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Some aspects of boundary layer evolution in Mexico City

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Abstract

Measurements of chemical species and meteorological parameters were made at a site located 440 m above the mean basin level of Mexico City, over a two-week period in November during Project Azteca. Data from three of the stations of Mexico City's air quality monitoring network (Red Automática de Monitoreo Ambiental, RAMA) were also used to estimate the dilution in concentration experienced by pollutants as they are transported upslope during the course of the day. Both carbon monoxide and sulfur dioxide show a dilution of up to 50%, while ozone is usually more concentrated at the elevated site. These comparisons clearly highlight the intrinsic differences between primary and secondary gases, which are supported also by time–space, cross correlation analysis. The thermal mesoscale wind circulation dominates concentrations of pollutants at the research site: upslope during the day and downslope during the night. The data present clear evidence that downslope flows during the night contribute to ozone concentration at basin sites.

Keywords: Air quality; Pollution transport in complex topography; Megacity pollutants

1. Background

Mexico City is well known for its pollution problem, mainly due to photochemically produced gases, such as ozone, and also due to the presence of aerosol particles. High pollution episodes are the result of the city's geographical location at an elevation of 2240 m above sea level and due to the mountains that almost completely surround the flat-based basin. Its tropical location (19°N) also contributes to the problem, given that incident radiation is strong and does not vary significantly throughout the year. During the last decade, a large effort was made to measure and to try to understand the extent of the ozone and airborne particle problems (EGCA/MARI, 1994; IMADA, 1998). Mexico City is subjected to the influence of thermally driven, terrain-induced mesoscale circulations (e.g. up/downslope winds), that influence dispersion and transport of pollutants, as was first suggested by Jáuregui (1988) and recently modeled by Fast and Zhong (1998).

In this paper we further examine this hypothesis, aided by data collected at an elevated during a two-week period in November 1997, in the context of Project Azteca. This pilot project was a collaborative effort between Universidad Nacional Autónoma de México (UNAM) and the National Center for Atmospheric Research (NCAR), characterizing the microphysical and optical properties of small particles and their relationships to other gaseous pollutants. This paper studies the meteorological aspects of the diurnal evolution of the boundary layer, while the in-depth studies of particle microphysical and optical properties and the characteristics of gaseous pollutants are the focus of a companion paper (Baumgardner et al., 1999).

2. Data description

The experimental site is located on the Southwest edge of the city, within an ecological reserve (19°15′N, 99°11′W), at an elevation of 440 m above the mean basin level of 2240 m. The site (which will be referred to as Ajusco throughout the paper, due to its location on the

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slopes of the Ajusco peak) was chosen so that it would be located above the polluted layer during the night and early morning. A comprehensive suite of instrumentation was deployed at the site. Measurements were made of the gaseous pollutants, carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO, NO_y) and ozone (O_3). Airborne particles were measured with a variety of instruments, to characterize the size distribution. Particle optical properties were determined from a 3-wavelength nephelometer and a soot photometer, and measurements were also made of visible and ultraviolet irradiance. The pollution layer evolution was also recorded on time-lapsed video (1 frame per minute) and on a digital camera (1 picture every 30 min). Measurements of wind speed and direction, temperature and relative humidity were made with a commercial weather station.

The field campaign lasted for two weeks, from 4 to 18 November 1997, near the end of the rainy season. The sampling strategy consisted of 24-h gas, radiation and particle optical property measurements, while automated particle spectra were sampled between 8 a.m. and 8 p.m. (local time). The cascade impactors were exposed for 7-h periods from 10 a.m. to 5 p.m., to include only samples from the polluted mixed layer. The equipment was installed in a house within the reserve, with all measurements made from a stack that extended above the building by approximately 2 m (to a total of ~ 8 m above the ground). Table 1 presents details of the equipment used at the research site, which is very similar to the equipment used at the RAMA stations. Note that the data utilized in this study corresponds to 6-min averages, both from the Ajusco research site and the RAMA sites. The meteorological measurements were made at the same elevation, about 3 m to the north of the stack where the gases were sampled, with a Weather Monitor II (Davis) unit.

Three stations from the RAMA network were selected for the study: Pedregal (19°19′N, 99°12′W, 2342 m), Plateros (19°22′N, 99°13′W, 2317 m), Cerro de la Estrella (19°21′N, 99°10′W, 2247 m), which measure all the gas pollutants and meteorological parameters. Fig. 1 shows a map with the location of all the sites as well as the topographical contours every 200 m. Pedregal is located in a wealthy residential area, characterized by large properties and with very few local emissions. In contrast, Plateros is located less than 500 m from an eight-lane freeway, and Cerro de la Estrella is located in a more industrialized area to the East of the other two stations.

