Atmosfera (1998), 11 pp. 95-108

On the vertical distribution of pollutants in Mexico City

H. PÉREZ VIDAL

Universidad Juárez Autónoma de Tabasco. División Académica de Ciencias Básicas. Km. 1 Carretera Cunduacan-Jalpa, Tabasco, México

G. B. RAGA

Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México, Circuito Exterior, CU, México, D. F., 04510, México

(Manuscript received June 16, 1997; accepted in final form October 10, 1997)

RESUMEN

El problema de la contaminación del aire en la Ciudad de México se estudia en este trabajo utilizando una base de datos obtenidos por un avión meteorológico instrumentado durante una campaña de muestreo en febrero de 1991. Estos datos constituyen una base única en México y permiten conocer la estructura vertical de la capa límite y de especies contaminantes que no han sido presentadas anteriormente.

Los resultados obtenidos en cuanto a la evolución y estructura de la capa de mezcla indican que su altura pasa de 100 m a las 8 de la mañana a más de 2000 m sobre el nivel de la superficie a las 5 de la tarde. Los resultados consistentemente presentan que el máximo en la concentración de ozono no se observa en superficie, sino a una altura de 700 m por encima de ella cerca del mediodía. Este pico, con una concentración promedio durante el período observacional de 167 ppb, parece ser un resultado transitorio, dado que las concentraciones se homogeneizan en la vertical por la tarde. Los perfiles verticales de óxidos de nitrógeno y de bióxido de azufre indican que las concentraciones son máximas durante la mañana y decrecen uniformemente con la altura, sugiriendo que las fuentes para estas especies están en la superficie, como era de esperar. No parece haber una correlación entre el contenido de óxidos de nitrógeno observado durante los sondeos de la mañana (durante el despegue del avión) y la concentración de ozono observada durante el aterrizaje (2 ó 3 horas más tarde). Cuando las variables son normalizadas por la altura de la capa de mezcla, los resultados indican que el ozono es independiente de la concentración de óxidos de nitrógeno observada durante el despegue. El rango de valores del cociente entre el ozono acumulado en la capa de mezcla y la altura de esa capa no es amplio.

Las partículas de aerosol cerca de la superficie presentan su máxima concentración durante la mañana, pero durante el transcurso del día, hay un marcado incremento en la concentración más arriba en la capa de mezcla, sugiriendo que posiblemente la conversión de gas a partícula sea responsable del incremento observado.

ABSTRACT

The problem of air pollution in Mexico City is studied through the analysis of a large dataset obtained by an instrumented aircraft during February 1991. These data constitute a unique set in Mexico and provide insight into the vertical structure of the boundary layer and the pollutant species which has not been previously discussed.

The results obtained on the evolution and structure of the mixed layer indicate that its height rises from 100 meters during the morning (8am) to over 2000 meters at 5 pm. Results consistently show that the maximum in ozone concentration is not observed at the surface, but at about 700 m on average above it near midday. This peak, with an average concentration over the observational period of 167 ppb, appears to be a transient feature, with concentrations becoming more uniform with height in the afternoon. The vertical profiles of nitrogen oxides and sulphur dioxide indicate that concentrations are highest during the morning and steadily decrease with height, suggesting that sources for these species are located near the surface, as was expected. There appears to be no correlation between the amount of nitrogen oxides observed during the take-offs and the ozone concentrations observed during landign (2-3 hours later). When the variables are normalized by the mixed layer height the results indicate that the ozone observed is fairly independent of the nitrogen oxide concentrations observed earlier.

A reduced range of values of the ratio of ozone accumulated in the mixed layer and the layer height is consistently day found during the observational period.

Aerosol particles near the surface show maximum concentration during the morning hours, but in contrast, during the course of the day, there is a marked increase in their concentrations at higher levels in the boundary layer suggesting that possibly gas to particle conversion is responsible for the observed increase.

1. Introduction

Atmospheric pollution in Mexico City is favored due to its geographical location at an elevation of 2.2 km above sea level and due to the mountains that surround the flat-based basin. The high elevation is couple with reduced water vapor content that during the night allows the infrared radiation to escape, and thus to give formation to strong surface temperature inversions. Its tropical location (at 19°N) also contributes to the problem, since it is mainly photochemical in nature and incident solar radiation does not vary significatly throughout the year. The extremely high emissions by mobile and fixed sources provide the needed conditions for very high 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 Petroleoum Institute) and Los Alamos National Laboratory (EGCA/MARI, 1995). The main objective of this study was to improve the understanding of the ozone problem in Mexico City. An instrumented aircraft participated during the project and flew 15 missions in a 3-week period. These data constitute a unique set in Mexico because they allow us to approach the problem from a different perspective, that is, not only including surface information which has been the subject of numerous studies (Bravo, 1986, 1989; Jáuregui *et al.*, 1981; Quadri and Sánchez, 1992; Raga and LeMoyne, 1996, among others). Nickerson *et al.* (1992) present a brief description of the data obtained, discussing only 2 of the 15 flights. In this study we build on their results to include all flights and to evaluate the relationship between meteorological and air quality variables in the vertical and determine their diurnal evolution.

