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OZONE AND ITS NIGHTTIME CONCENTRATION IN THE SOUTHERN MEXICO CITY METROPOLITAN AREA

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RESUMEN

Desde 1975 se han registrado los niveles de oxidantes en la atmósfera en varios puntos del área metropolitana de la ciudad de México. Se ha observado con evidencia el transporte atmosférico de contaminantes tales como el ozono hacia el extremo sur de la cuenca llamada Valle de México, alcanzando las montañas en esa área. Desde 1979 se ha efectuado el monitoreo continuo del ozono en la Ciudad Universitaria, situada en el sur de la ciudad de México, utilizando un analizador quimioluminescente.

Durante el período 1979-1981 se registraron pocos valores máximos horarios diurnos de ozono superiores a 0.12 ppm. Sin embargo, durante 1984, el 7% de los datos registrados superaron tal nivel.

También se han registrado las concentraciones de ozono durante la noche. Los datos meteorológicos sugieren una posible fuente nocturna de ozono como resultado del transporte de los contaminantes acumulados durante el día, por el viento catabático, desde las montañas que se encuentran al sur hacia la ciudad.

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ABSTRACT

Levels of oxidants in the atmosphere at several sites in the Mexico City Metropolitan Area have been recorded since 1975. Evidence of atmospheric transport of pollutants such as ozone have been observed towards the southern end of the México Valley Basin, reaching the mountains in that area. Continuous ozone monitoring at University City located in the south of Mexico City has been carried out since 1979, using a chemiluminescent analyzer.

During the period 1979-1981 few hourly values higher than 0.12 ppm of ozone were registered. However, during 1984, 7% of the year had a maximum hourly diurnal level of ozone higher than those values.

Ozone concentrations at night have also been recorded. Meteorological data suggest a possible ozone nocturnal source as a result of the katabatic wind transport of accumulated pollutants during the day from the mountains on the south side into the city.

INTRODUCTION

The transport of ozone to rural areas has been reported by several authors (Blumenthal *et al.*, 1974; Stasiuk and Coffey, 1974; Ripperton *et al.*, 1976; Wolff *et al.*, 1977). The reports mention that ozone concentration in rural areas can exceed the Air Quality Standard for Photochemical Oxidants at various sites in the United States.

The daily ozone cycle has been observed and studied for various locations since 1975 in the México City Metropolitan Area (Bravo *et al.*, 1978). There is an evident transport of air pollutants such as ozone to the southern mountains of the México City Basin (Bravo and Torres, 1984).

Ozone phytotoxicity damage has been observed in the Ajusco forest, located in the southern mountains, and it is associated to the transport of air masses from the urban area (Bauer *et al.*, 1985).

Also associated to the observations mentioned, nighttime events with large concentrations of ozone have been recorded at the University monitoring station located in the southern area of México City, considered some years ago as a rural area in terms of air quality.

Dimitriades and Altshuller (1977) have enumerated four possible sources for rural ozone: *(a)* air transport from urban areas, *(b)* local photochemical generation from urban ozone precursors, *(c)* local photochemical generation from precursors of rural origin which may be man-made or natural, and *(d)* injection of stratospheric ozone into the rural areas.

Photochemical oxidants result from a complex series of atmospheric reactions initiated by sunlight. When reactive organic substances and nitrogen oxides accumulate in the atmosphere and are exposed to the ultraviolet component of sunlight, the formation of new compounds including ozone, takes place (Cadle and Allen, 1970; Altshuller and Bufalini, 1971; Pitts *et al.*, 1972). Absorption of ultraviolet light energy by nitrogen dioxide results in its dissociation into nitric oxide and an oxygen atom. This reaction is the photolysis of NO_2,

$$NO_2 + h\nu \longrightarrow NO + O \tag{1}$$

Ozone, O_3, is then formed by reacting very quickly with the oxygen atom in the reaction,

$$O + O_2 + M \longrightarrow O_3 + M \tag{2}$$

where M is a third body needed to absorb the energy of the reaction.

