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On the formation of an elevated ozone peak in Mexico City

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Abstract

High ozone concentrations have been a major pollution problem in the Mexico City basin for at least 10 years, exceeding 110 ppbv (Mexican standard) more than 300 days per year. Aircraft observations obtained during February 1991 showed for the first time that vertical profiles of aerosol particles and ozone presented peak concentrations close to the top of the mixed layer. We hypothesize that the interplay between aerosol particles, solar radiation and photochemical processes is the key to the development of the elevated ozone peak. This peak is reproduced when a layer of highly absorbing particles, representative of Mexico City aerosols, is included in a 1-D turbulent transport and chemistry model of the boundary layer. The results suggest that the presence of large concentrations of absorbing particles within the mixed layer is likely inhibiting ozone formation that would otherwise reach even higher levels.

Keywords: Air pollution; Light absorbing particles; Photochemistry; Vertical profiles of actinic fluxes; Mexico City

1. Background

Atmospheric pollution in Mexico City is favored due to its elevation of 2.2 km above sea level and its location in a flat basin surrounded by mountains. Its tropical location (at 19°N) also contributes to the problem, mainly photochemical in nature, since the high incident radiation does not vary significantly throughout the year. The extremely high emissions by mobile and fixed sources provide the needed conditions for significant pollution events to develop.

During February 1991 a very large field project took place in Mexico City, co-sponsored by the Instituto Mexicano del Petróleo (IMP, Mexican Petroleum Institute) and Los Alamos National Laboratory (MARI, 1994), to improve the understanding of the ozone problem in the city. Several studies (e.g. Blake and Rowland, 1995; Elliot et al., 1997) discuss aspects of the particular characteristics of the atmospheric components in Mexico City that lead to the high ozone episodes frequently observed. An instrumented aircraft participated in the project and flew 15 missions in a 3-week period. The analysis of the data obtained by the aircraft (Nickerson et al., 1992; Perez Vidal and Raga, 1998) has indicated the presence of definite vertical structure in aerosol particles and gases in the thermodynamically well-mixed layer over Mexico City. Elevated layers with large concentrations of pollutants have been reported for other locations such as Los Angeles (Edinger et al., 1972; Lu and Turco, 1996) and Germany (Beyrich et al., 1996), but it is the first time that such a profile has been systematically observed in Mexico City's basin.

The Beechcraft King Air-100 aircraft, operated by the National Center for Atmospheric Research, participated in the project. It was equipped with the standard suite of meteorological instruments as well as instrumentation to measure gases such as carbon monoxide (CO), nitrogen oxides (NO_x and NO), and sulfur dioxide (SO_2). Aerosol particles were measured with an optical spectrometer (ASASP), to determine size distributions in the range of diameters between 0.12 and 3.0 μm and a total particle

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counter (CN). The vertical soundings during take-off and landing of the instrumented aircraft have been analyzed (Perez Vidal and Raga, 1998), and clearly show the complex vertical structure of pollutants over the city. Fig. 1a shows the vertical profiles of the potential temperature measured during take-off and landing on 13 February 1991. The mixed layer is clearly identifiable, rising from only a few meters at 8:45 a.m. (local time) to about 1 km above the surface at 11:20 a.m. The corresponding profiles for ozone are shown in Fig. 1b, where it is clear that the gas is not well mixed and presents a peak close to the top of the boundary layer at 11:20 a.m. The dark solid line corresponds to the profile measured later in the afternoon (14:30 local time), where a more homogeneous vertical distribution is observed. There were no wind shifts observed during the vertical profile and since the potential temperature was constant with height, it suggested that advection was not the reason for the ozone peak at the top of the mixed layer. The profiles of the aerosol particle concentration (from the size distributions measured by the ASASP) are shown in Fig. 1c and again indicate a non-uniform structure in the mixed layer. On this day, ozone concentrations aloft are about a factor of 2 larger than at the surface, while particle concentrations are about a factor of 3 larger. This elevated peak in particle concentration could be linked to the production of particles from the gas phase, either from sulfur dioxide and/or from hydrocarbons (Meng et al., 1997; Odum et al., 1997), or may just indicate the growth of smaller primary particles into the ASASP range. Fig. 1d shows the vertical profile of a surrogate for the ultraviolet (UV) actinic flux. This surrogate was calculated as the sum of the measured fluxes by the down and upward looking Eppley hemispheric broadband (295–385 nm) radiometers on the aircraft. The observed enhanced surrogate of the UV actinic flux directly corresponds to the peaks in particle concentrations in Fig. 1c, highlighting a process equivalent to the one described by Madronich (1987) near the tops of clouds. Wind direction and speed remained constant and very light during the period. Mexico City is the largest regional source and it is unlikely that the large concentrations aloft would be the result of differential advection, considering that the thermodynamic parameters are well mixed in the layer.

