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Measurements of C_1-C_4 carbonyls at forested regions in México

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RESUMEN

Se determinaron las concentraciones de formaldehído, acetaldehído, acetona, propionaldehído y butiraldehído en la atmósfera de cinco zonas boscosas de México. Se hicieron dos muestreos simultáneos en dos sitios localizados en el estado de México, el primero en Temascaltepec, un área semirural, y el otro en Rancho Viejo, un área boscosa. Se hizo otro muestreo simultáneo en el sur del estado de Veracruz en un área rural (Monte Pío) a la orilla del mar y en el interior de un bosque tropical en la Estación de Biología de la Universidad Nacional Autónoma de México y un muestreo en un sitio ubicado en la Sierra de Puebla (Cuetzalan). Los muestreos se realizaron entre el 12 de mayo de 2002 y el 8 de marzo de 2003. Las concentraciones de propionaldehído y butiraldehído no se reportaron porque siempre estuvieron abajo o cerca del límite de detección del sensor de cromatografía líquida. Las concentraciones más altas de los otros compuestos se encontraron en los intervalos de muestreo de las 7:00 a las 11:00 y de las 11:00 a las 19:00 h en todos los sitios de muestreo. La media aritmética de las concentraciones de acetona fue la más alta en casi todos los sitios variando de 0.5 a 8.4 μg m^{-3}. La media aritmética de las concentraciones de formaldehído y acetaldehído varió de 0.83 a 6 y de 0.53 a 4.7 μg m^{-3}, respectivamente. La correlación de Spearman entre formaldehído y acetona y entre acetaldehído y acetona fue estadísticamente significativa en casi todos los sitios ($p < 0.05$). Se observó una correlación significativa ($p < 0.05$) entre formaldehído y acetaldehído en Rancho Viejo y Temascaltepec. La razón HCHO/CH_3CHO promedio de las concentraciones fue de 1.83 y 1.31 en Rancho Viejo, primer y segundo muestreo, respectivamente; 1.71 y 1.62 en Temascaltepec, primer y segundo muestreo, respectivamente; en Cuetzalan fue de 1.70, en Monte Pío de 2.90, y en La Estación de Biología fue de 1.61. Estos valores reflejan una mayor influencia de contaminantes atmosféricos transportados desde regiones con actividad antrópica, debido a que valores entre 1 y 2 de la razón de la concentración HCHO/CH_3CHO son típicos del aire urbano. Durante el inicio de vientos fuertes del sur (localmente conocidos como ''surada'') se observó un incremento significativo en la concentración de carbonilos, con respecto a los días previos a la ''surada'', como resultado de un posible transporte de contaminantes emitidos por fuentes antrópicas distantes tales como la carretera cerca del poblado de Catemaco y los complejos industriales cercanos a Coatzacoalcos. Se calcularon las trayectorias 24 horas hacia atrás de las masas de aire para Rancho Viejo, Temascaltepec y Cuetzalan y las concentraciones de carbonilos en el aire se discutieron de acuerdo al origen de las masas de aire.

ABSTRACT

Measurements of formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde concentrations were made at five different forested regions in México. One set of two simultaneous samplings was performed at two sites located in the México State, one semi-rural area (Temascaltepec), and the other, a forested area (Rancho Viejo). A second set of two simultaneous samplings were made in southern Veracruz State, in one rural area (Monte Pío) and inside a tropical rainforest (at the Biology Station of the University of México). Finally, one sampling was performed in the Sierra of Puebla State (Cuetzalan). Propionaldehyde and butyraldehyde were not reported because their concentrations were always below or near the detection limit of the technique. The highest concentrations were found from 7:00 to 11:00 h and from 11:00 to 19:00 h in all the sampling sites. Arithmetic mean concentrations of acetone were the highest observed among the detected carbonyl compounds in almost all sites, ranging from 0.5 to 8.4 μg m^{-3}. Arithmetic mean concentrations of formaldehyde and acetaldehyde ranged from 0.83 to 6 μg m^{-3} and 0.53 to 4.7 μg m^{-3}, respectively. The Spearman's correlations between formaldehyde and acetone, and between acetaldehyde and acetone were statistically significant at $p < 0.05$ in almost all sites. A significant correlation ($p < 0.05$) between formaldehyde and acetaldehyde was observed in México State at Rancho Viejo and Temascaltepec. The mean ratio HCHO/CH_3CHO of concentrations was 1.83 and 1.31 in the forested area of Rancho Viejo, first and second sampling periods, respectively; 1.71 and 1.62 in the semi-rural area of Temascaltepec, first and second sampling periods respectively; 1.70 in Cuetzalan; 2.90 in the rural area of Monte Pío; and 1.61 in the Biology Station tropical rainforest. These values show a greater influence of atmospheric pollutants transported from sites with anthropogenic activities, because HCHO/CH_3CHO concentration ratios between 1 and 2 are typical values of urban air. During the onset of strong winds from the south (locally known as "surada") a significant increase in carbonyl concentration was observed, in relation to the days before the "surada", as a result of a possible transport of pollutants emitted by distant anthropogenic sources such as the highway near Catemaco town and industrial complexes near Coatzacoalcos city. The air mass back trajectories were calculated for Rancho Viejo, Temascaltepec and Cuetzalan, and average carbonyl concentrations in air were discussed according to the air mass origin.

Key words: Carbonyl, forests, tropical forest, México

1. Introduction

Carbonyl compounds are of interest because of their potential toxicity, their ability to photolyze, to produce free radicals and to form stable atmospheric products, and their interactions in the smog cycles (Singh *et al.*, 1994).

In spite of their great importance, in the last 20 years, the knowledge of ambient levels and diurnal profiles of lower carbonyls has been limited to urban areas (Grosjean and Fung, 1984; Salas and Singh, 1986; Kalakobas *et al.*, 1988; Tanner *et al.*, 1988; Grosjean *et al.*, 1990; Grosjean *et al.*, 1993; Báez *et al.*, 1995, 2001). Some investigations have also been carried out on the presence of lower carbonyls in rural and marine environments (Lowe *et al.*, 1981; Neitzer and Seiler, 1981; Lowe and Schmidt, 1983; Shepson *et al.*, 1991; Zhou and Mopper, 1993; Singh *et al.*, 1994). In rural continental areas, additional oxidation of natural and anthropogenic non-methane hydrocarbons (NMHC) including the biogenically emitted NMHC, isoprene and terpenes, contributes significantly to the formation of carbonyl compounds (Fehsenfeld *et al.*, 1992).

The present paper reports the results of measurements of carbonyls in five forested sites of México. These sampling sites were chosen because at mountainous regions as well as coastal regions, the atmospheric circulation exhibits marked diurnal cycles with the alternation of high stability conditions during the night and strong vertical mixing during the day. Ground level concentrations and temporal evolution of air pollutants are strongly influenced by mesometeorological conditions involving local land-sea and mountain-valley breezes.

