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CO_2 concentrations in the highly polluted atmosphere of Mexico City

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RESUMEN

Durante los años de 1981-1982 se llevaron a cabo medidas de la concentración del CO_2 atmosférico durante el día en la Ciudad de México. Los resultados indicaron que el 82% de los niveles de CO_2 fueron mayores que 330 ppmv, que es la concentración de fondo del CO_2 atmosférico que ha sido reportada.

Durante el día las concentraciones de CO_2 mostraron tres máximos: el primero entre las 9:30 h y 10:30 h, el segundo entre las 12:00 h y las 13:00 h, y el tercero entre las 15:00 h y las 16:00 h, tiempo local. Los picos coincidieron con las horas de intenso tráfico de la ciudad.

Las curvas anuales de CO_2 indicaron una variación estacional con valores bajos durante el invierno y con un máximo en primavera encontrándose los valores más bajos en la parte media de la estación lluviosa.

En vista de que las fuentes naturales de CO_2 durante el día son probablemente insignificantes, el uso del contenido del CO_2 atmosférico como un indicador de la contaminación del aire en la Ciudad de México parece ser factible.

ABSTRACT

Measurements of CO_2 concentrations in the atmosphere of Mexico City were carried out through the years 1981-1982, during daylight hours. The results indicate that 82% of the CO_2 levels were above 330 ppmv, which is the reported approximate atmospheric background.

During daylight hours CO_2 concentrations show three maxima: the first between 9:30 and 10:30 h, the second between 12:00 h and 13:00 and the third between 15:00 and 16:00 h local time. The peaks coincide with the rush hours in the city.

The annual curves of CO_2 show a seasonal variation with low values during the winter and a maximum in spring, the lowest values corresponding to the middle of the rainy season.

Since natural sources during the daylight hours are probably negligible, the applicability of CO_2 data as an indicator of air pollution in Mexico seems to be feasible.

Introduction

Since CO_2 is an easily measured, and relatively stable constituent of the atmosphere, measurements of this gas have been utilized in studies related to air pollution (Clark and Faoro, 1966), the natural cyclic processes of vegetation (Lieth, 1963, Spittlehouse and Ripley, 1977), the heat balance of the atmosphere (Plass, 1959; Idso, 1983; Woodwell, 1978; Manabe and Wetherald, 1980; Adem and Garduño, 1984) and the variation in the concentration of CO_2 at both Mauna Loa, Hawaii, and the South Pole (Ekdahl and Keeling, 1973) among other studies.

The observed systematic variations of the content of CO_2 in the atmosphere with season, latitude and altitude are the result of sources and sinks which exist only at the surface of the earth and that induce regular variations in the lowest layer of the atmosphere (Bolin and Keeling, 1963). Measurements of CO_2 have been made in many regions and oceans (Takahashi, 1961; Kanwisher, 1963), in the surface boundary layer over crops and natural vegetation (Lieth, 1963; Spittlehouse and Ripley, 1977), over and in the oceans (Bolin, 1960; Kanwisher, 1963; Takahashi, 1961) and in the

upper troposphere and stratosphere (Bischof and Bolin, 1966); and have been related to atmospheric turbidity (Baez and Fournier D'Albe, 1959).

The results reported by different authors show that the annual cycle has a minimum during summer or early autumn in the northern hemisphere, due to the removal of atmospheric CO_2 by photosynthesis and its incorporation into plant tissues. The maximum concentration occurs in winter to late spring as the CO_2 is replenished through the vegetation decay and the burning of fossil fuel mainly. Bolin and Keeling (1963) also indicated that there was only a small annual variation in mid-day CO_2 concentration in the free atmosphere in the southern hemisphere, probably because most of this hemisphere is oceanic. Goldman (1974) at Mauna Loa, Hawaii, noted day-to-day variation of CO_2 concentrations as well as the periodic variations described above. It has been found a gradual increase in mean annual CO_2 concentrations (Pales and Keeling, 1965). This is believed to be a result of the addition of CO_2 to the atmosphere by the combustion of fossil fuels, the deforestation and the humus oxidation. This yearly increment has increased from 0.5 ppmv per year during the last decade to an excess of 1 ppmv per year (Bischof and Bolin, 1966; Goldman, 1974).