2. Data utilized

The king Air from NCAR participated in the project and flew 15 missions in 13 days in the period from February 9 to 27, 1991. The standard suite of instrumentation was installed in the aircraft (for meteorological parameters), as well as instrumentation to measure ozone (O_3) carbon monoxide (CO), nitrogen oxides (NO_x and NO), sulphur dioxide (SO_2) and aerosol particles with an optical spectrometer (ASASP, which measures particles with diameters between 0.12 and 3 μm) and a total particle counter (CN). Broad band radiometers were also mounted, for UV, visible and IR radiation.

In this study we analyze only the segments that correspond to take-offs and landings, which provide a fairly good representation of a vertical sounding. The level segments are being currently analyzed and results on the export of pollutants from the urban area into the surrounding mountains will be reported shortly. Table 1 presents a summary of the flights analyzed.

Table 1. Summary of flights carried out during February 1991.

Flight	Date	Local time (ascent)	Local time (descent)
01	9	11:40:30	13:25:21
02	11	10:00:26	13:36:31
03	13	08:20:04	11:18:48
04	13	14:13:22	16:40:05
05	15	10:41:39	13:44:22
06	17	09:28:22	12:03:05
07	18	09:51:25	13:17:32
08	19	09:01:16	11:43:07
09	19	13:55:48	16:25:42
10	21	09:48:26	13:07:29
11	22	10:01:28	12:25:51
12	23	09:59:50	13:28:17
13	25	10:03:40	11:55:15
14	26	10:04:21	13:28:44
15	27	08:02:54	09:30:00

3. Results

a. Surface observations

Table 2 presents the observed values of meteorological and pollutant parameters at he surface (before take-off or after landing). Potential temperatures range from 302°K early in the morning to 320°K in the mid-afternoon, while the specific humidity ranges from 3 to 11 g/kg. Note that the surface winds are always very light and predominantly from the NE at the airport (45% of the cases). The observed particle concentrations are quite high, ranging from 2000 to 12000 per cubic centimeter. Gases show moderate to high concentrations at the airport. Ozone in particular, exceeded the Mexican standard in 6 instances during this observing period.

Table 2. Meteorological and pollutant data obtained by the aircraft at the airport before take-off and after landing.

Date	Local Time	Potential Temp (θ,°K).	Specific humidity (gr/kg)	Wind speed (m/s)	Wind direction	Mixed layer height (m)	NOx (ppb)	PST (#/cc)	O_3 (ppb)	SO_2 (ppb)
09	11:48	312	5.5	3	NE	460	30	10000	70	15
09	13:25	315	5.5	7	NE	960	-	2000	70	10
11	10:00	309	5.5	2	NW	300	-	6000	70	60
11	13:36	315	6.0	5	NE	1460	-	4000	80	20
13	08:20	305	4.8	2	NE	100	80	4000	20	25
13	11:18	312	6.0	4	NE	760	40	4000	100	20
13	14:13	318	-	5	NW	1100	100	4000	130	40
13	16:40	320	7.0	6	NE	2000	11	2000	130	15
15	10:41	310	8.0	3	NW	560	40	4000	100	35
15	13:44	315	7.0	3	NE	1760	35	2000	80	15
17	09:28	309	7.0	2	SE	250	340	8000	40	35
17	12:03	315	6.0	3	NE	1260	25	4000	110	10
18	09:51	310	6.0	2	SE	360	90	9000	120	25
18	13:17	318	4.0	2	NE	2360	15	2000	70	5
19	09:01	306	5.0	1	NW	100	170	12000	50	30
19	11:43	314	3.0	4	SE	760	30	4000	120	10
19	13:55	316	-	6	SW	1460	9	4000	60	4
19	16:25	320	3.5	6	SE	2360	20	2000	50	4
21	09:48	302	6.0	2	SW	-	90	12000	100	25
21	13:07	316	3.5	4	NE	-	20	2000	80	5
22	10:01	308	6.5	1	NW	260	180	10000	120	70
22	12:25	314	5.0	5	NE	1160	60	8000	150	55
23	09:59	308	10.0	3	NW	360	240	2000	60	5
23	13:28	314	4.0	6	SE	2260	25	4000	90	5
25	10:03	310	11.0	2	SW	260	85	6000	60	20
25	11:55	314	5.8	7	NE	1560	20	2000	80	5
26	10:04	310	7.0	4	NE	560	200	8000	60	45
26	13:28	318	6.5	6	SW	1760	7	2000	60	10
27	08:02	310	6.0	5	SE	200	45	2000	18	15

Figures 1a and 1b present the diurnal evolution of potential temperature and horizontal wind speed at the surface, obtained combining data from all 15 flights. There is an increase as the day progresses, as expected, and for the potential temperature it is well represented by the empirical relationship:

$$\theta_{surf} = 310 + 10 \sin[15(x - 11)] \quad (1)$$

where x is the time in hours, for the month of February between 8am and 5pm, for which there are flights available. Table 3 presents the linear correlation between different meteorological and pollution variables observed at the surface. it is clear that when conditions show moderate wind speeds the concentrations of NO_x, SO_2 and particles at the surface are reduced (negative value of correlation coefficient), as would be expected. In contrast, the correlation between wind speed at the surface and O_3 concentrations is virtually nil, which is an interesting result, since we would have expected lower O_3 concentrations with increasing wind speed. The same pattern of correlations is observed between the potential temperature and NO_x, SO_2 and particles. A small positive correlation is observed with ozone,

also as expected given that ozone is the resultant of photochemical processes that evolve in time and not a direct emission. Also listed in this table is the height of the mixed layer, determined from the aircraft soundings. Again, anticorrelations are obtained between mixed layer height and NO_x, SO_2 and particles, indicating a dilution effect. Correlation is positive with ozone concentrations, highlighting the different nature of this pollutant.