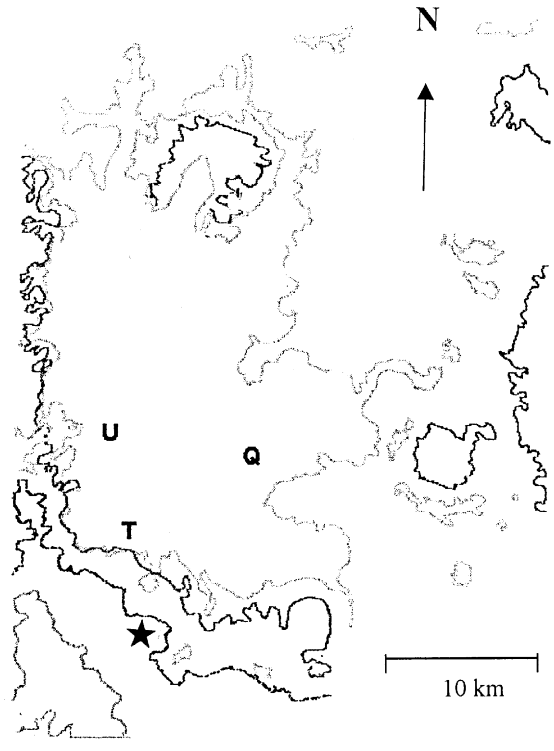

Fig. 1. Topographical map of the southwest corner of the Mexico City basin showing the RAMA (denoted by letters: T for Pedregal, U for Plateros and Q for Cerro de la Estrella) and research sites (denoted by a star).

Table 1
Equipment utilized for chemistry measurements at the research site

Gas species	Measurement method	Comments
O_3	UV absorption	With and without 5 μm inlet filter
NO	Chemiluminescence	
NO_y	Chemiluminescence	Gold/CO reduction
SO_2	Pulsed fluorescence	Carbonate zero trap
CO	Gas filter correlation	Heated Pd zero trap

3. Results

Fig. 2 shows the ozone time series over the 2-week period of the project for the research site Ajusco and the three basin stations, from 3 to 18 November. The diurnal pattern of O_3 is observed at all stations, directly linked to photolysis of anthropogenically produced nitrogen dioxide. Daily O_3 maximum concentrations ranged from almost 300 ppbv down to 80 ppbv, during a cloudy and windy 2-day period (10–12 November, due to the proximity of a tropical storm in the Pacific). Note also that the Ajusco site (Fig. 2a) always shows much higher concentrations during the night than the basin sites, which had already been observed by Bravo et al. (1992). During the

evening, the site remains in the residual layer, while the basin sites are all located within the stable nocturnal layer. Vertical soundings made at the airport (located within the basin) at 6 a.m. local time show this vertical structure very frequently, particularly in the fall and winter months. Basin sites typically show lower O_3 concentrations than the research site during the night, because O_3 destruction is more efficient in the nocturnal stable layer than in the residual layer aloft. Nevertheless, during several nights it is possible to detect rising O_3 concentrations at the basin sites and we will discuss these occurrences in more detail later in this section.

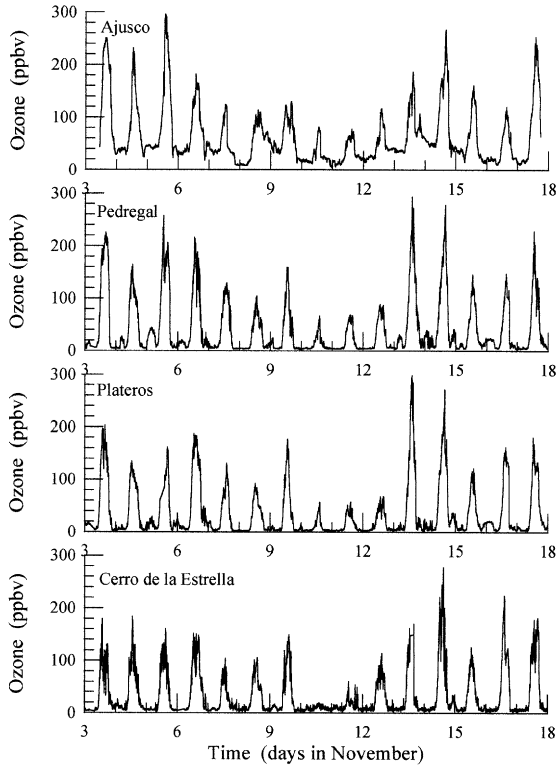

Fig. 2. Time series of ozone concentration at (a) the research site at Ajusco; (b) Pedregal site; (c) Plateros site; and (d) Cerro de la Estrella site.