In the air the M body will probably be N_2 or O_2 since these accounts for most of the available molecules. The third reaction is one which completes the cycle

$$O_3 + NO \longrightarrow NO_2 + O_2 \tag{3}$$

However, if a hydrocarbon is added, the dynamic equilibrium is lost, much more quickly if an olefin or an alkylated benzene is introduced (both of which are common components of gasoline), and the following events take place:

(*a*) The hydrocarbons are oxidized and disappear,

(*b*) Reaction products, such as aldehydes, nitrates and others are formed,

(*c*) NO is quickly converted into NO_2, and

(*d*) When all the NO has been used up, substantial amounts of O_3 begin to appear.

On the other hand, low concentrations of peroxyacetonitrile and the aldehydes are formed from the beginning of the reaction.

Anderson (1978) reported that surface ozone is destroyed at night by a combination of gas-phase reactions, primarily with NO emitted in the urban area, mainly by the reaction (3) and by iteration with the earth surface.

During the day the air is mixed through greater heights. Within this mixing zone, the ozone concentration becomes fairly homogeneous. At night, a nocturnal inversion is often produced near the ground. Within this inversion, vertical mixing is greatly reduced and ozone destruction occurs by contact with the ground and by gas phase reactions. The nocturnal inversion protects the ozone aloft from destructive agents being injected into the layer and from contact with the surface.

Therefore, the ozone above the inversion may persist longer than the ozone within the inversion (Anderson, 1978). Above the nocturnal inversion there is little decay of ozone giving a half life for ozone of about 20 hours. The same author (Anderson, 1978) suggests that above the nocturnal inversion most of the ozone present when the inversion is formed will persist through the night and will be transported wherever the air mass is transported during the night.

METHODOLOGY

The monitoring station is located at the Centro de Ciencias de la Atmósfera (University of México). The data were obtained with a Beckman Ozone Analyzer Model 950. The basic operating principle is the chemiluminescent gas-phase reaction of ozone with ethylene. The analyzer is equipped with an internal ozone generator to provide an upscale calibration gas (the internal generator is a secondary calibration device specified by the EPA in the Federal Register, Vol. 36, No. 84, 1974). The sampling port is located 8 meters above ground level, the sample travels about 4 meters to the monitor. An Eppley Ultraviolet radiometer which covers the broad band from 295-386 nm and a meteorological tower 20 meters high equipped with Teledyne instruments to measure wind speed and direction, temperature and relative humidity were operated on the roof of the building.

RESULTS

Continuous monitoring of ozone has been carried out at the monitoring station since 1979 (Bravo *et al.*, 1984), and until 1981 hourly diurnal levels higher than 0.1 ppm of ozone were not observed.

A number of concentrations higher than 0.1 ppm of ozone have been observed since 1982. Figure 1 indicates the maximum hourly concentrations per day during 1984 recorded at the University Station in a 336 day sampling period. A set of maximum concentrations found at the UAM Azcapotzalco (Baz and Spitia, 1984), located in the northwest industrial area of México City, are compared with the same records obtained at the University Station (located 19 km south of the UAM Azcapotzalco location) (Figure 2). Baz and Spitia used a thermoelectron Ozone Analyzer

Fig. 1. Ozone maximum hourly concentrations per day during 1984 at the University Station of the Mexico City Area (336 days sampled).