This paper reports the results of CO_2 measurements in the atmosphere of Mexico City. The purpose of this study has been focused primarily on establishing the daylight hours variation, the annual cycle of the CO_2 and to what extent the combustion of fossil fuels and the stability of the air layer near the ground affect the atmospheric CO_2 levels, as well as to explore the possibilities of using the CO_2 data as indicator of air pollution in Mexico city.

Materials and methods

Sampling sites

Samples were taken at different locations of the Mexico City Valley: The Atmospheric Science Building, University of Mexico, at the southern part of the city; Lecheria Town (industrial area), and Satelite County (residential area) both at the northern part; Tacubaya section (western part) and downtown. All samples were taken on the roof of selected buildings, at different hights (6 to 15 m above ground level).

During 1981-1982, atmospheric samples were also obtained from maritime and forest places. (Table II).

Sampling

Because an infrared non dispersive analyser was not available, samples were taken with 20 ml air tight polyethylene syringes. Samples were taken 50 cm above the operator head and against the direction of the wind. Four to five strokes were made, before having the final sample; after that, the syringe was stopped with its own needle which was previously cut out and sealed to avoid gas leaks. The samples were sent to the laboratory for analysis. For each sample, place, date, hour, temperature, wind direction and other meteorological conditions were recorded.

Analytical method

A gas chromatograph Pye Unicam with flame ionization detector was used for CO_2 analysis.

The operating conditions of the instrument were: stainless steel column, 1.70 m long, 4 mm internal diameter packed with Poropak Q 80-100 mesh. Column temperature, 105°C, injector temperature 125°C. Detector temperature 125°C. Carrier gas: ultrapure nitrogen. Carrier gas flux 30 ml min^{-1}.

A nickel catalitic cell to convert CO_2 to metane was installed before the column.

A 99.95% purity CO_2 gas diluted in ultrapure nitrogen was used for instrument calibration. Mylar bags and microsyringes were used to prepare standard mixtures of CO_2– Nitrogen, from 275 to 400 ppmv. Correction for temperature and atmospheric pressure were made. After the standards were permitted to be homogeneous, they were injected through a 5 ml calibrated loop into the cromatograph.

The well known chromatographic technics for quantitative gas analysis were applied (Adlar *et al.*, 1972; Lown *et al.*, 1977). Standard CO_2 peak heights versus standard concentration were used for the curve construction, from which sample values were obtained. Standards were prepared before running a set of samples, but during the analysis the instrument was periodically recalibrated. Samples were analysed by duplicate and only a deviation of less than ± 1%, 3 ppmv was allowed, value a little larger than the deviation of 0.15 ppmv reported in double analysis made in flask on a DC-8 flight. (Bischof, 1970).

Results and discussion

To study the shape of the distribution of the atmospheric CO_2 level concentration data, an histogram-like display was generated for the batches of data and shown in Fig. 1. Such labeled bar charts are called stem-and-leaf diagrams (Tuckey, 1977). From this figure it is observed that only 16.0 percent of the CO_2 concentrations were below 330 ppmv and 58.5 percent of the values were grouped between 330 to 359 ppmv, 25.5 percent being above this last value. The concentrations of importance in this study are those above 330 ppmv - which is the reported approximate atmospheric background level of CO_2 (Woodwell, 1978). From this value the relative contribution of fuel combustion emissions could be considered.