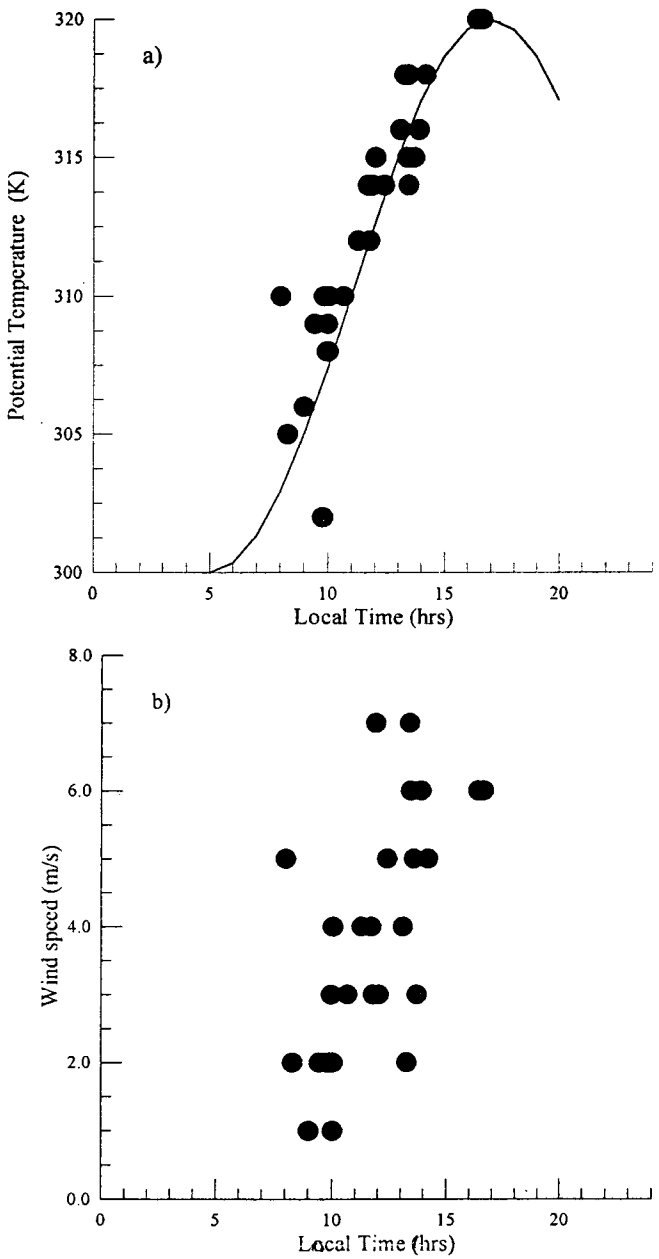

Fig. 1. Diurnal evolution of a) surface potential temperature and b) horizontal wind speed.

Table 3. Linear correlation between meteorological parameters and pollutants at the surface.

	NOx	PST	Ozone	SO_2
Specific humidity	0.4070	0.0538	-0.0917	0.1545
Wind speed	-0.5104	-0.6035	0.0737	-0.4492
Mixed layer height	-0.5912	-0.5799	0.2135	-0.5078
Potential Temperature	-0.5638	-0.6560	0.2515	-0.4280

b. Aircraft soundings

Figure 2 shows the vertical profiles of the thermodynamic variables as well as the pollutants measured for the take-off at 10:03 am on 25 February 1991. The mixed layer height was about 300m, overlayed by the residual layer (slightly stably stratified) from the previous day to about 4000m. The strong stable layer at 4000 m indicates the top of the boundary layer, with the free atmosphere above it. Figures 2b and 2c show vertical profiles of sulphur dioxide and nitrogen oxides, all of which are emitted at the surface and presenting maximum values there. In contrast, the ozone profile shows a more complicated vertical structure, with ozone remaining overnight in the residual layer. There is a suggestion at this time that ozone is forming more rapidly aloft in the mixed layer than at the surface. This will appear more clearly later on Figure 2d shows the vertical structure of the aerosol particle concentrations. As in the ozone case, there is much more structure observed, with an elevated small particle peak between 3200 m in the residual layer.

The boundary layer height evolution can be parameterized from the observations (Fig. 3a) as:

$$Z_{ML} = 1245\ \{1 + \sin[15(x - 13)]\} \tag{2}$$

where x is the time in hours, for the month of February between 8am and 5pm, for which there are flights available. The mixed layer height varies from less than 100 m during the morning to 2.0 km in the afternoon. The derived empirical function (2) would provide valuable information when trying to estimate the diurnal evolution of pollutants emitted at the surface due solely to dilution. Figure 3b presents the time evolution of the vertical profiles of the potential temperature, and shows a fairly reproducible vertical structure regardless of the day that it was obtained (note that the profiles are shown as function of take-off/landing time and not in a particular order with respect to days of the month). This observation will allow us to make further assumptions for pollutant data analysis, as is described in Section 4.