2. Experimental

2.1 Sampling sites description

A summary of the sampling conditions, specific characteristics for each sampling site and general considerations used to calculate the air mass back trajectories is shown in Table 1.

Table 1. Characteristics of the sampling sites, sampling conditions, and general considerations used to calculate the air mass back trajectories at 1000, 2000 and 3000 m AGL[1] at 0h UTC (local time = UTC - 5 or - 6)[2].

Site	Specific characteristics for each sampling site	Sampling date	Sampling time interval [3] (local time)	Number of samples	Air back trajectories
Rancho Viejo	Rural site with mixed woodland and grassland vegetation	May 12-18, 2002	07:00-11:00	5	YES
First sampling			11:00-19:00	5	
Second sampling			19:00-07:00	6	
		Jul 21-28, 2002	07:00-11:00	6	NO
			11:00-19:00	5	
			19:00-07:00	4	
Temascaltepec	Semi-rural site	May 12-18, 2002	07:00-11:00	5	YES
First sampling			11:00-19:00	5	
			19:00-07:00	6	
Temascaltepec	Semi-rural	Jul 21-28, 2002	07:00-11:00	6	YES
Second sampling		Jul 21-28, 2002	11:00-19:00	6	
			19:00-07:00	5	
Cuetzalan	Semi-rural	Sep 23-27, 2002	07:00-11:00	3	YES
			19:00-07:00	4	
Monte Pío	A coastal town, located 100 m away from the coast of the Gulf of México	March 3-8, 2003	07:00-11:00	5	NO
			11:00-19:00	5	
			19:00-07:00	5	

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Table 1. Characteristics of the sampling sites, sampling conditions, and general considerations used to calculate the air mass back trajectories at 1000, 2000 and 3000 m AGL[1] at 0h UTC (local time = UTC - 5 or - 6)[2].

Site	Specific characteristics for each sampling site	Sampling date	Sampling time interval [3] (local time)	Number of samples	Air back trajectories
Biology Station	A site inside a tropical jungle at the facilities of the Biology Station of the University of México located in the ecological reserve ''Los Tuxtlas'', around 8 km from the coast in Veracruz State	March 3-8, 2003	07:00-11:00 11:00-19:00 19:00-07:00	5 5 5	YES

[1] Meters above ground level. [2] Five hours from the 1st Sunday of April to the last Sunday of October, 6 h for the rest of the year. [3] Four, six, and twelve hours sampling time intervals, respectively. YES: back trajectories have been calculated. NO: no computation of air mass back trajectories.

Temascaltepec is located at 1900 m above sea level, 140 km away from México City and 66 km away from Toluca City, in a narrow canyon at 19°02'14" N latitude and 100°02'47" W longitude. The sampling site is at 1767 m above sea level (Fig. 1) with a sub-humid climate according to humidity level and a semi warm climate according to temperature. The climate of this site according to the Köppen Classification modified by García (1973) is (A)C(w_0), where: (A)C means that the climate is semi warm with a mean annual temperature higher than 18 °C, showing temperatures lower than 18 °C in the coldest month, and (w_0) is used to denote that rains occur in summer with a P/T < 43.2 [ratio of total annual precipitation (mm) to mean annual temperature (°C)]. The existent vegetation includes ash trees, oyamel, oak, cedar, ocote pine, ceiba, guava tree, banana tree, willow, cypress, eucalyptus, avocado, peach, lemon and myrtle.

Rancho Viejo is a forested area 80 km away from México City and 30 km from Toluca City, with a mean annual rainfall of 1400 mm, located at 2700 m above sea level (Fig. 1). The climate of this location is C(w_0)(w)b´g, where: C is used for temperate climates; (w) indicates that winter rains accounts for less than 5% of the annual precipitation, b´ indicates long and fresh summers with a mean temperature of the warmest month between 6.5 and 22 °C, and g means that the highest temperature occurs just before the rainy season (García, 1973). The prevailing vegetation includes ash trees, pines, oyamel, oaks and vegetative communities of high mountain like moss, lichens and herbaceous plants. Rancho Viejo is situated at 19°06' N latitude and 99°55' W longitude.

Cuetzalan is located at the northeast of the State of Puebla, at 20°05'18" N latitude and 97°34'54" W longitude (Fig. 1) and at 1000 m above sea level. The climate of this location is (A)C(fm)w´´(e)g, where: (A) is used for warm climates; C(fm) means that rains occur in summer being the precipitation amount greater than 40 mm during the driest month and the winter precipitation less than 18% of the annual precipitation; w´´ indicates a well defined dry period in winter and another short dry