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                    Unit = 1.0
                32 2 represents 322.0
-------------------------------------------------------------------
 15   32   .    0 0 0 0 0 1 2 2 2 3 3 3 3 3 4
 31        *    5 5 5 5 5 5 5 5 6 7 7 7 8 8 8 9
 48   33   .    0 0 0 1 1 1 1 2 2 2 3 3 3 3 4 4 4
 69        *    5 5 5 6 6 7 7 7 7 7 8 8 8 8 8 9 9 9 9 9 9
 94   34   .    0 0 0 0 0 1 1 1 1 1 1 1 1 2 2 2 2 2 3 3 3 3 4 4 4
(12)      *    5 5 5 5 7 7 7 7 7 7 8 9
 83   35   .    0 0 0 0 0 0 0 1 2 2 2 2 3 3 3 3 3 3 3 3 3
 62        *    5 5 5 5 5 5 5 6 6 7 7 7 9 9 9
 48   36   .    0 0 0 0 0 1 1 1 1 1 1 1 2 2 2 4 4 4
 30        *    5 5 5 7 7 7 8 8
 22   37   .    0 0 0 0 0 2 2 2 4
 13        *    5 5 5 5 8 9
  7   38   .    0 0 1 1 2
  2        *    5 8
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Figure 1. Stem-and-leaf display of atmospheric CO_2 concentration data.

Associated to the stem-and-leaf diagram of CO_2 concentration data, some useful statistics were computed to achieve and overall understanding of the distributional properties of data. Mean, median (μ), lower and upper fourths (Hi, Hu, similar to 25th and 75th percentiles respectively), fourth spread (OH = Hu - Hi), and standard deviation were calculated and listed in Table I.

Table I also contains sample size (η) minimum and maximum values, and shows that the CO_2 values range from 320 to 388 ppmv with a median (μ) of 344.5, and a mean of 347.3; a standard deviation of 17.04 and a spread of 68 ppmv.

Table I. CO_2 data useful statistic.

Sample size	189
Mean	347.3
Standard deviation	17.04
Median (μ)	344.5
Lower fourth (Hi)	334
Upper fourth (Hμ)	360
Minimum	320
Maximum	388
Spread	68

Daylight-hour-variation

Fig. 2 shows the daylight hours variation of the mean CO_2 concentration during the years 1981 and 1982 in Mexico City. Three maxima occur: one between 9:30 and 10:30 h, the second and the biggest between 12:00 and 12:30 h and the third between 15:30 and 16:00 h local time.

Most of the authors have indicated that the diurnal cycle has a maximum CO_2 concentration at night and a minimum usually in the afternoon (Hasselbarth and Fittbogen, 1879; Reinau, 1930, 1954; Huber, 1952). Spittlehouse and Ripley (1977) found that at night the maximum is atributed in rural areas to respiration by animals and plants and diffusion of CO_2 from the soil into the atmosphere, while the minimum during the daylight hours is mainly due to photosynthesis and atmospheric difussion. However, in an urban area two sources must be considered to account for the diurnal CO_2 cycle: natural sources (parks, lawns, animal and plant respiration, etc.) and anthropogenic sources (combustion of fossil fuels).

The contribution of natural CO_2 sources in metropolitan areas is variable and reliable data pertaining to the rate of exchange of CO_2 through the natural cycle processes of vegetation are not readily available.

Clark and Faoro (1966) have pointed out that although there can be no doubt of their existence, the effects of natural emissions on urban levels of CO_2 is still a matter of speculation. Normally the vertical turbulent exchange existing at night is larger over an urban area than over a rural one, and would produce concentrations below those expected simply from advection of rural concentrations into an urban area.

The effect of natural sources on nocturnal urban concentrations of CO_2 has been estimated by Clark and Faoro (1966) by utilizing Huber's vertical measurements of rural concentrations up to 100 m. They found that this gas may be used as a gross indicator of total pollution in an urban area, during the winter season, in northern latitudes, and in all seasons during afternoon hours, because all the time the contribution from natural sources is probably negligible (Huber, 1952).