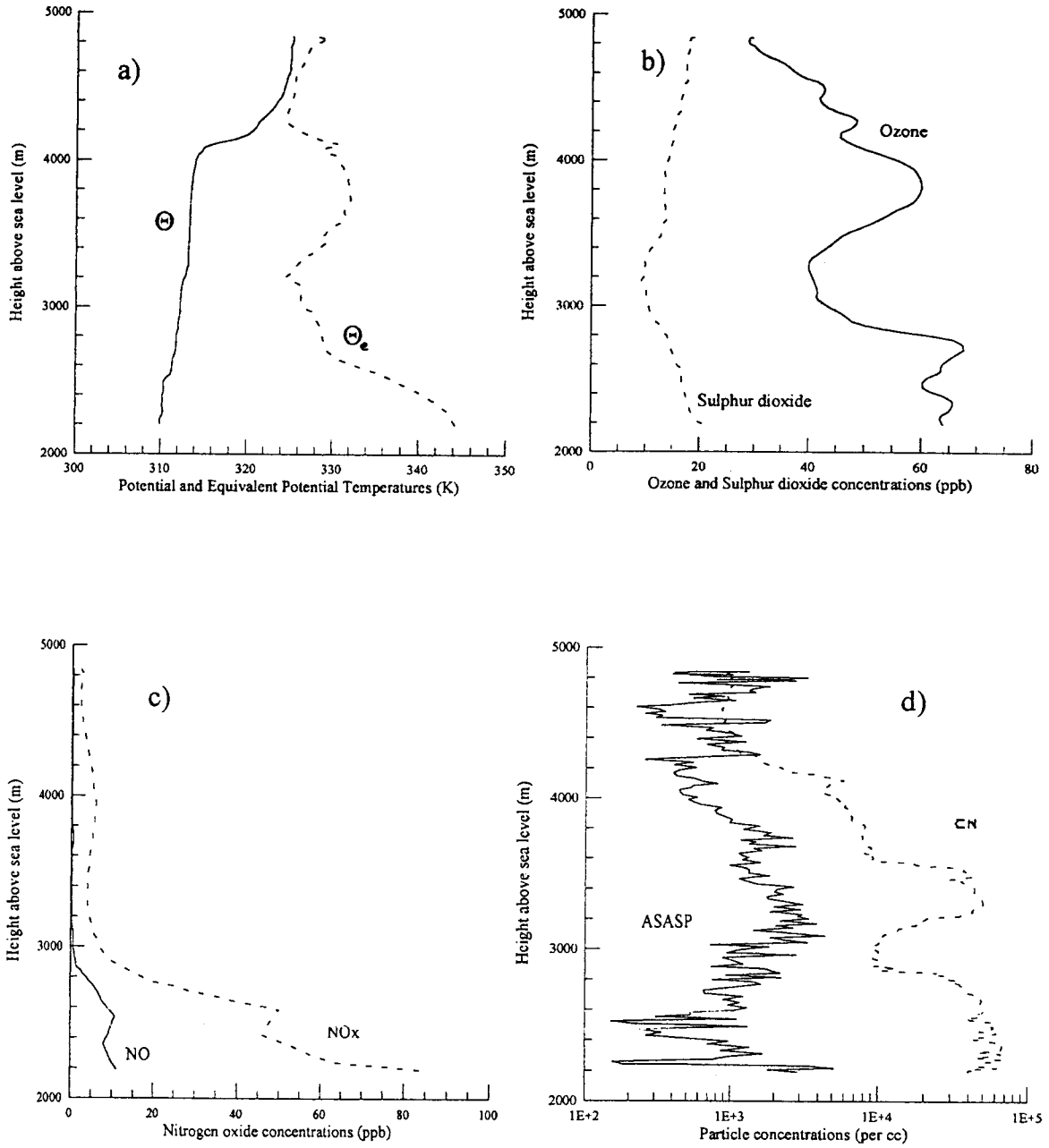

Fig. 2. Thermodynamic and chemical variables with height for flight 13 at 10:03 am on 25 February 1991. a) Potential (θ) and equivalent potential (θ_e) temperatures; b) ozone (θ_3) and sulphur dioxide (SO_2) concentrations; c) nitrogen oxides (NO and NO_x), and d) total aerosol particles (CN) and particles in the size range 0.12 to 3.0 μm (ASASP).