3.1. Mean characteristics

Figs. 3 and 4 provide an overview of the conditions observed at the research site during the whole project, showing the daily mean (denoted by the square symbols), maximum and minimum values for a number of different variables. Fig. 3, showing CO, NO_y, accumulated visible (SW) and ultraviolet (UV) radiation and ozone, indicates the variability observed during the field project. The days with clouds and rain (10–12 November), had lower radiation and consequently lower maximum O_3 concentrations. The CO and NO_y (indicative of primary pollutants) had higher than average concentrations for the period, but since they corresponded to the cloudy period, O_3 concentrations were low even though precursors were a bit higher than average.

Fig. 4 shows the corresponding values for CO, SO_2, particle volume (from the automated spectral measurements, for particles smaller than 3.0 μm in diameter) and particle mass from the Andersen impactor (total, corresponding to particles with aerodynamic diameter smaller than 10 μm; small, corresponding to diameter smaller than 3.3 μm). Both CO and SO_2 are approximate surrogates for primary particle emissions and gas-to-particle conversions (secondary particle formation), that can be related to the direct particle measurements (Baumgardner et al., 1999). The large maximum concentrations of

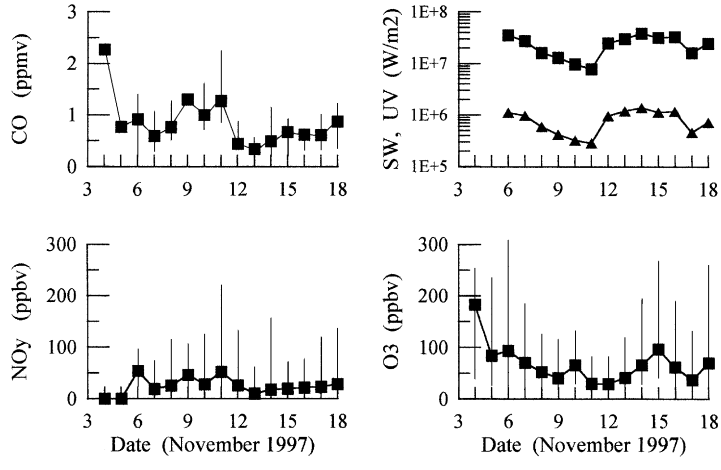

Fig. 3. Time series of average, maximum and minimum values measured at the research site for (a) carbon monoxide (CO), (b) nitrogen oxides (NO), (c) accumulated visible (SW) and ultraviolet (UV) radiation and (d) ozone (O_3).

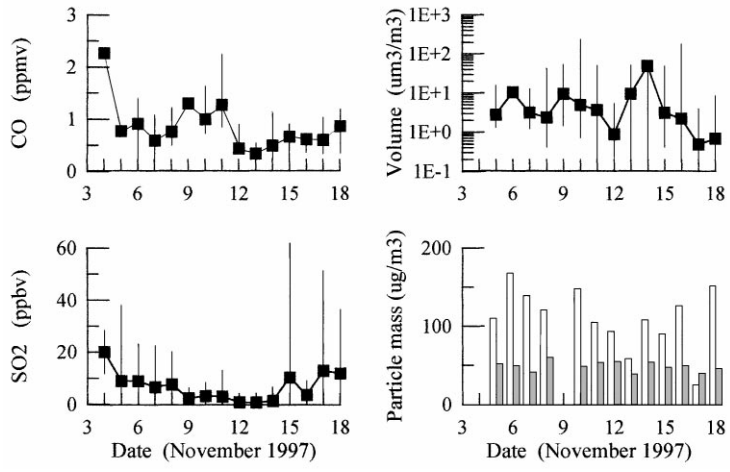

Fig. 4. Same as Fig. 3 but for (a) carbon monoxide (CO), (b) sulfur dioxide (SO_2), (c) volume of particles with diameters in the range from 0.02 to 3.0 μm and (d) mass of particles in Andersen impactor (white bar: total mass, particles with aerodynamic diameter smaller than 10 μm; shaded bar: small particle mass, particles with diameter smaller than 3.3 μm).

SO_2 towards the end of the sampling period are linked to natural emissions by the Popocatepetl volcano (about 60 km from the experimental site), rather than to anthropogenic sources within the city (Raga et al., 1999). Total particle mass shows a rather large variability during the sampling period, ranging from 250 to 60 $\mu g\, m^{-3}$. This variability is very much reduced in the small particle fraction, which shows a fairly constant concentration of around 50 $\mu g\, m^{-3}$. This difference in the traces could be indicative of the different origin of the particles in those two fractions, the larger particles having a larger geological component than the smaller ones.