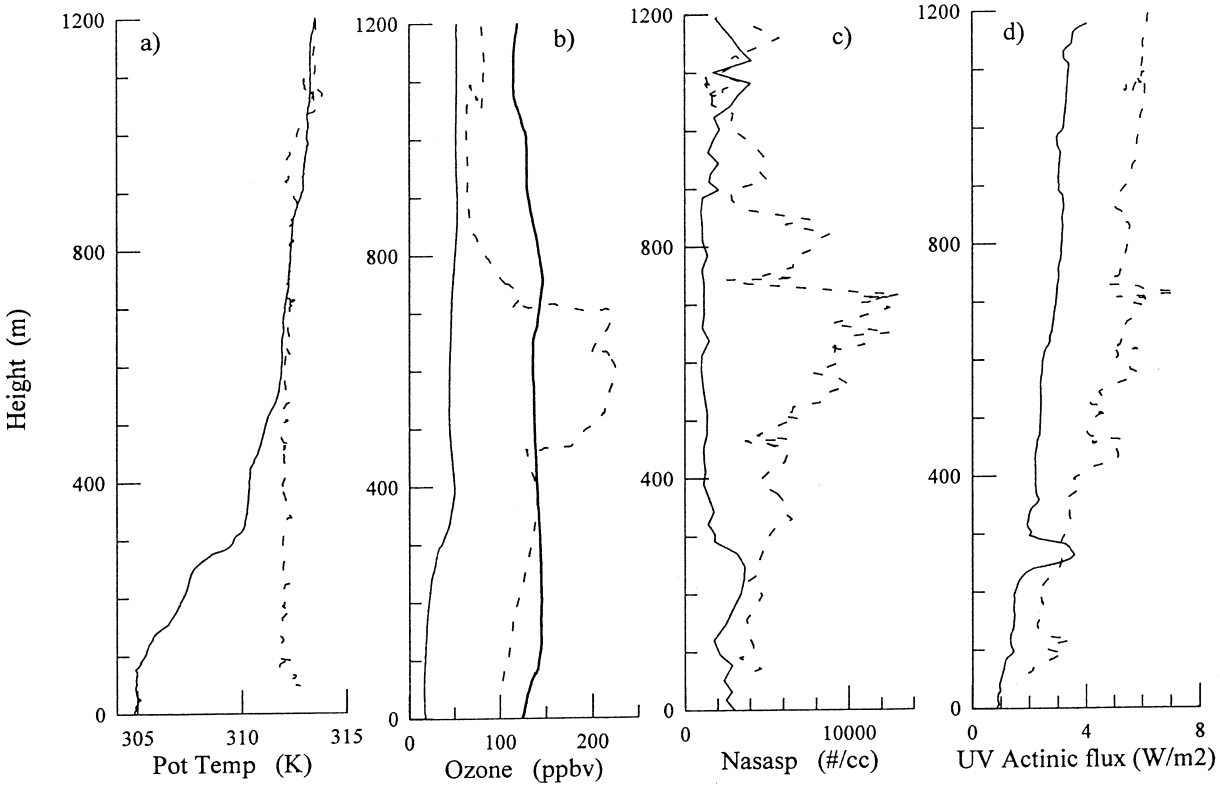

Fig. 1. Vertical profiles of (a) potential temperature (K), (b) ozone concentration (ppbv), (c) particle concentration (cm^{-3}), and (d) 'surrogate' UV actinic flux ($W\,m^{-2}$). Solid curves correspond to take-off sounding at 8:45 a.m. (local time) and dashed curves correspond to landing period (11:20 a.m.). In Fig. 1(b), the dark solid line corresponds to the profile observed during the afternoon (14:30).