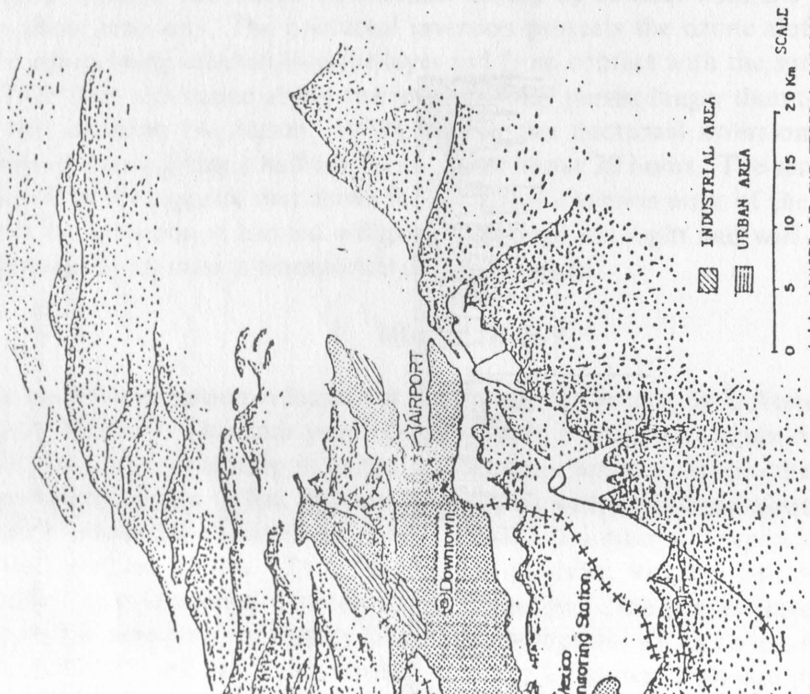

Fig. 2. Schematic representation of the México City metropolitan zone in the México City Valley.

Model 101-D to measure the ozone concentration, the analyzer was calibrated according to the EPA ozone reference method. Table 1 shows these data.

Table I

Maximum ozone concentrations at Azcapotzalco compared to University Station in the MZMC

Date	Azcapotzalco	University Station
	Concentration ppm	
7/10/83	0.075	0.12
27/2/84	0.095	0.23
28/2/84	0.047	0.14
29/2/84	0.033	0.09
1/3/84	0.037	0.13
21/3/84	0.040	0.10
5/3/84	0.065	0.08
4/4/84	0.071	0.08
5/4/84	0.040	0.09

The data indicate that the concentration of ozone is higher at the University Station compared with levels found at the Azcapotzalco area. The air mass transport in the México City Basin is predominantly from the north-northwest to the south (Campos *et al.*, 1973). The wind rose for several years of statistical data is shown in Figure 3. This suggests a transport of pollutants generated in the north to the south, and at the same time, formation of ozone as a product of photochemical reactions involving NOx, hydrocarbons, ultraviolet radiation plus meteorological factors such as temperature inversion and low wind speed. This transport is shown schematically in Figure 4.

Unexpected events of high ozone concentrations have been observed during the night at the University Station since 1982, and cannot be attributed to *in situ* photochemical formation at the surface level (Bravo and Torres, 1985). Figure 5 shows an

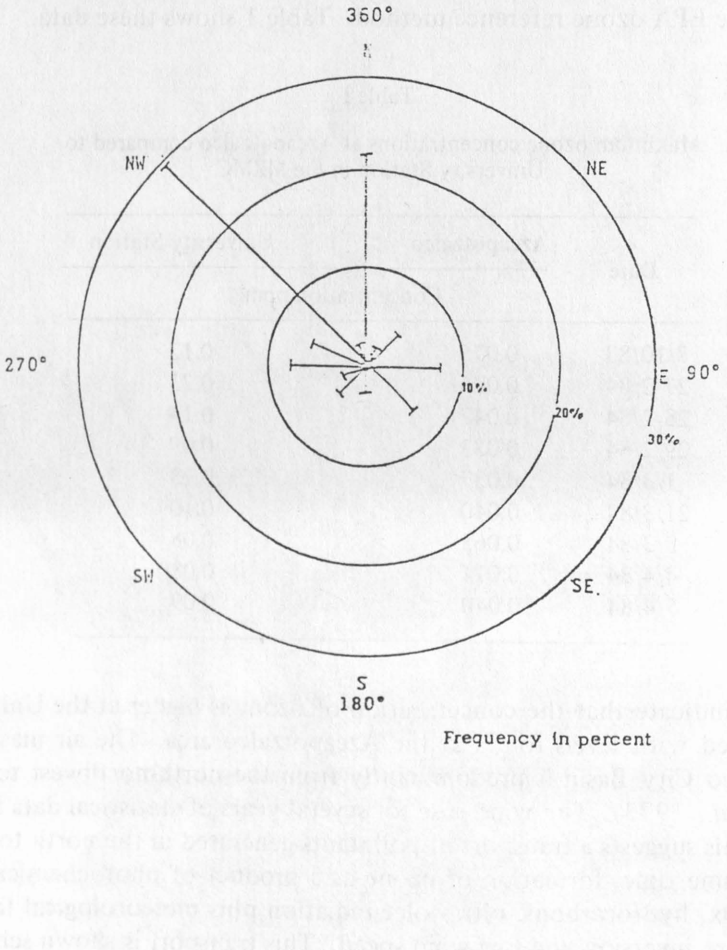

Fig. 3. Wind rose for the Mexico City metropolitan zone annual average (from Campos *et al.*, Modelo de Dispersión de Bióxido de Azufre en el Valle de México, Memorias de la I Reunión Nacional de Contaminación Ambiental. México. Enero. 1973, pp. 941-955).