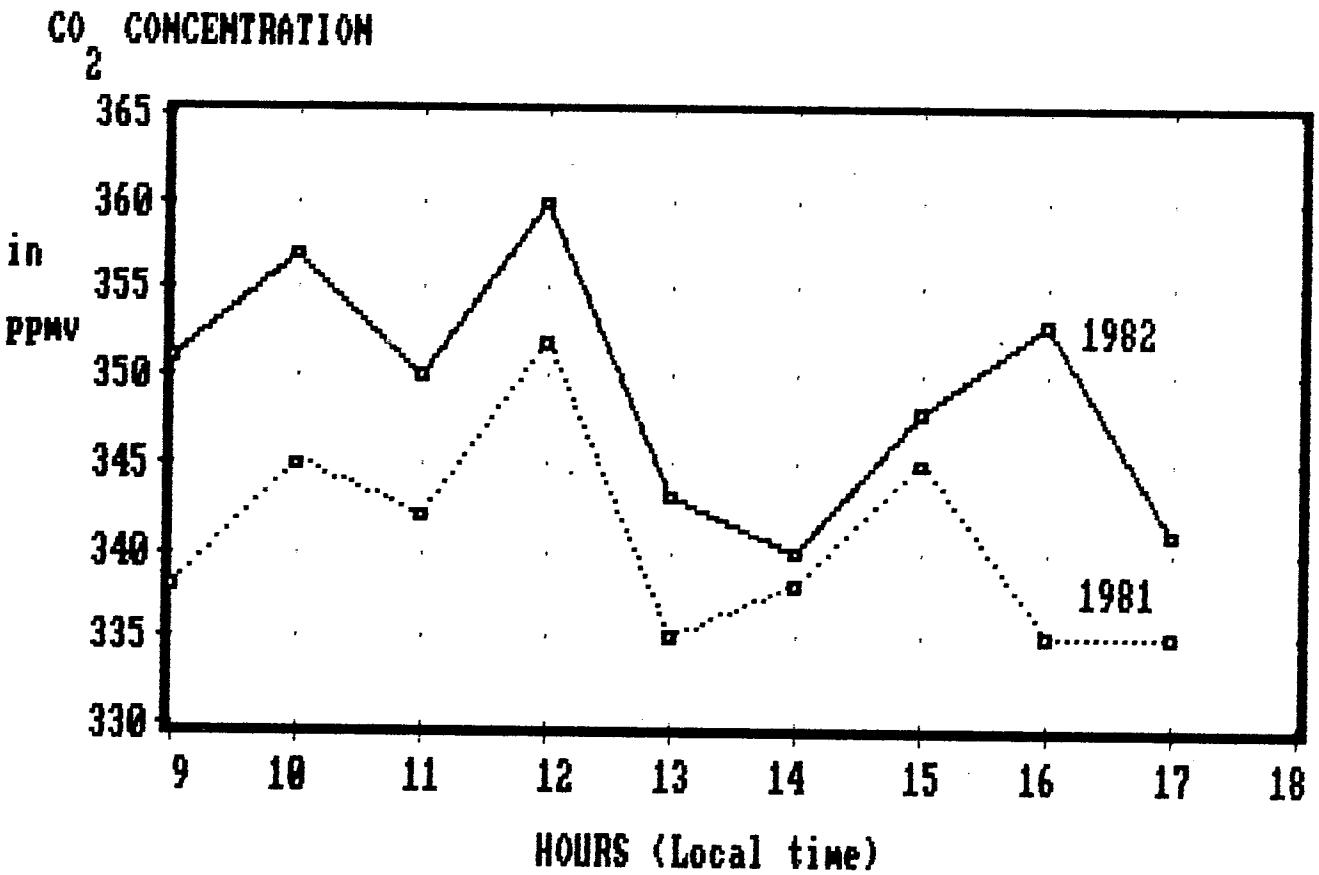

Figure 2. Daylight hours variation of mean CO_2 concentrations for 1981-1982.

Mexico City is located in a valley sorrounded by a chain of forested mountains to the West, South, and East and lower hills at the northern part of the valley.

In the metropolitan area exist around 870 ha of green areas corresponding to 0.2 - 1.6% of the total surface of the metropolitan area considered to be about 1482 km^2 (García, 1977).