2. Theoretical model

A one-dimensional Eulerian model of turbulent diffusion in the boundary layer is used to simulate the vertical transport within it. The time evolution of a chemical species C_i is modeled by the following equation:

$$\frac{\partial C_i}{\partial t} = S_i + K_i \frac{\partial^2 C_i}{\partial z^2}, \quad (1)$$

where S_i represents the combination of chemical sources and sinks for species C_i. The mixed layer (ML) was allowed to grow from 300 to 755 m in the 2 h of simulation (consistent with observed values), and the turbulence levels within the ML and in the free troposphere aloft were simulated by different ratios of the diffusion coefficient K_i (10 : 1 and 100 : 1).

The chemistry model for the production/destruction of ozone is highly parameterized and was selected in order to test the hypothesis that the presence of particles was important in the development of an elevated ozone peak. The reactions included are shown in Table 1. It includes oxides of nitrogen, in the presence of formaldehyde and hydroxyl and peroxy radicals, giving a total of 15 species in 11 reactions. Formaldehyde has frequently been detected in Mexico City (Baez et al., 1989, 1995, 1999). The rate constants also shown in Table 1 were obtained from Seinfeld and Pandis (1997), while the initial conditions for the simulations are based on the observed profiles of NO, NO_2 and O_3 (listed in Table 2). The computational domain has a free boundary at the top of the domain (located at 1 km above the surface), numerically imposed by extrapolating the gradient to the last grid point. Vertical fluxes at the surface simulate the continuous emissions within the city.

The presence of aerosol particles in the boundary layer will scatter and absorb solar radiation, and thus, modify the vertical profile of the radiative fluxes within it. A simplified, linear vertical profile of the UV actinic flux based on the observations (Fig. 1d) was used as input in the

Table 1
Chemical reactions used in the model

Reaction		Rate constant	Units
$O_3 + NO \rightarrow$	$NO_2 + O_2$	$2.2\times10^{-12}\exp(-1400/T)$	$cm^3\ molec^{-1}\ s^{-1}$
$NO_2 + h\nu \rightarrow$	$NO + O$	Depends on light intensity	s^{-1}
$O + O_2 + M \rightarrow$	$O_3 + M$	$6.0\times10^{-34}(T/300)^{-2.3}$	$cm^6\ molec^{-2}\ s^{-1}$
$O_3 + h\nu \rightarrow$	$O_2 + O(^1D)$	Depends on light intensity	s^{-1}
$R^aH + OH \rightarrow$	$RO_2 + H_2O$	2.63×10^{-11}	$cm^3\ molec^{-1}\ s^{-1}$
$HCHO + OH \rightarrow$	$HO_2 + CO + H_2O$	1.1×10^{-11}	$cm^3\ molec^{-1}\ s^{-1}$
$HCHO + h\nu \rightarrow$	$2HO_2 + CO$	Depends on light intensity	s^{-1}
	$H_2 + CO$	Depends on light intensity	s^{-1}
$RO_2 + NO \rightarrow$	$NO_2 + RO$	8.9×10^{-12}	$cm^3\ molec^{-1}\ s^{-1}$
$RO + O_2 \rightarrow$	$RCHO + HO_2$	1.9×10^{-15}	$cm^3\ molec^{-1}\ s^{-1}$
$HO_2 + NO \rightarrow$	$NO_2 + OH$	$3.7\times10^{-12}\exp(250/T)$	$cm^3\ molec^{-1}\ s^{-1}$
$NO_2 + OH \rightarrow$	HNO_3	$2.6\times10^{-30}(T/300)^{-3.2}$	$cm^6\ molec^{-2}\ s^{-1}$

[a] $R = CH_3$, except in reaction 4 where the OH rate corresponds to propene; $T = 283$ K (Seinfeld and Pandis, 1997).