3.2. Variability in terms of wind direction

Preliminary inspection of the diurnal wind direction data at the research site suggested that winds were predominantly from the SW, followed by NE and SE, with very few occurrences of NW winds, as can be seen in Fig. 5. Pedregal site within the basin is similar to the Ajusco site, while Plateros experiences more SW and NW occurrences. In contrast, the frequency distribution at Cerro de la Estrella (the site furthest to the East and away from the mountains) is clearly dominated by SW flow. These distributions suggest that the mountain topography is determining the dominant wind patterns: NE winds corresponding to upslope flow and SW winds corresponding to downslope flow. Further inspection reveals a clear time separation for these wind directions: southwesterly during the late afternoon and evening and easterly (both NE and SE) during the daytime. This particular 'dipolar' pattern in wind direction is directly related to the concentration of pollutants at the research

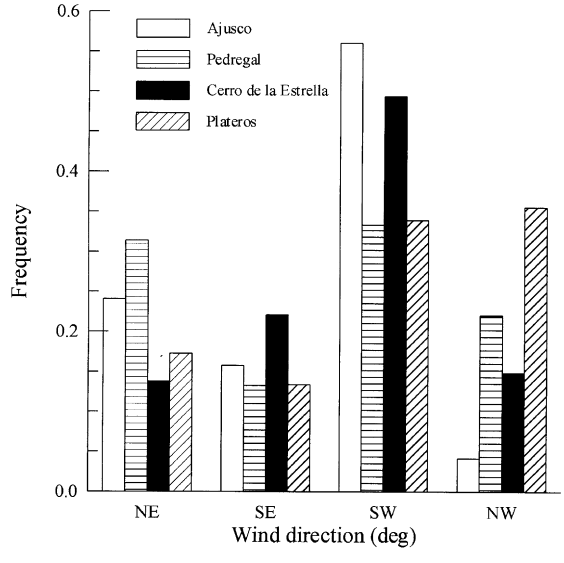

Fig. 5. Frequency distribution of wind direction at the research site and at the three sites within the basin.

site, as can be appreciated in Fig. 6. The majority of points in the night period (from 6 p.m. to 6 a.m. local time) are clustered between 180 and 270°, the southwesterly flow that corresponds to downslope flow at the site. Higher concentrations, as well as larger variability, are observed during the daytime period, but nevertheless, the majority of the observations cluster in the northeasterly quadrant.

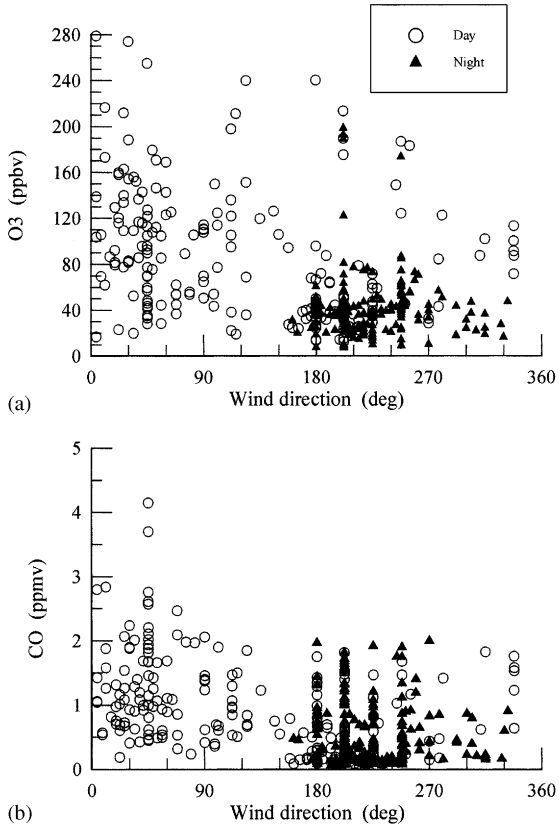

Fig. 6. (a) Ozone concentration at the research site Ajusco as a function of wind direction for daytime (6 a.m.–6 p.m.) and nighttime (6 p.m.–6 a.m.); (b) same as (a) but for carbon monoxide.