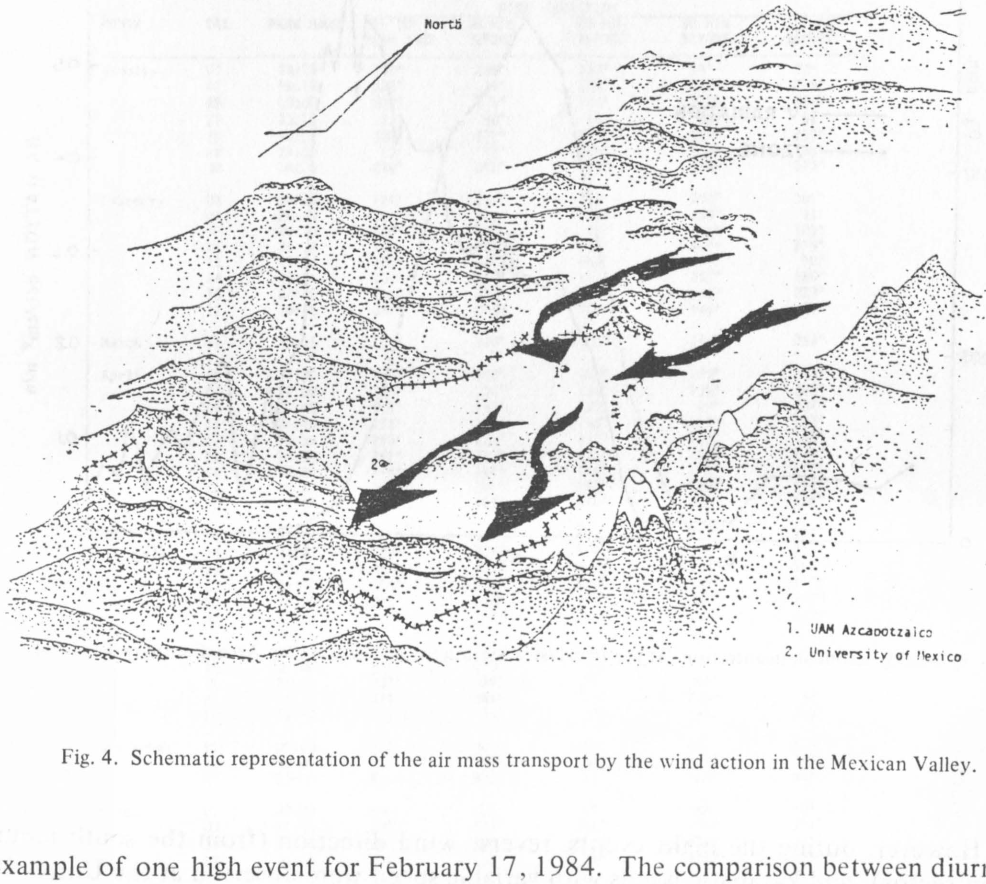

Fig. 4. Schematic representation of the air mass transport by the wind action in the Mexican Valley.

example of one high event for February 17, 1984. The comparison between diurnal and nocturnal maximum ozone concentrations recorded during 1984 is shown in Figure 6.

During the days with night events, the vertical temperature gradient measured at the México City Airport at 0600 hours local time, indicates strong temperature inversions; but temperature profiles at the 1800 hours (local time) did not show any kind of inversion. Also, low wind velocities (0.05 m/s) with the prevailing wind direction from the north sector (downtown and industrial area) were present during the day.