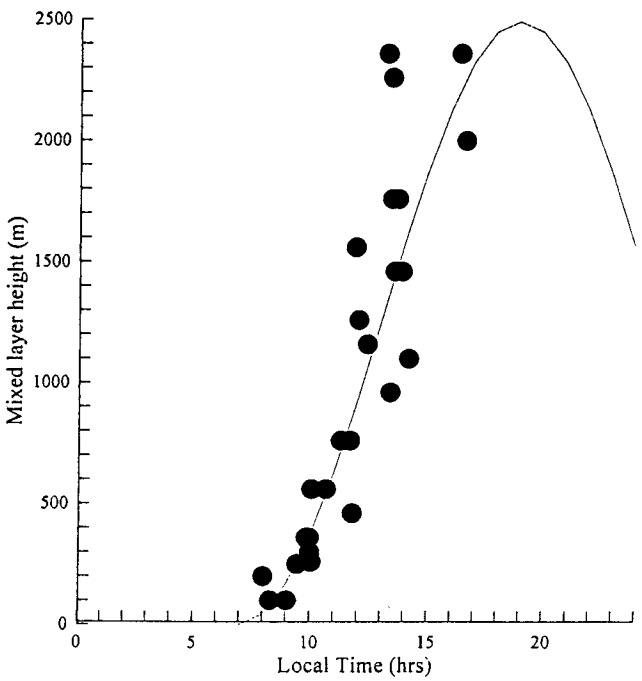

Figure 3a

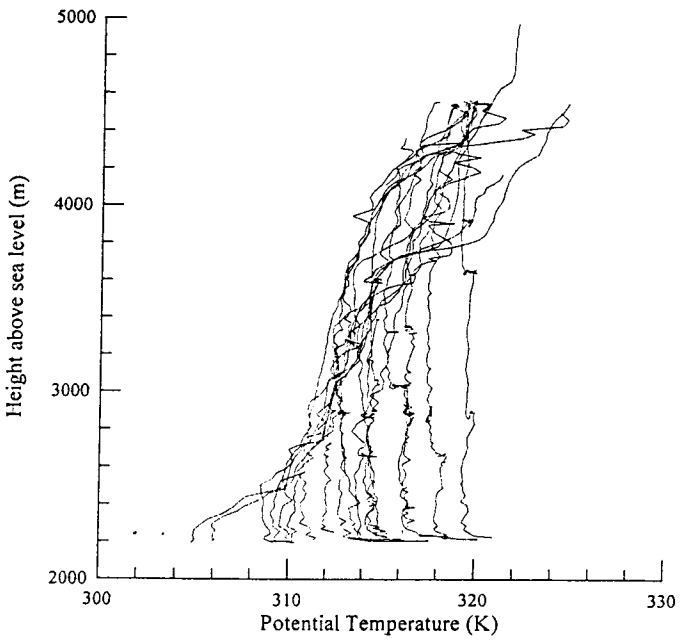

Figure 3b

Fig. 3. Time evolution of a) the mixed layer height (Z_{ML}) and b) the potential temperature profile.

Table 4 presents the heights at which the peak concentrations of ozone and particles were observed. Note that consistently the concentrations of ozone and particles are observed above the surface. This constitutes a very important finding. Elevated 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), in the last few years. The average heights at which O_3 and particles have maximum concentrations

Table 4. Heights where peak ozone and particle concentrations are observed.

Date	O_3 concentration (ppb)	height of O_3 peak (m)	Particle concentration (#/cm^3)	Height of particle peak (m)
9	180	560	12000	560
11	160	560	12000	860
13	220	560	12000	560
15	140	360	15000	760
17	120	260	12000	560
18	150	1060	10000	760
19	180	560	14000	560
21	200	760	12000	560
22	240	160	14000	560
23	160	1760	16000	760
25	140	560	16000	560
26	120	1560	15000	1260

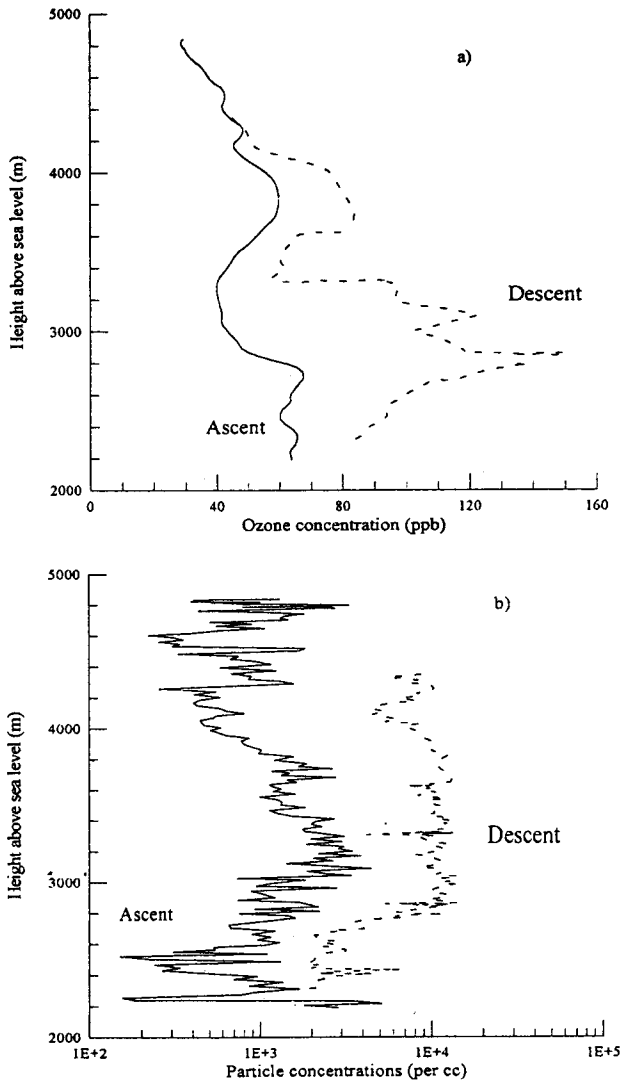

Fig. 4. Profiles of a) ozone and b) aerosol particles observed during take-off (at 10:03 am) and landing (at 11:55 am) on 25 February 1991.

are 727 and 693 m, respectively. As a representative example, Figure 4 presents the vertical profiles of ozone and particles observed during take-off (at 10:03 am) and landing (11:55 am) for flight 13. It is clear that both ozone and particles have increased significantly in concentration in the lapsed period of 2 hours. It is also clear that maxima for both pollutants are not observed at the surface, and exceed the surface values by almost a factor of 2 in the ozone case and by almost and order of magnitude in the case of particles. The elevated peak in particle concentration is very likely linked to the production of particles from the gas phase, either from sulphur dioxide and /or from hydrocarbons. The mixed layer height has risen from 300m to 1200m above the basin level in the same period. In a more theoretical paper (Raga *et al*, 1998) we explore the possible causes for the formation of an elevated ozone peak.