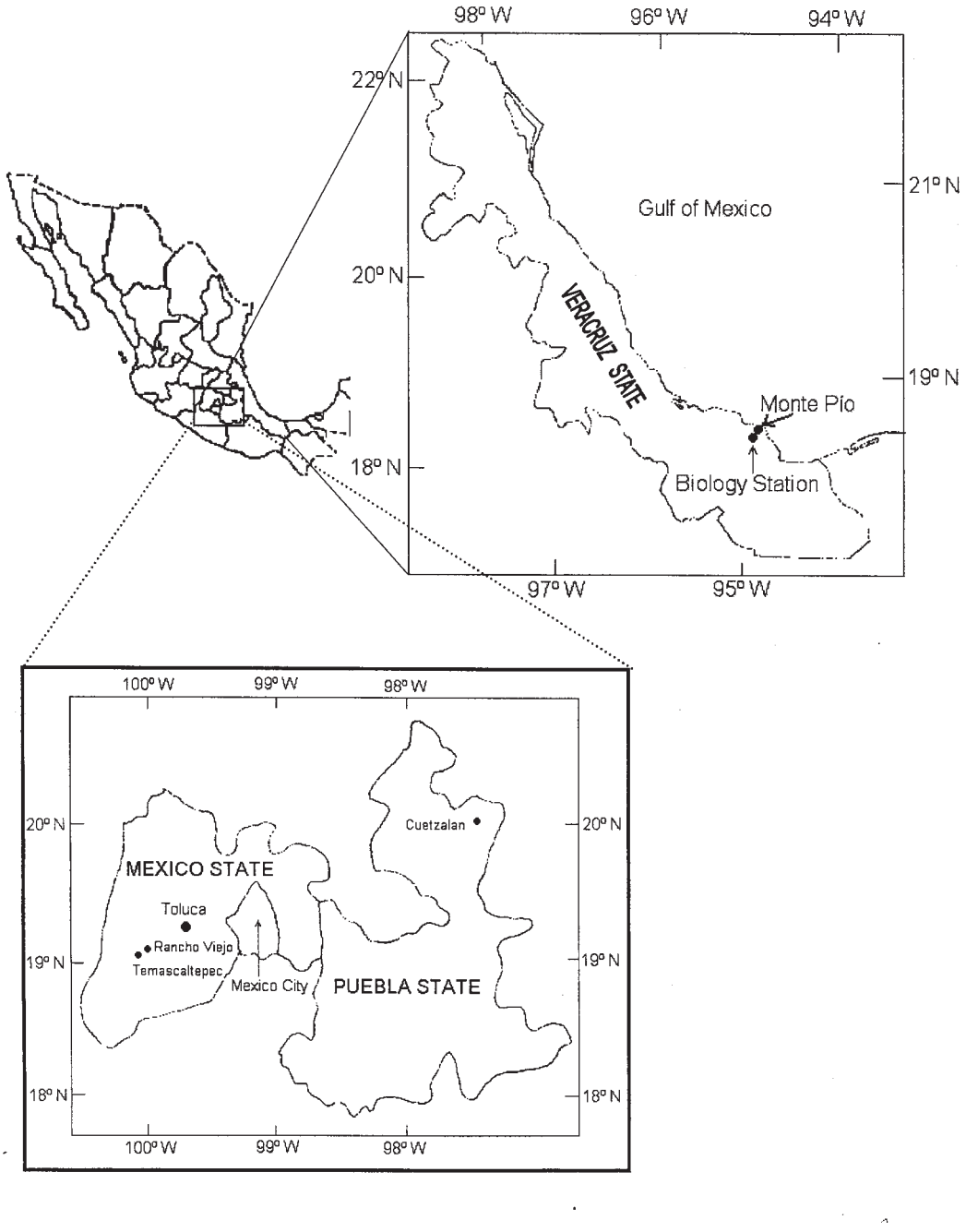

Fig. 1. Sampling sites location.

period in summer, (e) is used for regions with an annual oscillation of the mean monthly temperatures between 7 and 14%, and g means that the highest temperature occurs just before the rainy season (García, 1973). This municipality has lost the majority of its forested areas, however, it preserves mesophyl vegetation of the mountain type with liquidambar species at the riverside of the Apulco River as well as communities of pine-oak at the south-southwest of the city.

Monte Pío is a small town located at the south of Veracruz State, 100 m away from the coast of the Gulf of México, 50 m above sea level, at 18°38'34" N latitude and 95°05'50" W longitude (Fig. 1). Its climate is Am(f)i, where Am(f) means a warm-humid climate with the heaviest rains occurring in summer and the winter rains accounting for more than 10.2% of the annual precipitation; the precipitation in the driest month is less than 60 mm; and i is used for regions with an annual oscillation of the mean monthly temperatures less than 5 °C (García, 1973). Its average annual precipitation is 3216 mm. The prevailing vegetation includes that of coastal dunes and secondary vegetation. This site is located 8 km away from the Biology Station.

The Biology Station is located at the south of the State of Veracruz, inside the ecological reserve Los Tuxtlas (Fig. 1). It is located at 300 m above sea level, at 18°35' N latitude and 95°04' W longitude. Its climate is Af(m), which denotes a warm humid climate with rains throughout the year, the precipitation in the driest month is less than 60 mm, and winter rains account for less than 18% of the annual precipitation (García, 1973). The mean annual temperature measured in situ is 23.3 °C and its average annual precipitation is 4419.8 mm. The prevailing vegetation is evergreen high forests and secondary vegetation. The evergreen tropical high forest includes cedar, small hat species, real palm, rubber, ojite, ojuela and marayo.

2.2 Sampling and analysis

Carbonyls C_1- C_4 were sampled at the five afore mentioned sites in 2002 and 2003. Three sampling time intervals were conducted during each one of the periods of study: from 07:00 h to 11:00 h, from 11:00 h to 19:00 h, and from 19:00 h to 07:00 h. Measurements were made for formaldehyde, acetaldehyde, and acetone. Propionaldehyde and butyraldehyde were also measured, however, were not considered because their concentrations were below or near the limit of detection of the UV detector. Samples were collected with Sep-Pack DNPH-Silica cartridges (Waters, 1994). The sampling airflow was 1 L min^{-1}. An ozone scrubber was connected to the upstream end of the cartridge to avoid degradation of hydrazone derivatives (Waters, 1994). Each cartridge was sealed with Teflon caps immediately after sampling, then wrapped in aluminum foil and refrigerated.

The formed 2,4-dinitrophenylhidrazones were analyzed by high-performance liquid chromatography. Cartridges were eluted with 10 ml of HPLC-grade acetonitrile, and 20-ml aliquots were injected into a liquid chromatograph. The analytical conditions were as follows: a Spherisorb S5 ODS2 reverse phase analytical column, water/acetonitrile, 45/55 v/v as a mobile phase, and a flow rate of 1 ml min^{-1}. The derivatives were detected at 360 nm with a GBC LC 1200 UV/VIS detector. Calibration was done by direct injection of standard mixtures with known amounts of solid hydrazones dissolved in acetonitrile.

Cartridge blanks were analyzed to determine background levels of DNPH derivatives (Table 2). Ambient carbonyl concentrations were nevertheless corrected for cartridge blanks. The cartridge collection efficiency and the sampling precision (Table 2) were determined by connecting two cartridges in series and from the results obtained from four sampling devices co-located and simultaneously operated on six occasions, respectively. Also, in Table 2 are shown the analytical detection limits for formaldehyde, acetaldehyde and acetone. The analytical detection limits for propionaldehyde and butyraldehyde were 0.023 and 0.042 g per cartridge, respectively.

Table 2. Cartridge background carbonyl concentrations, cartridge collection efficiency, sampling precision, and analytical detection limits.

Parameter	Formaldehyde	Acetaldehyde	Acetone
Cartridge background (µg/cartridge)[a]	0.038	0.09	0.26
Cartridge collection efficiency (%)[b]	96.9	93.8	95.3
Sampling precision (% RSD)[c]	1.7-7.9	0.7- 8.2	1.3-9.6
Analytical detection limit (µg/cartridge)	0.035	0.061	0.075

[a]Arithmetic mean concentration (six cartridges from different lots). [b]Arithmetic mean of five independent determinations obtained by connecting two cartridges in series. [c]Arithmetic mean concentration obtained from 4 sampling devices colocated and simultaneously operated on six occasions.

The detection limits corresponding to sampling air volumes corrected for STP conditions for formaldehyde, acetaldehyde and acetone are shown in Table 3. The sample breakthrough of the cartridges is 83 ppbv (considering the combined concentrations of all carbonyls) when 720 L of air are sampled, which is the maximum sample volume at sampling conditions.