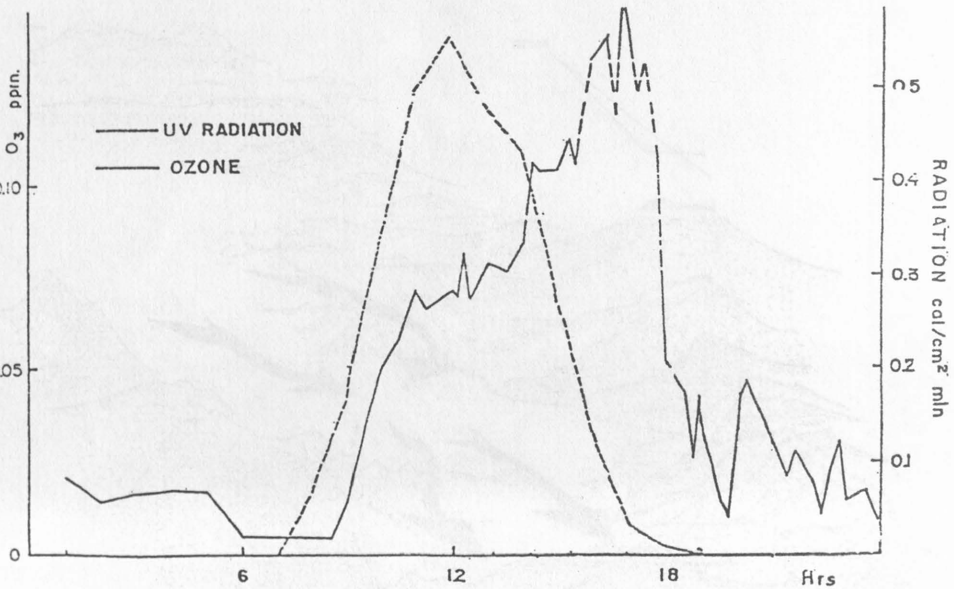

Fig. 5. Hourly ozone concentrations at the University Station in the México City Area, February 17, 1984.

However, during the night events, reverse wind direction (from the south mountain sector), and katabatic winds with variable speed were observed at the University Meteorological Station (70% frequency).

Figure 7 shows schematically the latter situation, and the data are presented in Table II.

CONCLUSIONS

There is evidence of reverse transport of rural ozone to the Metropolitan Area and for the possible sources for ozone night concentrations. The transport of air masses

Table II. Wind direction during and before night ozone events at the University meteorological and monitoring station, 1984.

MONTH	DAY	PEAK HOUR	WIND DIRECTION AT THE PEAK HOUR	30 MIN BEFORE	60 MIN BEFORE	90 MIN BEFORE	120 MIN BEFORE
January	01	18:25	252°	256°	297°	18°	23°
	07	19:10	324°	14°	225°	225°	219°
	26	19:00	333°	279°	288°	279°	261°
	27	23:15	13°	90°	94°	99°	49°
	28	19:55	350°	229°	279°	255°	239°
	29	24:00	13°	40°	148°	170°	108°
	30	18:30	238°	240°	229°	243°	279°
February	03	02:30	274°	297°	299°	297°	301°
	04	20:45	103°	112°	94°	283°	31°
	07	20:30	144°	130°	144°	140°	189°
	11	20:30	198°	207°	230°	247°	279°
	13	19:50	266°	261°	252°	247°	90°
	14	19:55	184°	158°	161°	257°	180°
	16	02:30	265°	292°	301°	296°	283°
	17	19:50	351°	315°	167°	148°	31°
March	11	23:15	171°	270°	263°	256°	252°
April	02	23:30	102°	144°	234°	229°	148°
	07	22:00	238°	234°	225°	135°	243°
	09	22:45	103°	193°	173°	27°	234°
	11	04:00	234°	261°	193°	189°	135°
	17	19:30	268°	231°	272°	162°	45°
	21	18:30	297°	207°	130°	265°	279°
	24	18:30	144°	144°	144°	171°	175°
	26	19:30	189°	225°	212°	198°	193°
	29	22:45	225°	189°	274°	220°	225°
May	13	01:00	171°	302°	270°	273°	290°
	14	01:00	283°	229°	274°	278°	297°
	19	00:00	261°	279°	270°	257°	266°
	21	03:00	288°	294°	337°	332°	117°
	23	22:30	315°	328°	328°	337°	342°
	31	01:00	265°	254°	270°	250°	292°
June	02	23:45	207°	247°	257°	13°	92°
	15	01:00	890°	279°	285°	283°	283°
	26	01:00	308°	310°	306°	301°	306°
	27	19:30	221°	292°	279°	285°	36°
	28	18:45	297°	236°	94°	85°	189°
September	01	01:00	NDA	NDA	NDA	NDA	NDA
	13	18:00	263°	168°	153°	153°	167°
	29	23:30	NDA	NDA	NDA	NDA	NDA
October	01	02:00	NDA	NDA	NDA	NDA	NDA
	03	21:00	261°	281°	272°	276°	276°
	20	21:30	NDA	NDA	NDA	265°	211°
	22	20:00	144°	135°	92°	276°	315°
November	02	03:00	38°	45°	58°	119°	140°
	20	19:00	166°	81°	286°	279°	322°
	23	04:00	301°	288°	267°	310°	310°
	25	19:30	243°	225°	107°	207°	119°
	27	19:30	231°	234°	353°	211°	211°
December	07	19:30	162°	126°	123°	58°	42°
	08	19:00	293°	257°	126°	32°	20°
	16	20:30	229°	247°	NDA	NDA	NDA
	19	18:30	243°	229°	184°	193°	126°
	20	19:30	270°	223°	238°	162°	69°
	21	18:30	225°	247°	360°	9°	22°