3.3. *Transport and dilution: primary vs. secondary pollutants*

In order to investigate the role of dilution as the air is transported up the slope from the polluted basin to the research site, we have calculated the ratio of concentrations observed at the site to those measured at the three basin stations. In particular, we selected CO, SO_2 and O_3 to highlight the differences observed between primary and secondary pollutants. Fig. 7 presents these ratios for CO and SO_2 as a function of the wind direction at the research site and as a function of time of day (daytime vs. nighttime conditions). The dipolar pattern of upslope flow (from the NE quadrant) during the day and downslope flow (from SW quadrant) during the late afternoon and evening mentioned earlier is very obvious when displayed in this manner. Note that the circles correspond to values of the ratio equal to 0.5, 1 and 1.5. Maximum values for the ratios exceed one on very few occasions, with the exception of SO_2 ratios at night when the influence of volcanic emissions is evident. The average value for the ratio between the research site and the basin stations Pedregal and Plateros is 0.45 for both CO and SO_2 during the daytime, indicating an average dilution of about 55% (assuming that sinks as well as extra sources can be neglected). In contrast, the O_3 ratios (Fig. 8) present a very interesting pattern: during the day, instead of showing dilution with respect to basin sites, the ratios are predominantly larger than 1. Note that the circles in Fig. 8 correspond to values of the ratio of 1, 5 and 10. This is even more remarkable during the night, when ratios of over 10 are observed. The nighttime observations are easily explained by the fact that the research site, being 440 m above the basin, is located within the nocturnal residual layer while pollutants in the basin (within the stable surface layer) are destroyed more efficiently. The 6 a.m. (local time) soundings from the airport within the basin typically show a stable layer in the first 200 m above the surface and a residual layer aloft. The daytime observations indicate that O_3 has higher concentrations aloft than at the surface in direct contrast with the observations of CO and SO_2. Aircraft observations taken in February of 1991 showed peak O_3 concentrations at the top of the mixed layer (Pérez Vidal and Raga, 1998). One possible explanation is that O_3 is being produced more efficiently at the top of the mixed layer rather than near the surface. The boundary layer in Mexico City is characterized not only by high concentrations of gaseous pollutants, but also of particulate matter. During Project Azteca, measurements of particle optical properties indicated a large light-absorbing component in particles with diameter less than 1 μm. These absorbing particles will modify the vertical profile of the solar actinic flux, and thus, the photodissociation rates. Even though O_3 precursors are emitted close to the surface, the presence of absorbing particles within the boundary layers creates a gradient in the photodissociation rates such that the production of O_3 is more efficient aloft. This hypothesis was presented by Raga et al. (1997) and continues to be explored in the light of new measurements made during Project Azteca.

This intrinsic difference in the transport and dilution of primary and secondary pollutants as they move up the slope was further investigated by calculating the cross correlation between parameters at the research site and at basin stations. These cross correlations were calculated using data at 6-min temporal resolution, and are presented in Fig. 9 as a function of time lag (in hours) for CO and O_3. Positive values of the lag correspond to the time series at Ajusco leading the time series at the basin site. The actual magnitude of the correlation coefficients is much lower for CO than for O_3, and this is related to the larger variability observed in the CO time series. Being a primary emission, CO concentrations at basin sites will be affected by very localized sources (such as the nearby passage of heavy trucks). Such short events will