The meteorological parameters play an important role in the dispersion not only of CO_2 but of other air pollutants. During the nocturnal hours it occurs the advection of air from the mountains into the valley that can transport additional significant masses of CO_2 that probably results from the natural cyclic processes of vegetation.

Since no measurements were made by night it is not possible to estimate the CO_2 contribution of those sources during the night. However daylight measurements of CO_2 at the forested areas gave an average concentration of 370 ppmv, much higher than the mean value of 347 ppmv (Table II) found at Mexico City. It was statistically significant at beyond $p = 0.05$.

Table II. Atmospheric CO_2 concentrations at different sampling sites of Mexico.

SAMPLING SITES	CO_2 CONCENTRATION (ppmv)
Mexico City	347
Forest places	370
Maritime	334

During daylight hours the air stability conditions are reversed. After sunrise the temperature increases and a vertical turbulent exchange occurs, and light upper air winds drain the air pollutants outside the valley. Also during daylight hours the assimilation of CO_2 by plants is generally greater than respiration, the result being a net loss of CO_2 in the surface layer so that the net concentration in the center of an urban complex is probably negligible during the daylight hours (Clark and Faoro, 1966). On the other hand, the role of production of CO_2 due to human breathing is estimated to be 1 kg per day, and for a city like Mexico with 18 million of inhabitants, the CO_2 production is roughly 16.5 x 10^3 metric tons per day. This natural source seems to be relatively important, since it contributes about 13% of the combustion source emissions that have been estimated, according to the emission factors given in Table III, to be roughly 122 x 10^3 metric tons per day.

Table III. CO_2 emission factors (Clark and Faoro, 1966.)

Coal	2.9 ton/ton
Oil	2.64 kg/1
Gas	2.24 kg/1000 1
Gasoline	1.73 kg/1
Diesel oil	3.0 kg/1
Incinerators	1.0 ton/ton

With respect to daylight hour variation, the occurence of the maxima observed, could be attributed in great part to vehicles exhaust emissions (more than 2.8 million vehicles in the metropolitan area), since CO_2 was well correlated with CO; $r = .356$ at $p = 0.01$.

During sampling, visibility was estimated from reference points, such as tall buildings and mountains, it was observed that with a poor visibility (3 to 5 km) high CO_2 concentrations occur (more than 360 ppmv), on the opposite, with very good visibility (more than 40 km) the lowest CO_2 values were measured.

If the important concentrations considered in this study are above 330 ppmv (the approximate atmospheric background), and the natural sources are negligible during daylight hours, then the applicability of CO_2 data as an indicator of air pollution in Mexico City seems to be feasible.

Annual variation

Several authors have found that besides of undergoing a daily variation, the CO_2 content in the atmosphere varies according to the season of the year for each hemisphere. Thus Fonselius (1956) shows that the annual cycle for the Scandinavian Peninsula is characterized by a high concentration of CO_2 during the winter season, decreasing in spring through early autumn, to start increasing toward the winter maximum. The same seasonal variation has been reported by Bolin and Keeling (1963) and by Woodwell (1978) for rural areas in the Northern Hemisphere, where the CO_2 concentration reaches its maximum at the end of winter or beginning of spring (April) due to the burning of fuel for house heating, the mixing with marine air masses and the decay of organic matter, descending hence toward a minimum at the end of the summer or the beginning of autumn, due to the removal of CO_2 by photosynthesis.

In Mexico it cannot be taken for granted the occurence of maxima and minima of weather elements at the same time of the year as they occur at middle latitude stations. The climate of Mexico City being one of a tropical high elevation station, shows only two contrasting seasons; the rainy season and the dry season. The latter can be further subdivided into two periods: one of increasing temperature

before the rainy period from February to May - this last being the month when the annual maximum in temperature occurs - an another period of decreasing temperature from November through to its minimum in January. Indeed, the development of weather process on the Mexican Plateau follows the pattern of the monsoon climates of the world, with rainfall in summer and early fall (June to October) and a marked dryness the remainder of the year, with an early maximum of air temperature before the summer solstice.