4. Discussion

The results presented above constitute an example of a first in depth evaluation of the measurements obtained by the aircraft in 1991. To further investigate the role of the emitted pollutants in the boundary layer in Mexico City we proceed to estimate what fraction of the observed concentrations with height is due merely to dilution and what fraction is due to photochemical reaction. For the sake of argument, let us assume that SO_2 and NO_x are conserved species. During the morning (take-off sounding), a certain concentration is emitted at the surface, when the mixed layer height is rather small. At the time of aircraft landing the mixed layer has grown significantly and a new profile of the contaminants is measured. In Figure 5, we present a scatter diagram of the observed NO_x concentrations during landing as a function of the calculated concentrations considering dilution in a larger volume, if no further emissions had taken place and assuming a conserved species. Note that the 1:1 line (that corresponds exactly to dilution)

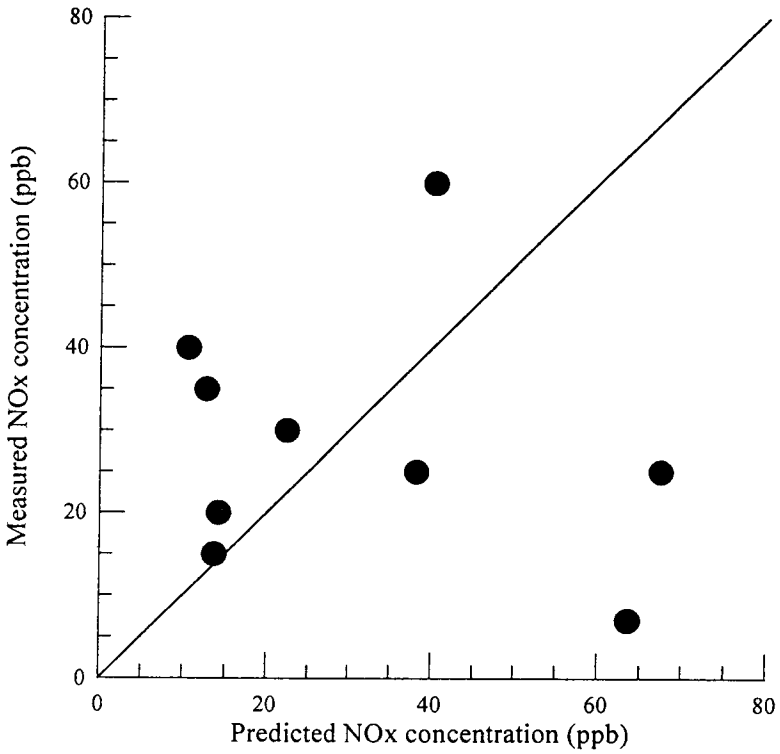

Fig. 5. Observed versus calculated NO_x concentrations for all flights. See text for details on the calculation.

separates two clear regimes: a) when the calculated concentrations are lower than the observed ones it implies that further emissions have taken place; and b) when calculated concentrations exceed observed values it implies that concentrations have been reduced by chemical reactions. A large scatter is shown which suggests that there is no consistent pattern during the observational period, perhaps implying the complexities both in the emissions and the photochemical processes. An equivalent diagram for SO_2 (Fig. 6) shows a very different distribution, with reduced scatter and most of the points lying above the 1:1 line. This indicates that further emissions (after the take-off observations are made) are needed to explain the observations at a later time (landing). Obviously, SO_2 can be considered a better tracer than NO_x, particularly during the dry season when very low relative humidities are observed and this difference is expressed in these two figures.