2.3 Statistical analysis

Non-parametric statistical methods were used to estimate whether there were significant differences between the concentrations of carbonyls at the different sampling times at each sampling site. The Kruskal-Wallis test was used to compare the concentrations of each carbonyl compound among the three sampling time intervals in each sampling site. The Wilcoxon-Mann-Whitney U Test (Sprent, 1989) was applied whenever significant differences were observed with the Kruskal-Wallis test. The Spearman's rank correlation was applied to compute the correlation between carbonyl concentrations.

3. Results and discussion

3.1 Diurnal variations

In Figures 2a to 2g are depicted the diurnal variations of carbonyl concentrations in function of the

Table 3. Detection limits.

Sampling site	Sampling air volume at STP (L)	Formaldehyde μg m^{-3}	Acetaldehyde μg m^{-3}	Acetone μg m^{-3}
Temascaltepec	203.19	0.17	0.44	0.72
Monte Pío	238.57	0.15	0.37	0.61
Biology Station	231.25	0.15	0.38	0.63
Cuetzalan	222.62	0.16	0.40	0.65
Rancho Viejo	182.78	0.19	0.49	0.80
Temascaltepec	406.37	0.09	0.22	0.36
Monte Pío	477.13	0.07	0.19	0.31
Biology Station	462.50	0.08	0.19	0.31
Cuetzalan	445.23	0.08	0.20	0.33
Rancho Viejo	365.55	0.10	0.24	0.40
Temascaltepec	609.56	0.06	0.15	0.24
Monte Pío	715.70	0.05	0.12	0.20
Biology Station	693.75	0.05	0.13	0.21
Cuetzalan	667.85	0.05	0.13	0.22
Rancho Viejo	548.33	0.06	0.16	0.27

sampling time intervals for each sampling site. The highest concentrations were found in all the sampling sites during daytime (7:00-11:00 and 11:00-19:00 h). In general, the maximum values for acetaldehyde and acetone were found at 07:00-11:00 h and the maximum for formaldehyde at 11:00-19:00 h. This behavior is expected because these carbonyls are photoxidation products of atmospheric hydrocarbons, and sampling diurnal periods coincide with high photochemical activity. On the other hand, the lower carbonyl concentrations from 19:00-07:00 are possibly due to the reaction with the NO_3 radical and deposition in the nocturnal boundary layer. However, part of nighttime concentrations could also be the remnants of daytime higher concentrations, since the loss rate by the NO_3 radical is slow compared to that of daytime reactions with OH and HO_2 in polluted atmospheres (Finlayson-Pitts and Pitts, 1986).

3.2 Correlation between carbonyl concentrations

It was found a statistically significant correlation ($p < 0.05$) between formaldehyde and acetaldehyde only in Rancho Viejo and Temascaltepec in the two sampling periods (Table 4). It was observed a statistically significant correlation ($p < 0.05$) between formaldehyde and acetone (Table 4) in almost all sites, except in the second sampling in Temascaltepec and Cuetzalan. The correlation between acetaldehyde and acetone was statistically significant ($p < 0.05$) at all sites. The correlation between these carbonyls suggests that they have common sources and sinks.

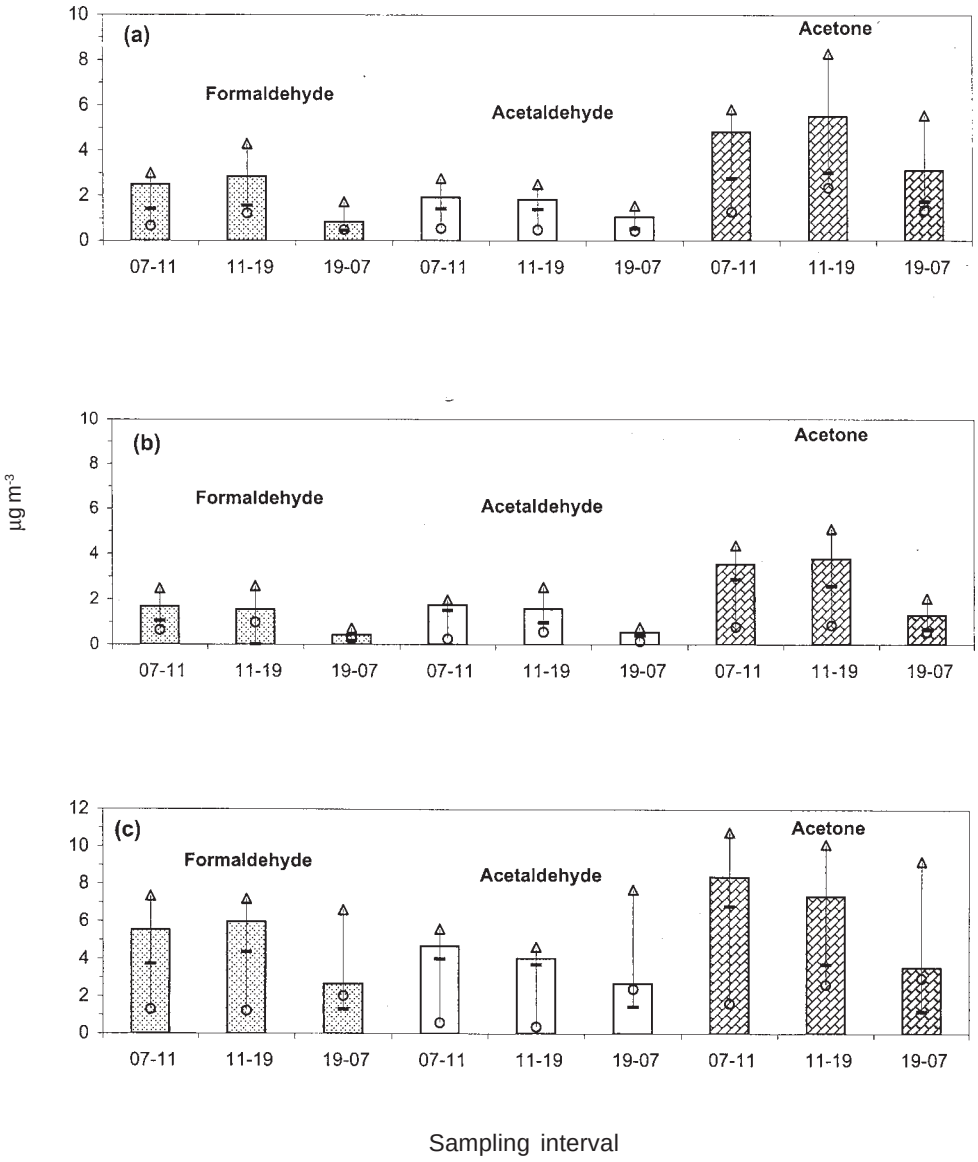

Fig. 2. Diurnal carbonyl mean concentration variations in each sampling site: (a) and (b) Rancho Viejo, first and second sampling, respectively (c) and (d) Temascaltepec, first and second sampling, respectively; (e), (f), and (g) Monte Pío, Cuetzalan, and the Biology Station, respectively. Columns indicate mean values; dashes-minimum values; triangles-maximum values; circles-standard deviation.