NDA: No data available

*Note: The Desierto de los Leones Forest is located in the 290° direction Ajusco Forest is located in the 210° direction with respect to the University Station. Others low altitude mountains are located in the 160°- 200°range.

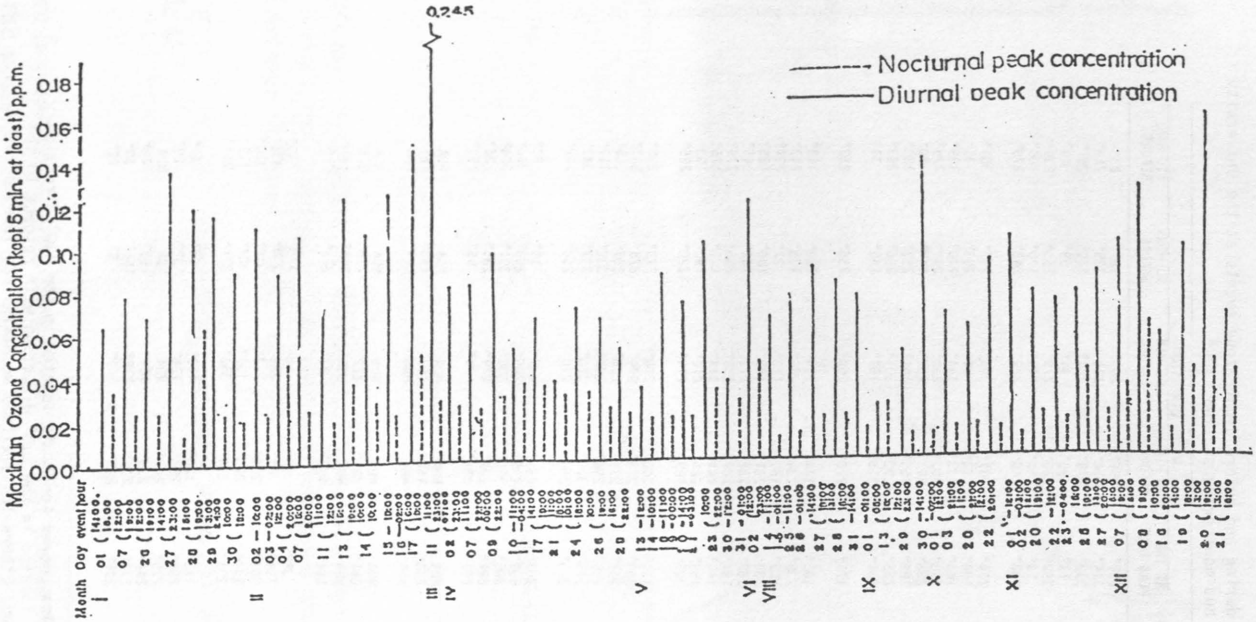

Fig. 6. Comparison between diurnal and nocturnal maximum ozone concentrations as recorded at the University monitoring station during 1984.