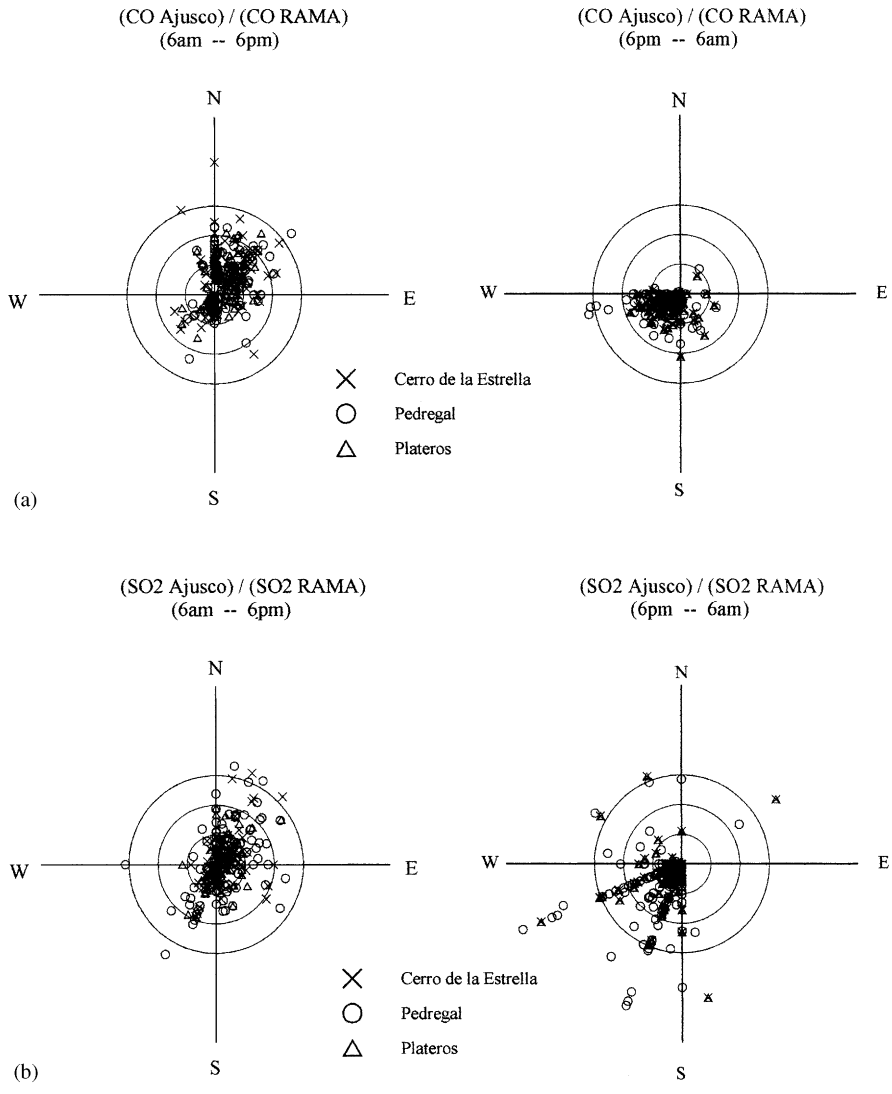

Fig. 7. (a) Ratio of carbon monoxide at Ajusco to carbon monoxide at basin stations as a function of wind direction and time of day (circles correspond to values of the ratio equal to 0.5, 1.0 and 1.5); (b) same as (a) but for sulfur dioxide.

not appear as peaks at the research site, but as an overall increase in concentration over a longer period of time, after the pollutant has been diluted and transported upslope. Concentrations at the research site lag those at the basin site Pedregal by about 1.25 h and site Plateros by 2 h (see Fig. 1 for site location). These values are consistent with the time that an air parcel would take travelling at the observed mean wind speed (1.42 m s^{-1}) from the basin sites to Ajusco (the distance from Pedregal to Ajusco is 7.8 km while the distance from Plateros to Ajusco is 12.4 km). The site Cerro de la Estrella to the East does not show correlation with the research site, which is consistent with the predominant winds at that basin site being away from the research site (see Fig. 5). In contrast, the cross correlations for ozone in basin sites Pedregal and Plateros have very significant peaks (correlation coefficient of about 0.8), but for lag = 0. This means that at the research site and at both basin sites the maximum ozone concentrations are observed at the same time, not showing any evidence of a time lag due to transport up the slope. This result is consistent with the hypothesis presented earlier that ozone is not produced at the surface within the basin and demonstrates the importance of including photochemistry and perhaps interaction between particles and radiation and not only transport when studying pollutant distributions in urban

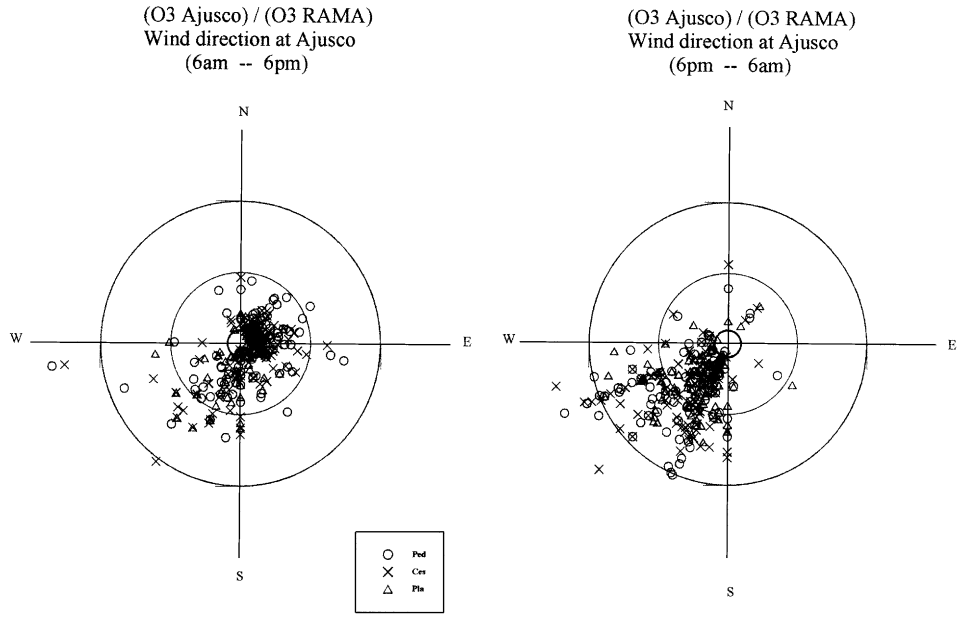

Fig. 8. Same as Fig. 7, but for ozone. The circles correspond to values of the ratio equal to 1, 5 and 10.

settings. The correlation between O_3 and CO presented in Fig. 10 at the research site also supports the argument that primary and secondary pollutants are not necessarily transported simultaneously up the slope. The low correlation obtained between O_3 and NO_y at the research site indicates that the ozone has been formed prior to arrival at the site.