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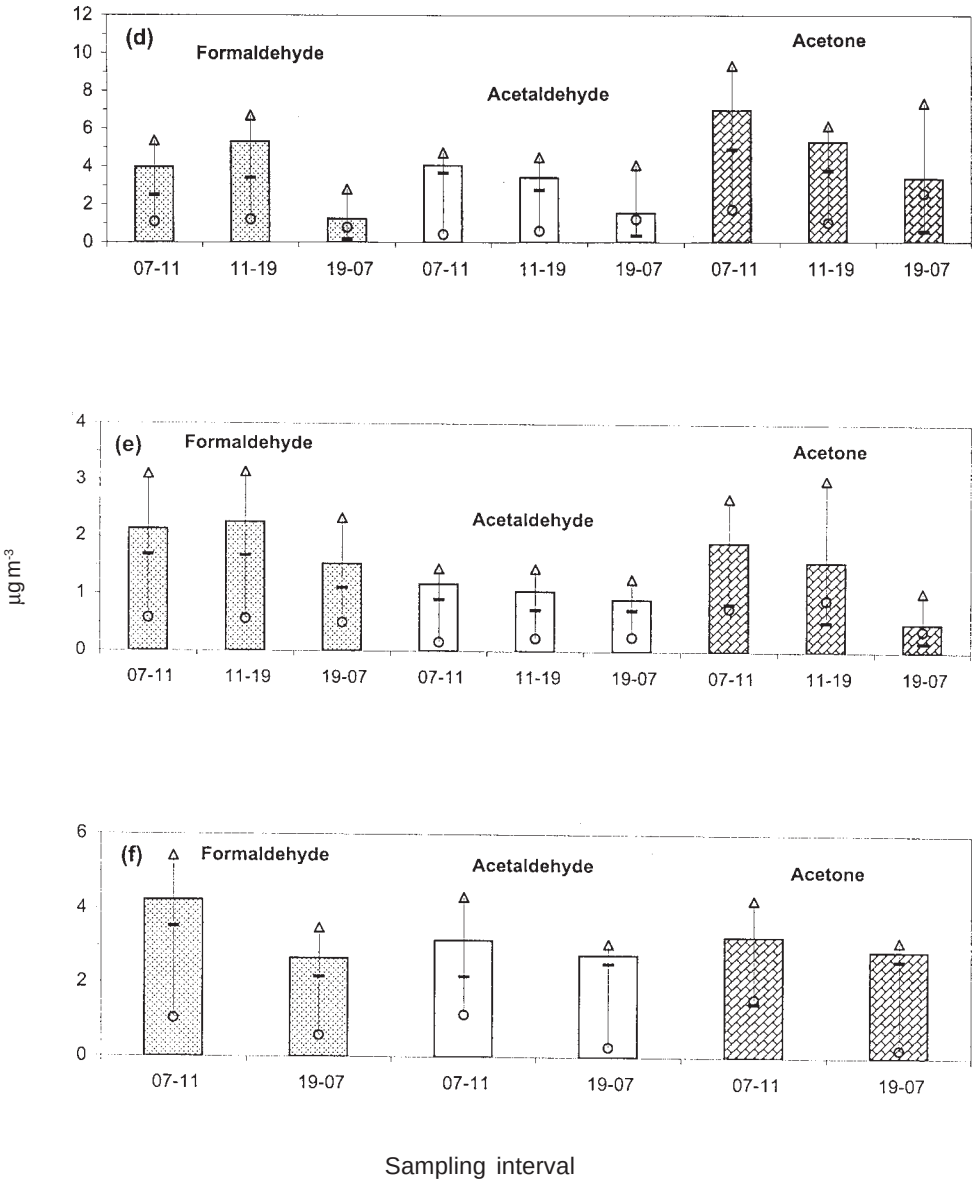

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Table 4. Spearman´s rho correlation between carbonyl concentrations.

Sampling site	N[a]	Formaldehyde: Acetaldehyde	Formaldehyde: Acetone	Acetaldehyde: Acetone
Rancho Viejo (first sampling)	16	0.780 [b]	0.785 [b]	0.889 [b]
Rancho Viejo (second sampling)	15	0.732 [b]	0.786 [b]	0.954 [b]
Temascaltepec (first sampling)	16	0.821 [b]	0.876 [b]	0.882 [b]
Temascaltepec (second sampling)	19	0.682 [b]	0.295	0.665 [b]
Monte Pío	15	0.097	0.561 [c]	0.617 [c]
Cuetzalan	7	0.357	0.500	0.964 [b]
Biology Station	15	0.493	0.727 [b]	0.675 [b]

[a] Number of samples. [b, c] Correlation is significant at 0.01 and 0.05 levels (2-tailed), respectively.

3.3. Carbonyl concentration ratios

Formaldehyde/acetaldehyde concentration ratios have been used to compare the results of carbonyl measurements studies at different locations (Grosjean *et al*., 1993). Relatively high values for this ratio may reflect the local participation of natural reactive hydrocarbons whose oxidation yields more formaldehyde than acetaldehyde. Measurements of formaldehyde and acetaldehyde in a forested (deciduous) site, in which isoprene chemistry often plays a dominant role, indicated a typical $HCHO/CH_3CHO$ ratio of 10 (Shepson, 1989). Grosjean (1982) and Salas and Singh (1986) found typical values for this ratio of approximately 2 in Southern California sites. Tanner and Meng (1984) reported for Long Island values for this ratio of 4.1 in winter and 1.9 in summer. Thus, since this ratio can vary between 1-2 (urban) and 10 (deciduous forest), it could be used as a measure of the possible impact of natural hydrocarbons on the oxidizing capacity of a particular air mass. The values of the mean ratio of $HCHO/CH_3CHO$ concentrations found in this study were: in Rancho Viejo (first and second sampling periods) 1.83, and 1.31, respectively; in Temascaltepec (first and second sampling periods) 1.71, and 1.62, respectively; in Cuetzalan 1.70; in Monte Pío 2.90; and in the Biology Station 1.61. These results reflect typical values of urban air (1-2), thus, it can be suggested that the local participation of natural reactive hydrocarbons was less than the local participation of anthropogenic hydrocarbons for all the sampling sites in this study.