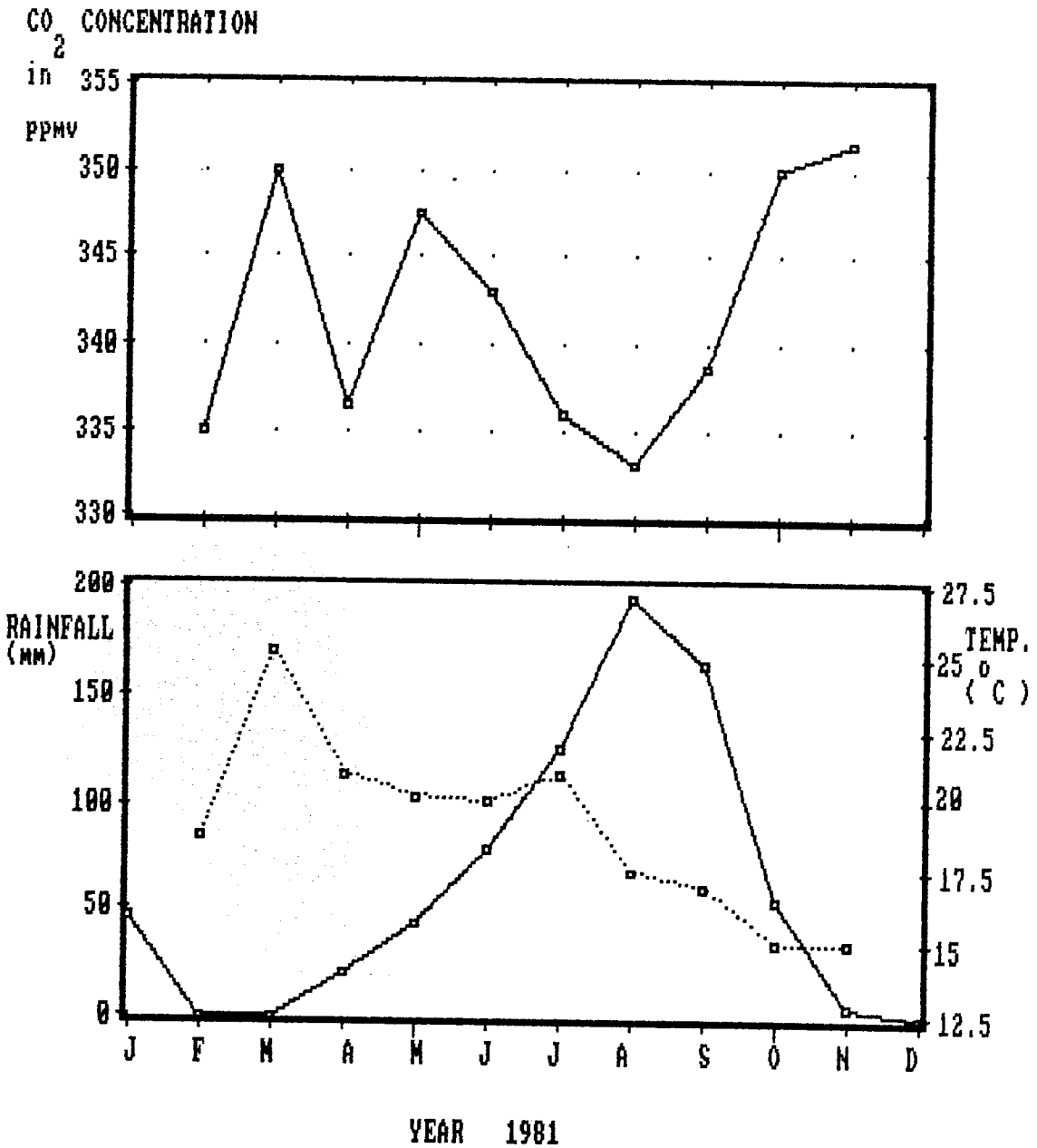

Figure 3. Comparison among CO_2 concentration, temperature and precipitation data for 1981.