3.4. Nocturnal downslope flows

The ozone time series presented in Fig. 2 indicate that the concentrations at the research site are always higher during the night than at the basin sites. This is explained by the fact that the site is located within the nocturnal residual layer, while the basin is immersed in the stable surface layer that develops throughout the night. The air in the surface layer is strongly stratified and less turbulent; therefore, pollutants are not easily mixed in the vertical. The titration of ozone by nocturnal NO emissions will significantly reduce O_3 concentration within the basin. Nevertheless, close inspection of the time series for Pedregal and Plateros shows evidence of increased ozone concentrations during the night, usually after midnight. In particular, the concentration at Pedregal on November 5th and 16th reached the same magnitude as that observed at the research site, as can be seen in Fig. 11a (for November 16th). In contrast, the site Cerro de la Estrella very rarely shows increased nocturnal ozone concentrations, and it is located furthest away from the mountains. We suggest that the nocturnal downslope flows are responsible for bringing down to the basin the higher ozone concentrations that are typical of the residual layer. Fig. 11b presents the scatter diagram for wind speeds at Ajusco and at Pedregal and Plateros, and there is a clear evidence of correlation between them, particularly when the magnitude is larger than 2 m s^{-1}. Wind direction remains constant during this period and is the same for all three sites. It is very likely that the air in the residual layer that is rushing down to the basin will transport not only ozone but also particles and other gaseous pollutants that could be important in the determination of pollution levels the following day.

4. Conclusions

A pilot project to determine the microphysical and optical properties of aerosol particles in Mexico City was carried out for a 2-week period in November 1997, at a research site 440 m above the mean basin level. The observing period was characterized by a range of pollution conditions, from days with very large ozone concentrations (above 250 ppbv) to days when the concentration was well below the Mexican standard (110 ppbv) coinciding with cloudy and windy days.

The results indicate that the diurnal upslope/downslope wind pattern (thermally forced circulation) is very important in the determination of pollutant concentrations at the research site. Analysis of the data from three

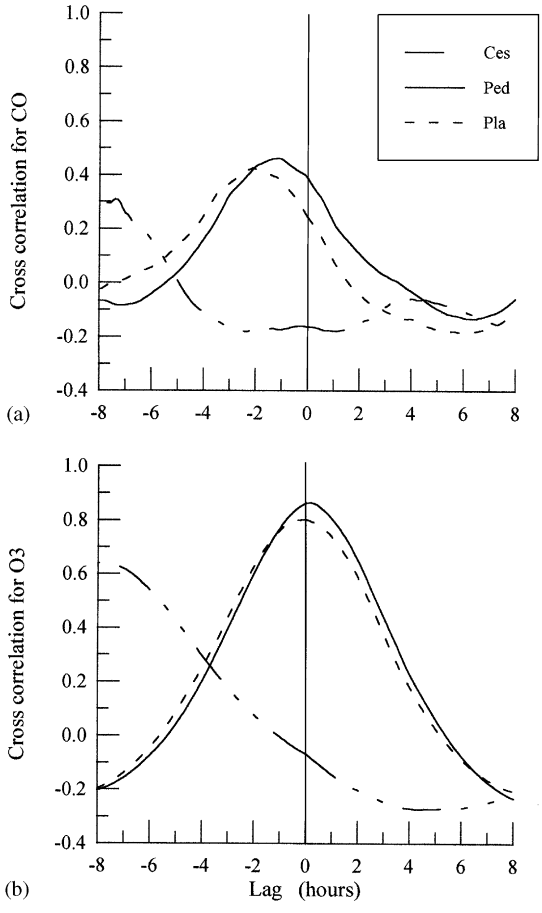

Fig. 9. Cross correlation between research site and basin sites for (a) carbon monoxide and (b) ozone.

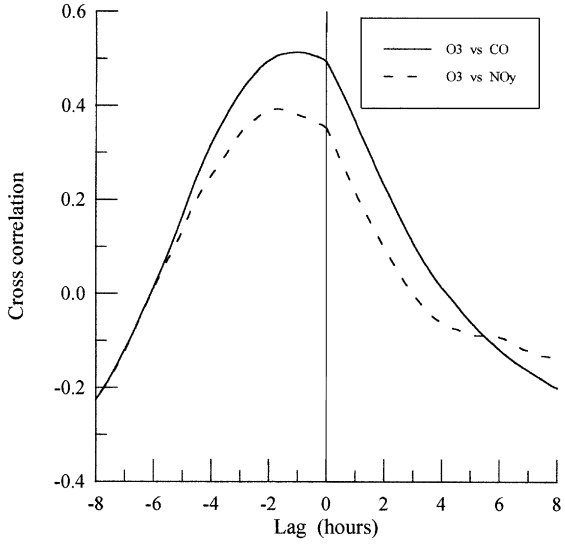

Fig. 10. Cross correlation between ozone and carbon monoxide (solid) and ozone and nitrogen oxides (dashed) at Ajusco.