3.4 Comparison of carbonyl concentrations at the different sampling sites

The Kruskal-Wallis test (Table 5) indicates that there were significant differences ($p < 0.05$) in the concentrations of carbonyls measured in Rancho Viejo and Temascaltepec in all cases, except for acetone in Rancho Viejo in the first sampling period and in Temascaltepec in the second sampling period. Such differences have also been reported in earlier studies (Slemr and Junkermann, 1996; Granby *et al*., 1997; Viskari *et al*., 2000). In Monte Pío and the Biology Station no significant differences were observed, except for acetone in Monte Pío. The Kruskal Wallis test was not applied to Cuetzalan data because this test requires at least three groups of data.

Table 5. Comparison of carbonyl concentrations among the sampling time intervals using the Kruskal-Wallis test.

Sampling site	H		
	Formaldehyde	Acetaldehyde	Acetone
Rancho Viejo (first sampling)	9.348[a]	7.371[a]	4.823
Rancho Viejo (second sampling)	6.083[a]	9.708[a]	9.458[a]
Temascaltepec (first sampling)	6.294[a]	5.981[a]	5.347
Temascaltepec (second sampling)	13.652[a]	9.697[a]	5.426
Monte Pío	3.620	3.829	7.440[a]
Biology Station	3.867	0.560	4.500

[a] Statistically significant difference at $p < 0.05$.

The Wilcoxon Mann-Whitney U Test (Table 6) was applied to determine if there were significant differences at the 0.05 level between daytime 3 (07:00 to 11:00 h and 11:00 to 19:00 h) and nighttime hours (19:00 to 07:00 h). Significant differences have been determined between daytime and nighttime hours for formaldehyde in Rancho Viejo, Temascaltepec and Cuetzalan, except in Rancho Viejo between 11:00 to 19:00 and 19:00 to 07:00 h during the second sampling period. For acetaldehyde, similar patterns were observed, except in Temascaltepec and in Cuetzalan during the first sampling period. Formaldehyde and acetaldehyde did not show any significant differences between daytime (from 07:00 to 11:00, and from 11:00 to 19:00 h) and nighttime (from 19:00 to 07:00 h) at Monte Pío and the Biology Station during both sampling periods. Acetone showed significant differences in the second sampling period in Rancho Viejo and in Monte Pío between 07:00 to 11: 00 and 19:00 to 07.00 h, and between 11:00 to 19:00 and 19:00 to 07:00 h, and in Temascaltepec and at the Biology Station between 07:00 to 11:00 and 19:00 to 07:00 h during the two sampling periods.

Although the sample number is low, some tendency in the variation of carbonyl concentrations seems to prevail: formaldehyde and acetaldehyde concentrations varied significantly between different sampling times in a more consistent way, only at the sampling sites relatively close to anthropogenic sources (Rancho Viejo and Temascaltepec). In Cuetzalan, which is a site that is farther away from pollution sources than Rancho Viejo and Temascaltepec, only formaldehyde concentrations varied significantly. Finally, in Monte Pío and the Biology Station, which are the farthest sites from anthropogenic sources, only acetone concentrations varied significantly between different sampling times. This could indicate that the variation of carbonyl concentrations throughout the different time intervals of the day, in Rancho Viejo, Temascaltepec and, to a lesser extent, in Cuetzalan, depends on short-range transport processes from pollution sources. A possible transport process is the movement of air pollutants, emitted in México City during morning hours, to nearby mountainous areas by a complex combination of mountain breezes (anabatic winds) and synoptic winds just over mountain ranges. This process could explain the higher concentrations of carbonyls observed in daytime hours, especially in Rancho Viejo and Temascaltepec. On the contrary, since

Table 6. Comparison of individual carbonyls concentrations between pairs of sampling time intervals using the Mann-Whitney test (07:00-11:00 morning, 11:00-19:00 noon and afternoon, 19:00-07:00 night).

Pair	Mann-Whitney U		
	Formaldehyde	Acetaldehyde	Acetone
Rancho Viejo (first sampling)			
Morning vs. noon and afternoon	10	12	10
Morning vs. night	1[a]	2[a]	5
Noon and afternoon vs. night	1[a]	3[a]	5
Rancho viejo (second sampling)			
Morning vs. noon and afternoon	12	8	10
Morning vs. night	0[a]	0[a]	0[a]
Noon and afternoon vs. night	5	0[a]	0[a]
Temascaltepec (first sampling)			
Morning vs. noon and afternoon	11	4	10
Morning vs. night	4[a]	5	4[a]
Noon and afternoon vs. night	3[a]	5	5
Temascaltepec (second sampling)			
Morning vs. noon and afternoon	6	5[a]	6
Morning vs. night	1[a]	4[a]	7[a]
Noon and afternoon vs. night	0[a]	5[a]	10
Monte Pío			
Morning vs. noon and afternoon	9	6.5	10
Morning vs. night	5	4	1[a]
Noon and afternoon vs. night	5	8	2[a]
Cuetzalan			
Morning vs. night	0[a]	5	4
Biology station			
Morning vs. noon and afternoon	12	12	7
Morning vs. night	5	9	3[a]
Noon and afternoon vs. night	4	10	7

[a] There is a statistically significant difference at $p < 0.05$ (2-tailed test). The smallest U value of the two groups is compared with the critical U value corresponding to a significant level. If the difference between the medians of the two groups is greater than would be randomly expected, such difference is statistically significant.

Monte Pío and the Biology Station are much farther from pollution sources, the effect of local winds is not strong enough to bring air pollutants from distant urban centers, therefore, the concentrations of carbonyls remains fairly constant throughout the day, in relation to the other sampling sites. At these sampling sites, larger scale phenomena (such as cold fronts) are the main transport processes that account for the observed carbonyl concentrations in these relatively isolated places.

3.5 Comparison of carbonyl concentrations with other sites

Although there are not many measurements of carbonyls performed in rural areas, it is interesting to compare the results of this paper with those reported in other rural areas (Table 7). The average carbonyl concentrations found in this study are in good agreement with those reported for other rural and clean areas around the world. The present work provides one of the first data set of measurements of carbonyl compounds in rural sites in México. It can be noted that the average carbonyl compounds concentrations were similar in all the stations. However, it is interesting to remark that formaldehyde concentrations in the tropical forest at Los Tuxtlas were similar to those observed in the Central Amazonian tropical forest (Kesselmeier *et al*., 2000). It is difficult to compare data obtained in different regions such as Los Tuxtlas and Central Amazonian tropical forests. It is nevertheless interesting trying to explain why formaldehyde concentrations were similar.