Table 2
Initial concentrations for all species included in the model

Species	Initial concentration
NO_2	Based on aircraft sounding (max conc. = 40 ppb)
NO	Based on aircraft sounding (max conc. = 40 ppb)
O_3	20 ppb, constant with height
RH	20 * (NO) + (NO_2)[a]
HCHO	40 ppb[b]
OH	$1.\times10^6$ molec cm^{-3}
HO_2, CO, H_2O, HNO_3, O, RO_2, RO, RCHO	$1.\times10^{-15}$
O_2	0.209

[a] Based on observations of (RH/NO_x) for Mexico City that range between 15 and 20 (M.E. Ruiz, pers. commun).
[b] Based on observations for Mexico City (Baez et al., 1989, 1995, 1999).

calculations described here. The flux at the top of the mixed layer changes with time according to the zenith angle of the sun (between 9 a.m. and 11 a.m.), and the flux at the surface is a fixed fraction of the flux at the top of the ML.

3. Results and discussion

Fig. 2 shows the time evolution of the vertical profiles of O_3, for the case when no aerosol particles are present in the boundary layer (left panel), when the incoming flux is reduced by 50% at the surface due to absorbing particles (central panel), and when a 80% reduction in the flux at the surface is included (right panel). The turbulent diffusion coefficient is set to $10\,m^2\,s^{-1}$ in these simulations (corresponding to moderate turbulence levels), and the dark solid lines represent the growth of the boundary layer in the 2-h period. A marked peak is observed when the aerosols absorb the incoming photons, in contrast to maximum O_3 concentrations observed at the surface when no aerosols are present. The simulated O_3 peak aloft is in qualitative agreement with observations; however, because these simulations represent only the evolution of precursors from the observed initial state, the model cannot produce the measured O_3 levels (of up to 200 ppbv in the peak). Two cases were run with fluxes at the ground simulating actual emission rates in the city. The model considers surface fluxes of nitrogen oxides and the lumped hydrocarbon category, and their values are: 1.1×10^{-6} and 1.1×10^{-5} ppb/s, respectively, for a moderate emissions case. An analysis of the annual emissions inventory for the city, assuming uniform emissions in space (over $1200\,km^2$) and time (annual estimates), yielded much higher emission rates. When these rates are included in the model, the maximum O_3 concentrations agree well with the observed ones in the city. The vertical profiles after 2 h of simulation for these continuous emission cases, as well as the initial puff case

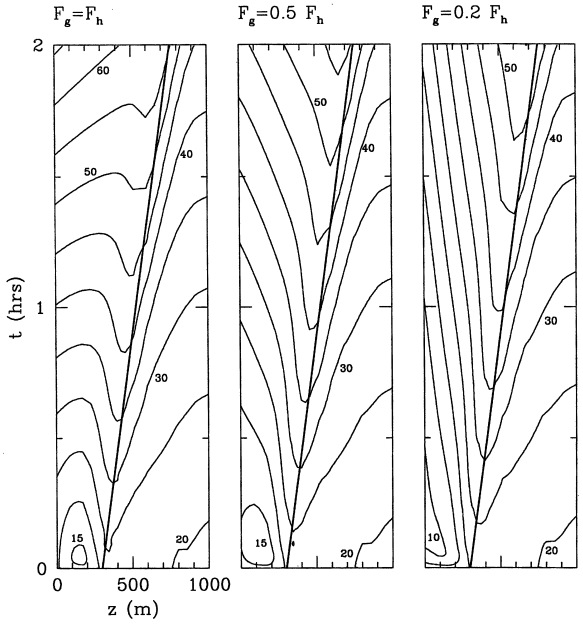

Fig. 2. Simulated ozone concentrations as a function of time and height for the case of no aerosols (left panel, when highly absorbing particles are included which result in an 50% reduction of the radiative flux at the surface (medium panel), and when a 80% reduction of the radiative flux at the surface is considered (right panel). The dark lines correspond to the top of the mixed layer and the contours have a linear spacing of 5 ppbv.