During the rainy season the air temperature maintains a high thermal level but it does not overcome the yearly maximum of the dry season. Because of these climate characteristics the stability of air at Mexico City can be expected to vary in a different way from that described for middle latitude stations. The time of incidence of maxima and minima CO_2 concentrations in a tropical environment is also different from that at middle latitudes.

The Mexico City annual curves of CO_2 concentrations, corresponding to monthly means for the period 1981-1982, show a seasonal variation with low values during the winter (December to February), that increases to a maximum in spring (March to May) decreasing hence toward a minimum in summer (June to August) to increase again to a maximum in the autumn (September to November).

Fig. 3 shows the curve of CO_2 concentration for 1981, together with the monthly temperature and precipitation curves. It is very remarkable that the mean monthly temperature of the air varied only 5° C through the rainy period from May to October, Fig. 4 shows the curves for 1982 with

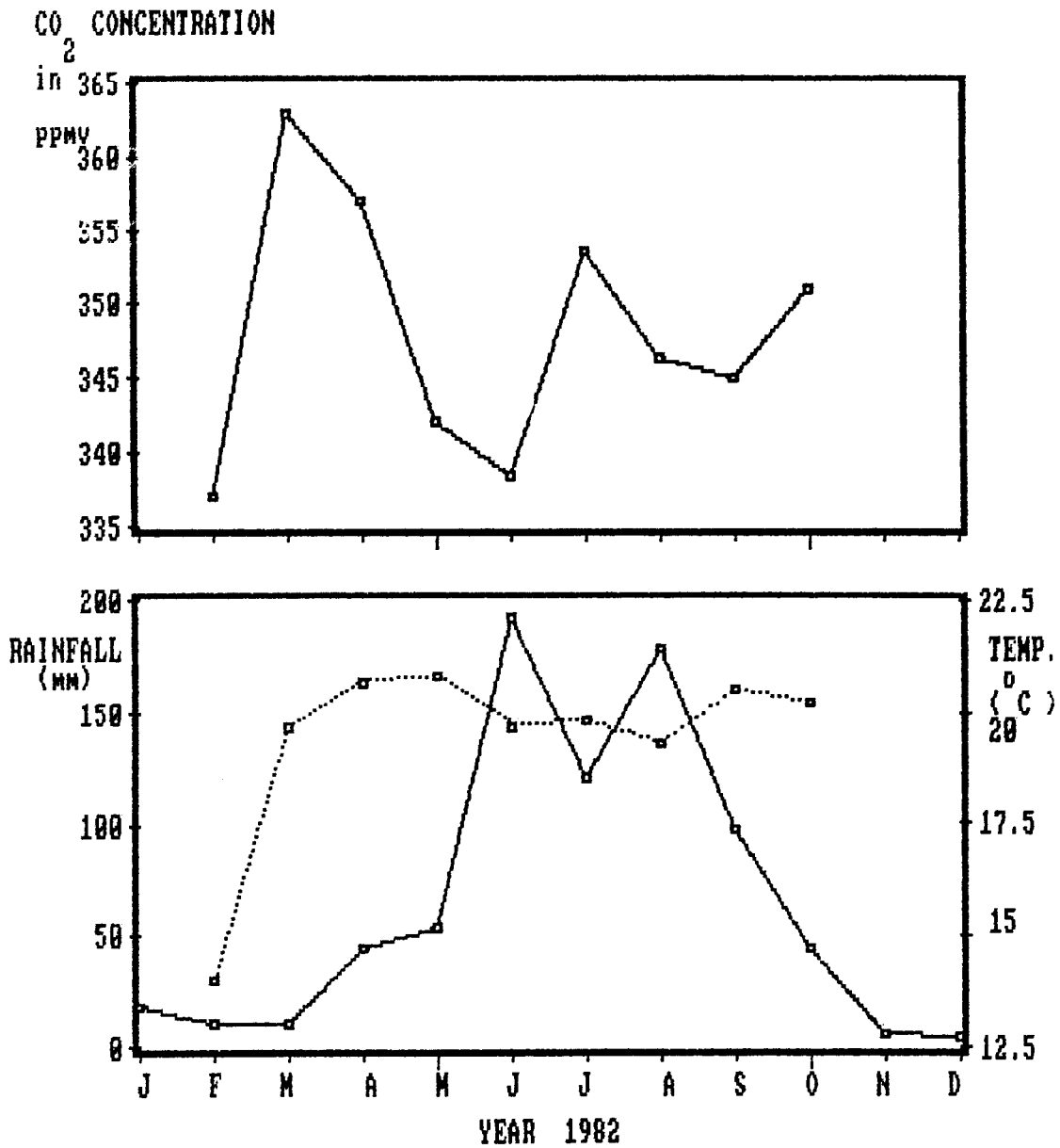

Figure 4. Comparison among CO_2 concentration, temperature and precipitation data for 1982.

the same variables as depicted in Fig. 3. Here also the mean monthly temperature remain almost without change through the rainy season. Both Figs. 3 and 4, after close inspection show an inverse relationship between CO_2 concentration and precipitation throughout the rainy season. Table IV gives the correlation coefficients obtained by application of the linear regression equations to the Mexico City data.

Table IV. Correlation (Pearson's r) between CO_2 concentrations at Mexico City and Rainfall at two different nearby raingauges[1]

Year	Sample size	r	Level of significane	Raingauge location
1981	8	-0.73	0.05	U. campus[a]
1982	7	-0.66	N.S.	U.campus[a]
1981	10	-0.34	N.S.	National Observatory[b]
1982	6	-0.87	0.05	National Observatory[b]

1 From June to middle of October (the rainy season in Mexico).

a University of Mexico campus at the southern part of Mexico city.

b National Meteorological Observatory at the western part of Mexico City.