The formaldehyde detected in Central Amazonia was attributed to atmospheric reactions of terpenes and isoprene emitted by vegetation, since upwind the sampling site there are large extensions of forests (Kesselmeier *et al*., 2000). On the other side, the similar concentrations of formaldehyde observed in Los Tuxtlas, must have come from anthropogenic sources, since the area covered by this forest is obviously much smaller than that covered by Amazonian forests. In other words, if the formation of carbonyls from photochemical reactions of vegetation hydrocarbons were the main source of formaldehyde in Los Tuxtlas forest, the concentrations of formaldehyde would be much lower than in Central Amazonian forests.

Table 7. Formaldehyde, acetaldehyde and acetone concentrations (ppbv) measured in other rural and clean areas.

Site	Formaldehyde	Acetaldehyde	Acetone	References
Point Barrow, Alaska (clean air)	- - -	0.2-0.3	- - -	Cavanagh *et al*. (1969)
Hunsrueck mountains, Finthen, Germany (rural area)	0.7-5	- - -	- - -	Neitzer and Seiler (1981)
West coast of Ireland (remote sites)	0.1-2.5	- - -	- - -	Lowe *et al.* (1981)
On the Atlantic (35°N)	- - -	- - -	500*	Penkett (1982)
Julich, Germany (continental rural)	1-10	- - -	- - -	Lowe and Schmidt (1983)
Whiteface Mountain, NY	- - -	0.3-0.7	- - -	Schulam *et al*. (1985)
Pennsylvania (rural site)	- - -	- - -	0.2-1.8	Shepson *et al*. (1991)
Central Ontario (two rural sites)				Shepson *et al*. (1991)
Egbert	1.6	0.16-1.92	1.6	
Dorset	- - -	0.13-1.66	- - -	
Venezuela (clean tropical atmoshpere)	2	- - -	- - -	Trapp and Serves (1995)
Schauinsland, Germany (rural site)		0.1-1.8	1.7	Schubert *et al*. (1988)
Nashville, Tennessee (rural site)	- - -	0.66-3.6	4.3	Riemer *et al*. (1998)

Continues in the next page.

Table 7. Formaldehyde, acetaldehyde and acetone concentrations (ppbv) measured in other rural and clean areas.

Site	Formaldehyde	Acetaldehyde	Acetone	References
Central Amazonian (tropical forest)	- - -	0.1-1.2		Kesselmeier *et al*. (2000)
Sierra Nevada Mountains (Ponderosa pine plantation)	- - -	- - -	1.4-7.8	Goldstein and Schade (2000)
Temascaltepec, México State				This study
First sampling period	1.06-5.99	0.8-4.28	0.5-4.54	
Second sampling period	0.14-5.46	0.19-263	0.24-3.94	
Rancho Viejo, México State				This study
First sampling period	0.36-3.5	0.29-1.54	0.73-2.82	
Second sampling period	0.01-2.11	0.22-1.41	0.27-2.16	
Cuetzalan, Puebla, México	1.75-4.41	1.16-2.42	0.61-1.79	This study
Monte Pío, Veracruz, México	0.90-2.56	0.35-0.77	0.07-1.27	This study
Los Tuxtlas, Veracruz, México (Biology Station)	0.23-2.98	0.15-2.88	0.01-1.27	This study

3.6 Back trajectory analysis

Twenty-four hours back air mass trajectories were calculated for Rancho Viejo, Temascaltepec and Cuetzalan. Average carbonyl concentrations in air are discussed according to the air mass origin estimated by using air mass back trajectories for the entire sampling periods for these sampling sites. The trajectories were calculated at 1000, 2000 and 3000 meters above ground level at 0:00 h (UTC) by using the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model) from the NOAA (Draxler and Hess, 1998). The average concentrations and the results of the air mass back trajectories analyses (air mass origin) are shown in Figures 3a to 3e. The discussion of the carbonyls concentrations and the air mass back trajectories was facilitated by the fact that modeling results showed somewhat similar trajectories for the 3 levels (low shear) during all the sampling periods. Six air mass back trajectories, which represent typical conditions, observed at each sampling site during the different sampling periods are shown in Figures 4a to 4f.

The average formaldehyde, acetaldehyde and acetone concentrations in Rancho Viejo were higher during the first sampling period when the air mass origin was located to the northeast (Fig. 3a), and the average acetaldehyde and acetone concentrations were higher during the second sampling period when the air mass came from the northeast. Formaldehyde concentrations were higher when the air mass came from the east (Fig. 3b). In Temascaltepec the average formaldehyde, acetaldehyde and acetone concentrations were higher during the first sampling when the air mass

came from the northeast (Fig. 3c), and the average formaldehyde and acetaldehyde concentrations were higher during the second sampling when the air mass came from the northeast (Fig. 3d). Acetone showed the highest concentrations when the air mass came from the east. As it was expected, all these results observed in Rancho Viejo and Temascaltepec in both sampling periods showed a consistent pollutant transport from México and Toluca cities to these sites. Figure 3e shows the results for Cuetzalan. The average formaldehyde, acetaldehyde and acetone concentrations at this site were higher when the air mass came from the southwest, indicating a pollutant transport from the state and the federal highways, and from Zacapoaxtla Village. The analysis of carbonyl concentrations in relation to air mass back trajectories obtained with the HYSPLIT model for the

