of results from the T0 and T1 sites. *Atmos. Chem. Phys.* 9, 189-206.
- Madronich S., 2006. Chemical evolution of gaseous air pollutants down-wind of tropical megacities: México City case study, *Atmos. Environ.* **40**, 6012-6018.
- Molina L. T. and Molina M. J., 2002. *Air Quality in the México Megacity: An Integrated Assessment*. Kluwer Academic Publishers, 384 pp.
- Paredes-Miranda G., 2009 (personal communication).
- Paredes-Miranda G., W. P. Arnott, J. L. Jimenez, A. C. Aiken, J. S. Gaffney and N. A. Marley, 2009. Primary and secondary contributions to aerosol light scattering and absorption in México City during the MILAGRO 2006 campaign, *Atmos. Chem. Phys.* 9, 3721-3730.
- Pope III C. A. and D. Dockery, 2006. Health Effects of Fine Particulate Air Pollution: Lines that

Connect. *Journal of the Air & Waste Management Association*; **56**, 6; ProQuest Agriculture Journals, pg. 709.

- Raga G.B., T. Castro, D. Baumgardner, 2001. The impact of megacity pollution on local climate and implications for the regional environment: México City. *Atmospheric Environment* 35, 1805-1811.
- Ramanathan V., P. J. Crutzen, J. T. Kiehl and D. Rosenfeld, 2001. Aerosols, climate, and the hydrological cycle. *Science* 7, 2119-2124.
- Ruiz-Suarez L.G., T. Castro and A. García 2008. Cuarta Comunicación Nacional de México ante la Convención Marco de Naciones Unidas sobre el Cambio Climático. Informe Final.
- Salcedo D., T. B. Onasch, K. Dzepina, M. R. Canagaratna, Q. Zhang, J. A. Huffman, P. F. DeCarlo, J. T. Jayne, P. Mortimer, D. R. Worsnop, C. E. Kolb, K. S. Johnson, B. Zuberi, L. C. Marr, R. Volkamer, L. T. Molina, M. J. Molina, B. Cárdenas, R. M. Bernabé, C. Marquez, J. S. Gaffney, N. A. Marley, A. Laskin, V. Shutthanandan, Y. Xie, W. Brune, R. Lesher, T. Shirley and J. L. Jimenez, 2006. Characterization of ambient aerosols in México City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite. *Atmospheric Chemistry and Physics*, 6, 925-946.
- SMA (Secretaria del Medio Ambiente, Gobierno del Distrito Federal), 2006. Inventario de Emisiones de la Zona Metropolitana del Valle de México. Online available at: (http://www. sma.df.gob.mx/sma/links/download/archivos/inventarioemisiones2006/007_zmvm.pdf, last access: September 2009.