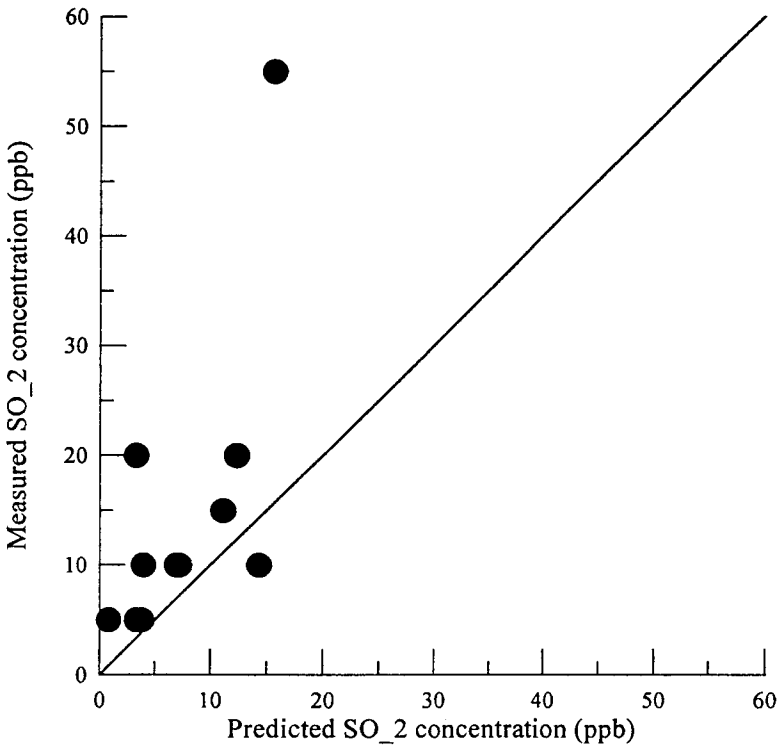

Fig. 6. Same af Figure 5, but for SO_2 concentrations.

We also investigate the role of NO_x emissions during the morning sounding in the ozone concentrations observed by the aircraft during landing. In order to do this, we estimate the amount of NO_x accumulated within the mixed layer during the take-off sounding and correlated it with the ozone integrated amount within the increased mixed layer at a later time. This accumulated concentration corresponds to the 'column amount', where the column is only the height of the mixed layer. Figure 7 shows this correlation and it is clear that there is no relationship between these two parameters. This result is a bit surprising since nitrogen oxides are precursors for ozone, but the conclusion has to be that the photochemical reactions are much too fast to be able to determine a relationship between them from the observations that we have (with typical time differences between take-off and landing of 2-3 hours). Also, NO_x are continued to be emitted throughout the period which is not taken into account in this simple exercise.

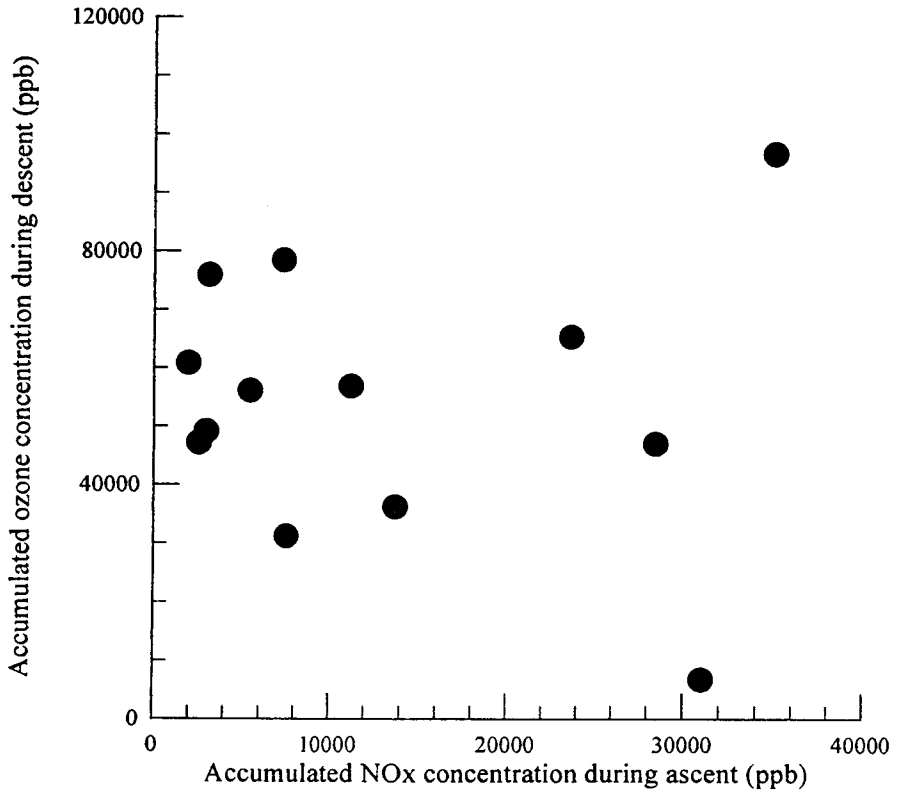

Fig. 7. NO_x concentration accumulated in the mixed layer during aircraft ascent versus O_3 concentration accumulated in the mixed layer during descent.