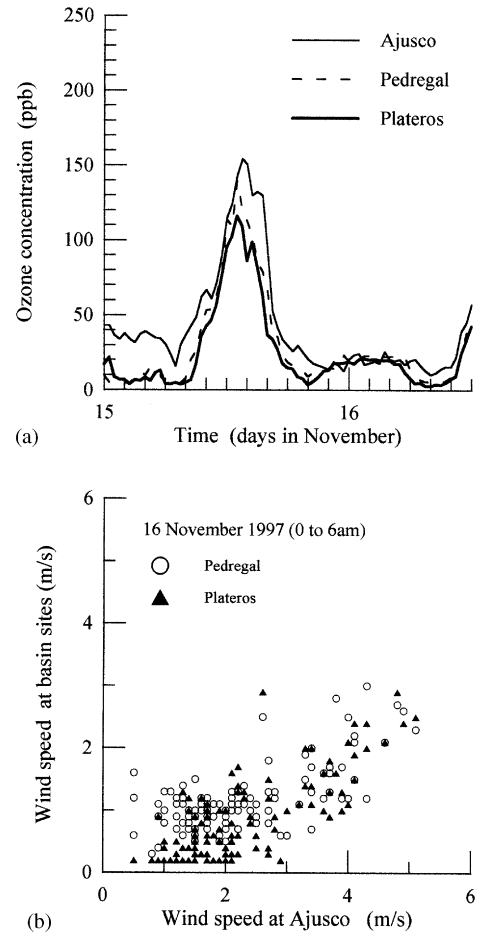

Fig. 11. (a) Ozone time traces measured at Ajusco (solid), Pedregal (dashed) and Plateros (heavy solid) corresponding to 15–16 November 1997. (b) Wind speed at basin sites Pedregal and Plateros as a function of wind speed at Ajusco.

stations of the monitoring network within the city indicate that the two sites closest to the research site (and thus to the mountains) also experience the thermal circulation, while the station furthest to the East does not show the aforementioned behavior.

The thermal circulation accomplished the transport of pollutants from the city to the research site and for carbon monoxide and sulfur dioxide it was accompanied by a dilution of about 50% (neglecting sinks and extra sources between the sites). Cross correlations between research and basin sites indicated a lag for maximum correlation of between 1 and 2 h for those gaseous pollutants. This is consistent with the time that an air parcel would take travelling at the observed mean wind speed from the basin sites to Ajusco. In contrast, ozone cross correlations were maximum for lag = 0 for the two closest sites. These contrasting results can only

be reconciled when one considers that ozone is a secondary pollutant, not primary as CO and SO_2. The results obtained in this study are consistent with the hypothesis presented by Raga et al. (1997) that in the presence of large concentrations of absorbing particles, ozone is formed more efficiently at the top of the boundary layer than near the surface, where precursors are emitted.

Finally, there is strong evidence that the nocturnal downslope flows may be playing a significant role in increasing pollutant concentrations in the stable surface layer, as was presented for ozone. It seems likely that small particles as well as other gas species (not measured by the monitoring network) may also be transported back to the basin during the night and this extra source may have important implications for photochemistry and particle spectral evolution the following day. Further theoretical studies are needed to quantify their possible importance.

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References

Baumgardner, D., Raga, G.B., Ogren, J., Kok, G., 1999. An evaluation of the microphysical and optical properties of Mexico City aerosols. Journal of Geophysical Research, (in press).

Bravo, H., Torres, R., Sánchez, P., Roy-Ocotla, G., Coutiño, M., 1992. Monitoreo de ozono en un sitio receptor de la Ciudad de México ubicado a 2726 msnm (Casa del Ajusco/UNAM). Internal Report, March 1992.

EGCA/MARI, 1994. Estudio Global de la Calidad del Aire/Mexico City Air Quality Research Initiative. Joint report Instituto Mexicano del Petróleo and Los Alamos National Laboratory, IMP/LA-12699.

Fast, J., Zhong, S., 1998. Meteorological factors associated with inhomogeneous ozone concentrations within the Mexico City basin. Journal of Geophysical Research 103, 18 927–18946.

IMADA, 1998. Investigación sobre materia particulada y deterioro atmosférico: Informe Final. Proyecto DOB-7238, Instituto Mexicano del Petróleo, México.

Jáuregui, E., 1988. Local wind and air pollution interaction in the Mexico basin. Atmósfera 1, 131–140.

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

Raga, G.B., Kok, G., Baumgardner, D., Báez, A., Rosas, I., 1999. Evidence for volcanic influence on Mexico City aerosols. Geophysical Research Letters 26, 1149.

Raga, G.B., Raga, A.C., Ruíz Suárez, L.G., 1997. The interaction of particles and gases with solar radiation in Mexico City. Proceedings of the Conference on Visual Air Quality: Aerosols and Global Radiation Balance, September 9–12, Bartlett, USA.