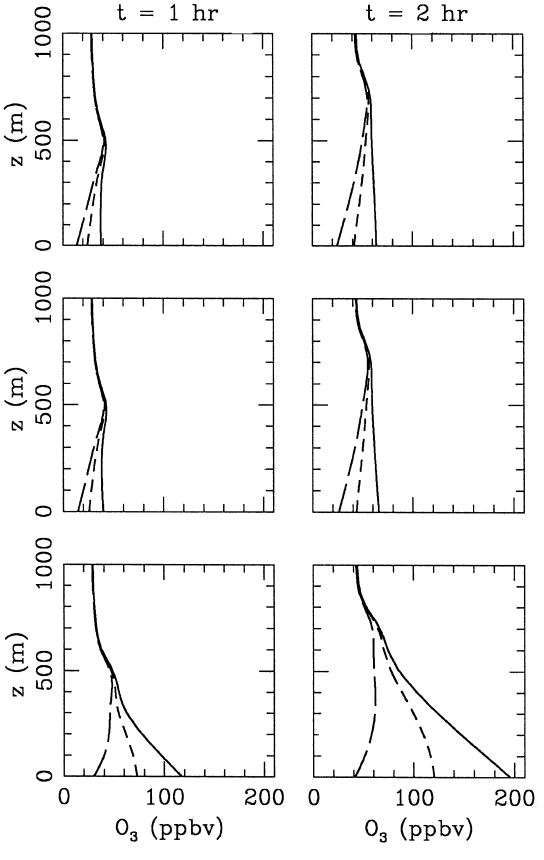

Fig. 3. Vertical cross sections of ozone for the no-aerosol case (solid line), absorbing aerosols present consistent with a 50% flux reduction at the surface (short dashed line) and consistent with an 80% reduction (long dashed line). The left panel presents results after 1 h of simulation and the right panel after 2 h. The two top panels correspond to results considering only an initial 'puff' of pollutants;the two middle ones show results with continuous moderate emissions at the surface, while the two bottom panels correspond to high surface emissions.

are presented in Fig. 3. Clearly, the presence of aerosols is enhancing O_3 production at the top of the ML with respect to production at the surface. The enhanced O_3 production at the top of the ML is the result of extra radiation at that level due to scattering by aerosols (Madronich, 1987; Dickerson et al., 1997) and because of the significant decrease in flux within the ML due to the absorbing particles, for the initial puff (top panels) and the moderate emissions (middle panels) cases. The high surface emissions case show a plateau (bottom panels) in O_3 concentration from 200 m to the top of the ML, as a result of the decrease of NO_2 photodissociation rates near the surface. A 50–80% reduction in the actinic flux is consistent with results of a 2-stream radiative transfer calculation (with δ-Eddington approximation), in which a 1–5% soot content in aerosol particles was included when estimating their single scattering properties (Raga et al., 1997). A reduction by 50% in the actinic flux corresponds to an aerosol optical depth (τ) of 0.69 for the boundary layer, while an 80% reduction corresponds to $\tau = 1.6$. These values are consistent with observations of spectral optical depths made by Vasilyev et al. (1995) in Mexico City for the June–July period in 1992. This period corresponds to the rainy season, when particles are more efficiently removed from the boundary layer by wet processes or simply by the strong vertical motions generated by the convective storms. It is reasonable to asumme that optical depths could be even higher during the dry season (November–May) when convective processes are not as strong and pollutants accumulate in the boundary layer, such as in the February case that we are considering here. The presence of absorbing aerosols is reducing the O_3 concentrations at the surface by about 40–66% after 2 h, suggesting that the ozone problem in Mexico City would be even worse if absorbing particles were not present in the ML. This result could have important implications for policymakers that are trying to implement measures to decrease ozone production in the city. Most of the measures tend to control gas emissions (particularly, vehicle NO_x and hydrocarbons), but soot particles are also emitted by the same vehicles. This situation is very different from that observed in the US (e.g., the Los Angeles basin and the Eastern seaboard), where light absorbing particles are a small fraction of all aerosols present. The high soot content observed in cities in the developing countries is indicative of less efficient combustion by older vehicles and reflects a socioeconomic situation very different from the prevalent one in the US. During a recent 2-week pilot project in Mexico City (Raga et al., 1999), the observed single scattering albedo of particles was on average 0.7, indicative of considerable absorption (Baumgardner et al., 2000). This value is much lower than 0.96 used for calculations in the Eastern US (Dickerson et al., 1997). Analysis with a thermographic technique (Novakov et al., 1998) indicated a large component of organic and elemental carbon in samples from Mexico City. Moreover, scanning and transmission electron microscope analyses of particles indicate a composition of predominantly carbon and oxygen and diffraction patterns are consistent with graphitic carbon.