Outside the rainy season a positive correlation coefficient is expected between CO_2 values and temperature, as the latter does vary during the dry season, characterized, as mentioned above, by one temperature decreasing period and another one of increasing temperature. Unfortunately no CO_2 samples were taken through the cool months of December and January for both years 1981-1982, so that, a significant correlation coefficient was not obtained between air temperature and CO_2 concentration. However, the relation between the former and latter follows the VantHoff rule according to which the rate of growth of plants is doubled with each increment of 10^oC in air temperature, provided there is an adequate amount of moisture and the air temperature is between 10 and 40^oC (Lieth, 1963).

Rainfall can influence the CO_2 concentrations through the following mechanisms:

1. It causes a decrease in air temperature by cooling up the rain drops by evaporation in their fall through the air (Kinzer and Ross, 1951).
2. It favours the growth of vegetation which becomes a sink of CO_2 during clear daylight periods between storms.
3. The cloudiness acompanying storms causes a decrease in temperature by screening of the short wave radiation from the Sun during the rainy season.
4. Rain water disolves a small amount of CO_2 in the air being the disolved amount inversely proportional to air temperature.

Points 1 and 3 may explain the early arrival of the maximum temperature before the summer solstice in monsoonal climates due to the fast rate of air temperature increase before the start of the rainy season. After it begins, the temperature remains almost constant or decreases slightly until the arrival of the next dry season in either September of October.

Concluding remarks

The present paper deals with both diurnal and annual variations of the CO_2 levels in the atmosphere of Mexico City. The diurnal CO_2 cycle contains three peaks corresponding to the rush hours in the City. On the other hand, the annual cycle differs somewhat from the middle latitude pattern on account of the diverse sequence of events in the meteorological processes that shows the atmosphere of the City. This sequence corresponds to the dominant dry and rainy seasons. Since the variation in temperature is almost negligible through the rainy season, a high inverse partial correlation coefficient is found between rainfall and CO_2 concentrations for both years 1981-1982. For this reason, it is considered that further continuous measurements of the CO_2 concentrations should demonstrate the feasibility of using CO_2 as an index of the air pollution in Mexico City.

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