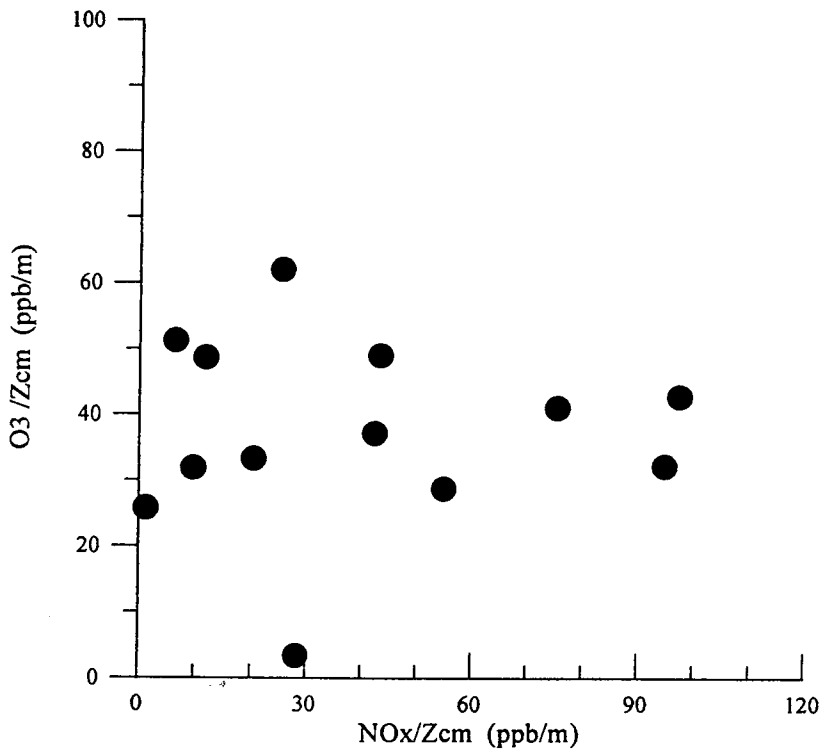

Fig. 8. Same as Figure 7, but both variables have been normalized by the height of the mixed layer in each case.

Another interesting result is shown in Figure 8 where we have normalized the integrated concentrations by the mixed layer height. These results indicate that the amount of ozone within the layer divided by this height is fairly independent of the ratio between NO_x and mixed layer height earlier in the morning. This would suggest that chemical species other than NO_x are the ones that play the limiting role in ozone production. It is also interesting to note the rather small range of values in the ozone axis, which would suggest that even though the formation processes are extremely complex, and even though there is variability in meteorological conditions the amount of ozone formed in the mixed layer remains fairly constant day after day during the observational period.

5. Conclusions

In this study we present the analysis of meteorological and pollution observations taken by an instrumented aircraft during a field campaign in Mexico City during February 1991. The results of the aircraft data provide insight into ozone and particle formation as a function of height, which have not been discussed previously in the context of the Mexico City air pollution problem.

The results from the surface data obtained before take-off and after landing, indicates that the NO_x, SO_2 and particles are anticorrelated with wind speeds and potential temperature, as was expected. In contrast, O_3 does not show a significant correlation with wind speed at the surface, which is contrary to what was expected. There is a positive correlation between potential temperature and O_3 concentrations, which highlights the fact that O_3 is the resultant of photochemical processes that take time to evolve and build up, hence the positive correlation. The correlations between pollutants and the height of the mixed layer are negative in the case of NO_x, SO_2 and particles (suggestive of a dilution effect) but are positive for O_3 concentrations, again highlighting the different nature of this pollutant.

The analysis of thermodynamic data (obtained during the take-offs and landings) allow us to determine the diurnal evolution of the mixed layer height near the airport, for the period of observation. This empirical function (Eq. 2) will be useful to others that need an estimate of such a height for their own studies.

The analysis of the air quality parameters has revealed the systematic development of an elevated ozone peak (at an average height of 727 m) and also a peak in the particle concentration (at an average height of 693 m). While the ozone peak appears to be transient in nature (more uniform concentrations with height are observed during the afternoon), the particles do not appear to mix much in the vertical. Because aerosol particles interact with solar radiation, both absorbing and scattering it, the presence of an elevated particle layer will affect the photochemistry within the boundary layer. This is further discussed by Raga *et al.* (1998), where the role that these particles play in the formation of ozone is studied.

Acknowledgements

This work was partially supported by Consejo Nacional de Ciencia y Tecnología (CONACyT) under grant # 0141P-T.

REFERENCES

Beyrich, F., K. Acker, D. Kalab, O. Klemm, D. Moller, E. Schaller, J. Werhahn and U. Weisensees, 1996. Boundary layer structure and photochemical pollution in the Harz Mountains: An observational study. *Atmos. Environ.*, **30**, 1281-1290.

Bravo A., H., 1986. Proc. of the APCA *International Conference on Particulate Matter and Fugitive Dusts, Tucson,* USA.

Bravo A., H., 1989. In: Problemas de la Cuenca de México. Kumate and Mazari, Eds.

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

EGCA/MARI, 1995. Estudio Global de la Calidad del Aire en la Ciudad de México. Informe conjunto del Instituto Mexicano del Petróleo y el Laboratorio Nacional de los Alamos, IMP/LA - 12699.

Jáuregui, E., K. Klaus and W. Lauer, 1981. Una primera estimación del transporte de SO_2 sobre Ciudad de México, *Geofis. Int.*, **20-1,** 55-79.

Lu, R. and R. P. Turco, 1996. Ozone distributions over the Los Angeles basin: Three-dimensional simulations with the SMOG model. *Atmos. Environ.*, **30**, 4155-4176.

Nickerson, C. E., G. Sosa, H. Hochstein, P. McCaslin, W. Luke and A. Schanot, 1992. Measurements of Mexico City air pollution by a research aircraft. *Atmos. Environ.*, **26B,** 445-451.

Quadri, G. and L. R. Sánchez, 1992. La Ciudad de México y la Contaminación Atmosférica. De. Limusa.

Raga, G. B. and L. LeMoyne, 1996. On the nature of air pollution dynamics in Mexico City. Part I: Nonlinear analysis. *Atmos. Environ.*, **30,** 3987-3993.

Raga, G. B., A. C. Raga and L. G. Ruíz-Suárez, 1998. On the formation of an elevated ozone peak in Mexico City. *Submitted to J. Geophys. Res.*