The absolute magnitude of the elevated peak is small compared to the observations when only an initial puff or moderate emission rates are considered, but nevertheless there seems to be a causal link between the presence of absorbing aerosol particles and ozone production taking place first aloft, even though the highest precursor concentrations are included at the surface. More realistic emission rates yield much higher O_3 concentrations, in agreement with observations and strongly suggest that the ozone problem in Mexico City would be much worse in the absence of absorbing aerosols.

4. Final remarks

The observation of an elevated ozone peak in the morning hours within the well-mixed boundary layer in Mexico City has led to the realization that the highly absorbing aerosol particles also present within the ML alter the height at which photochemical processes maximize their effect. Recently, Jauregui and Luyando (1999) presented climatological evidence that the global solar radiation within Mexico City is 21.6% lower than in rural areas surrounding the city, and they attribute this to the presence of urban atmospheric pollutants. The results presented in this study suggest that the presence of these aerosols is probably inhibiting total ozone production in Mexico City. These conclusions are opposite to those presented by Dickerson et al. (1997), who conclude that reducing sulfate aerosol loading would reduce photochemically produced smog in the Eastern United States, due to the differing aerosol optical properties there and in Mexico City. In addition, there is a possibility that reactions on the surface of soot particles could also contribute to inhibit ozone concentrations in Mexico City, as suggested by Aumont et al. (1999).

In addition to modifying photochemical processes, the optical properties of aerosols originated in Mexico City could have a large effect in the local and regional climates, given through localized heating of the atmosphere. The boundary layer over Mexico City (located in a basin at 2.2 km above mean sea level) reaches a maximum height of approximately 4–5 km above msl. Therefore, if some of these particles were injected above the boundary layer they would find themselves in the mid-troposphere only 200 km downwind of the city. At those heights, they would have much longer residence times and a potentially significant climatic effect. This potential impact is investigated in a recently submitted companion paper (Raga et al., 2000).

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References

Aumont, B., Madronich, S., Ammann, M., Kalberer, M., Baltensperger, U., Hauglustaine D., Brocheton, F., 1999. On the NO_2 + soot reaction in the atmosphere. Journal of Geophysical Research 104 D1, 1729–1736.

Baez, A., Belmont, R., Gonzalez, O., Rosas, I., 1989. Formaldehyde levels in air and wet precipitation at Mexico City. Environmental Pollution 62, 153–169.

Baez, A., Belmont, R., Padilla, H., 1995. Measurements of formaldehyde and acetaldehyde in the atmosphere of Mexico City. Environmental Pollution 89, 163–179.

Baez, A., Torres Barrera, M.C., Garcia Martinez, R., 1999. Calculo de la velocidad fotolitica total Kp y vida fotolitica total del formaldehido y del acetaldehido en la atmosfera de la Ciudad de Mexico. Proceedings of the Third Symposium on Air Pollution, Mexico City, 17–19 February.