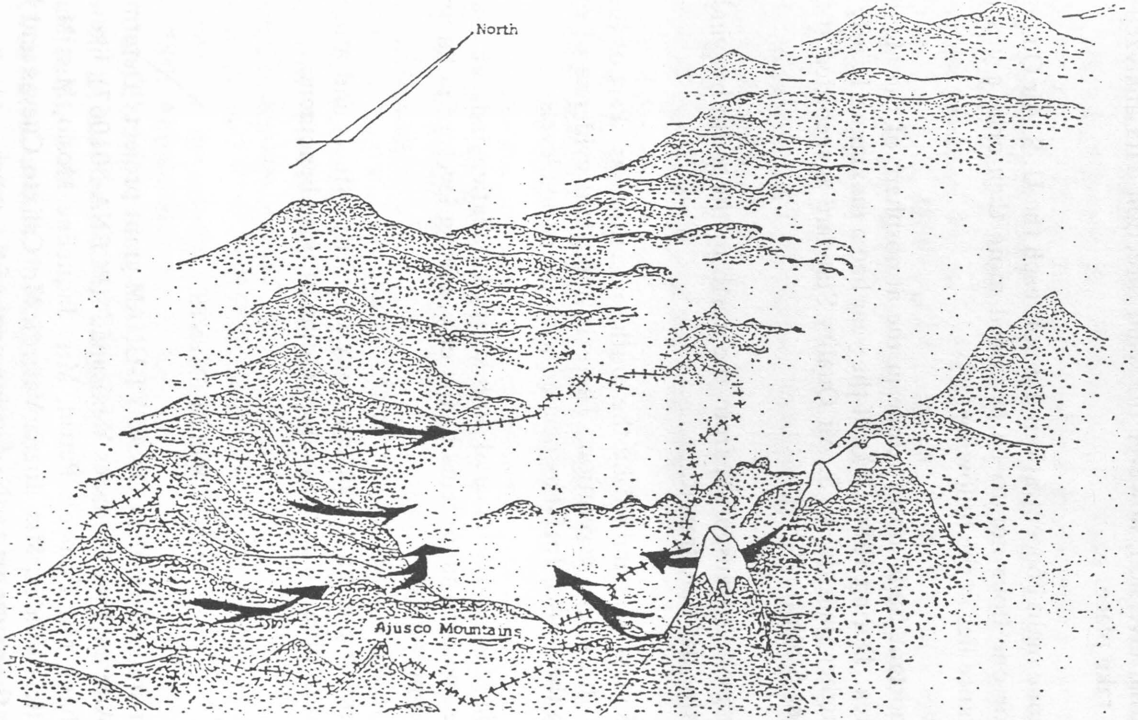

Fig. 7. Schematic representation of the nocturnal winds in the México City Basin.

by the wind from the southern mountains is the most probable in the case of México City Basin. The night events observed at the University Station do not seem to be related to a nocturnal inversion, however the wind direction data analyzed suggest that transport may take place.

Although the ozone night concentrations did not reach the U. S. Air Quality Standard (0.12 ppm for one hour not to be exceeded more than once a year) in any event, their importance lies in the following facts:

1. There is an important build up of ozone in the atmosphere of the México City Metropolitan Area. During 1984, 7% of the year had a maximum hourly diurnal level of ozone higher than the U. S. Air Quality Standard as recorded at the University Monitoring Station.

2. The polluted air mass is transported from the north to the south by wind, building up ozone during daytime transit.

3. The polluted air mass is contained by the southern mountains. Part of the ozone is destroyed by the native vegetation. There is important evidence of phytotoxicity damage to the Ajusco forest associated with the ozone levels.

4. At the end of the day, and associated with strong katabatic winds. air masses are carried from the southern mountains to the city, raising levels of pollutants such as ozone in the atmosphere.

More research on air pollutant transport, phytotoxicity effects and atmospheric chemistry is needed to obtain a better understanding of this phenomenon.

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