Baumgardner, D., Raga, G.B., Kok, G.L., Ogren, J., Rosas, I., Baez, A., Novakov, T., 2000. On the evolution of aerosol properties in Mexico City. P. Journal of Geophysical Research, submitted for publication.

Beyrich, F., Acker, K., Kalab, D., Klemm, O., Moller, D., Schaller, E., Werhahn, J., Weisensees, U., 1996. Boundary layer structure and photochemical pollution in the Harz Mountains: an observational study. Atmospheric Environment 30, 1281–1290.

Blake, D., Rowland, S., 1995. Urban leakage of liquefied petroleum gas and its impact on Mexico City air quality. Science 269, 953–956.

Dickerson, R., Kondragunta, S., Stenchikov, G., Civerolo, K., Doddridge, B., 1997. The impact of aerosols on solar UV radiation and photochemical smog. Science 278, 827–830.

Edinger, J.G., McCutchan, M.H., Miller, P.R., Ryan, B.C., Schroeder, M.J., Behar, J.V., 1972. Penetration and duration of oxidant air pollution in the south coast basin on California. Journal of Air Pollution Control Association 22, 882–886.

Elliot, S., et al., 1997. Ventilation of liquefied petroleum gas components from the Valley of Mexico. Journal of Geophysical Research 102D, 21197–21207.

Jauregui, E., Luyando, E., 1999. Global radiation attenuation by air pollution and its effects on the thermal climate in Mexico City. International Journal of Climatology 19, 683–694.

Lu, R., Turco, R.P., 1996. Ozone distributions over the Los Angeles basin: three-dimensional simulations with the SMOG mode. Atmospheric Environment 30, 4155–4176.

Madronich, S., 1987. Photodissociation in the atmosphere. 1. Actinic flux and the effects of ground reflections and clouds. Journal of Geophysical Research 92, 9740–9752.

MARI, 1994. Mexico City Air Quality Research Initiative. LA-12699; Los Alamos National Laboratory.

Meng, Z., Dabdub, D., Seinfeld, J., 1997. Chemical coupling between atmospheric ozone and particulate matter. Science 277, 116–119.

Nickerson, C.E., Sosa, G., Hochstein, H., McCaslin, P., Luke, W., Schanot, A., 1992. Measurements of Mexico City air pollution by a research aircraft. Atmospheric Environment 26B, 445–451.

Novakov, T., Raga, G.B., Baumgardner, D., Ogren, J., 1998. Size resolved carbonaceous aerosols in Mexico City. American Geophysical Union, Spring Meeting, Boston, USA, 26–29 May.

Odum, J., Jungkamp, T., Griffin, R., Flagan, R., Seinfeld, J., 1997. The atmospheric aerosol-forming potential of whole gasoline vapor. Science 276, 96–99.

Perez Vidal, H., Raga, G.B., 1998. On the vertical distribution of pollutants in Mexico City. Atmósfera 11, 95–108.

Raga, G.B., Kok, G.L., Baumgardner, D., Rosas, I., 1999. Some aspects of boundary layer evolution in Mexico City. Atmospheric Environment 33, 5013–5021.

Raga, G.B., Raga, A.C., Ruiz-Suarez, L.G., 1997. The interaction of particles and gases with solar radiation in Mexico City. AWMA Specialty Conference on Visual Air Quality, Aerosols and Global Radiation Balance Bartlett USA, 9–12 Sept., pp. 459–468.

Raga, G.B., Castro, T., Baumgardner, D., 2000. The impact of megacity pollution on local climate and implications for the regional environment. Atmospheric Environment, submitted for publication.

Seinfeld, J., Pandis, S., 1997. Atmospheric Chemistry and Physics. From Air Pollution to Climate Change. Wiley, New York, 1326 pp.

Vasilyev, O., et al., 1995. Spectral optical properties of the polluted atmosphere of Mexico City (spring–summer 1992). Journal of Geophysical Research 100, 26027–26044.