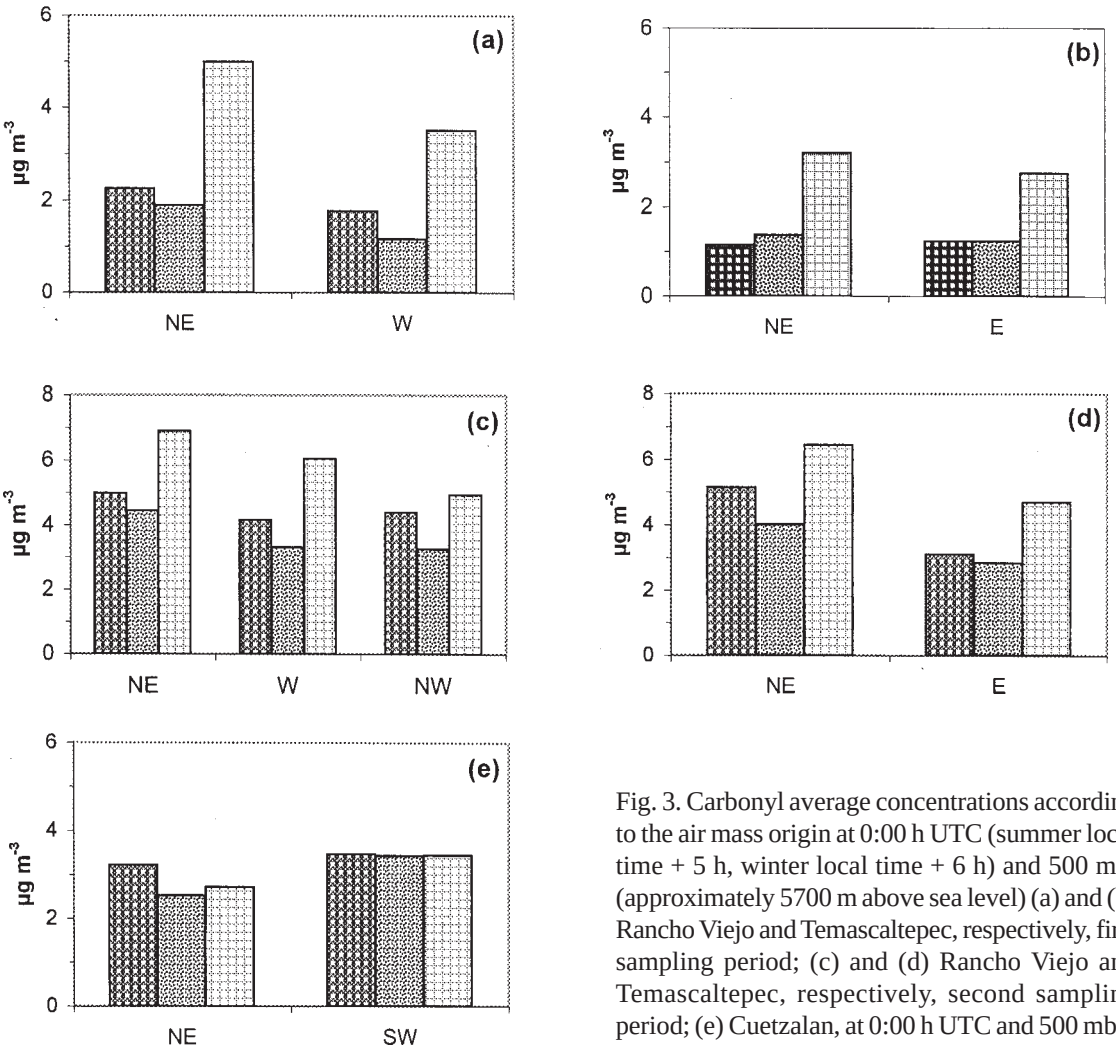

Fig. 3. Carbonyl average concentrations according to the air mass origin at 0:00 h UTC (summer local time + 5 h, winter local time + 6 h) and 500 mb: (approximately 5700 m above sea level) (a) and (b) Rancho Viejo and Temascaltepec, respectively, first sampling period; (c) and (d) Rancho Viejo and Temascaltepec, respectively, second sampling period; (e) Cuetzalan, at 0:00 h UTC and 500 mb.

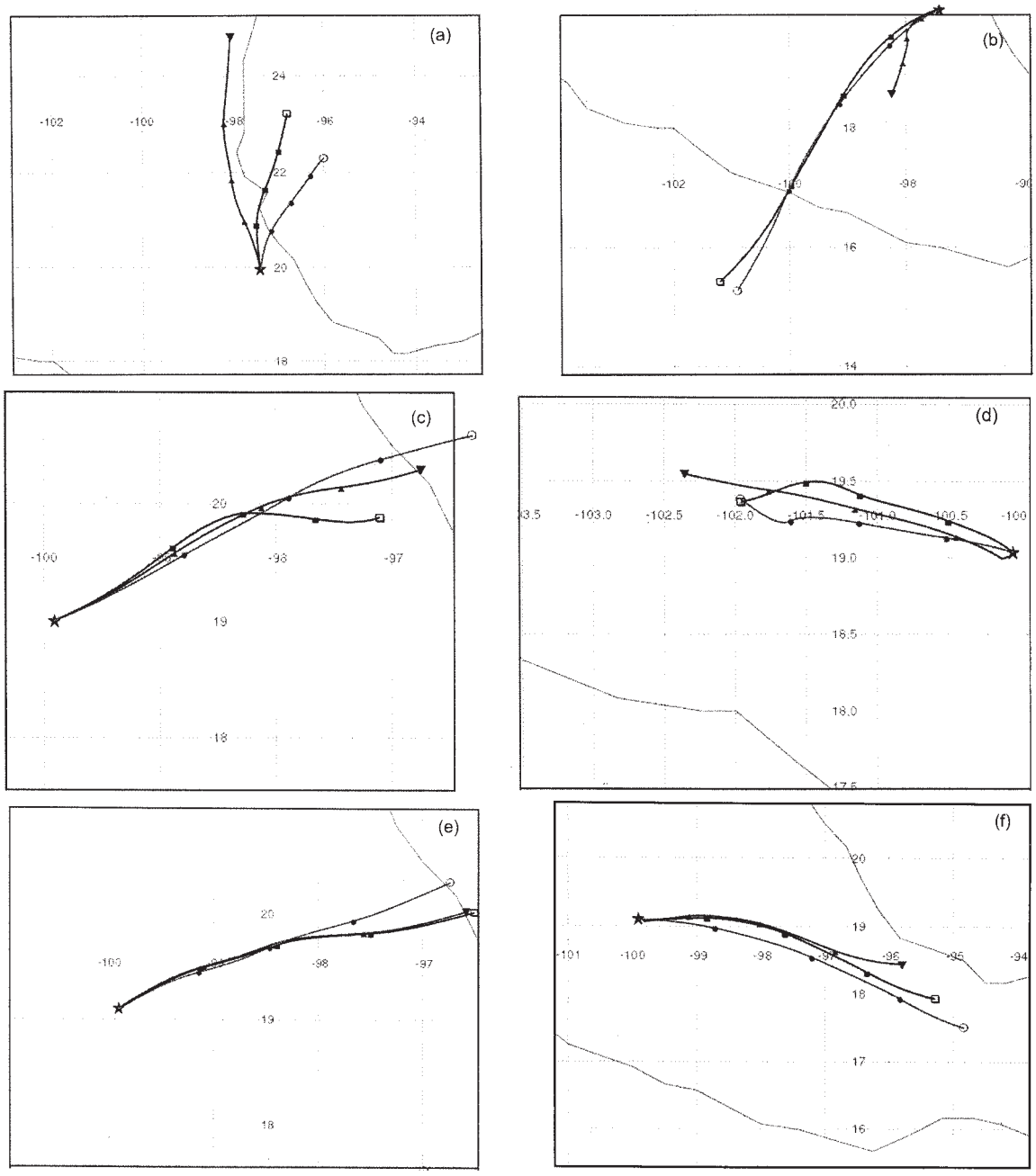

Fig. 4. Typical air mass back trajectories: (a) and (b) for Cuetzalan, (c) and (d) for Rancho Viejo and Temascaltepec during the first sampling period, (e) and (f) same as (c) and (d) except for the second sampling period. Triangles, squares, and circles indicate 1000, 2000 and 3000 m above ground level, respectively.

Biology Station and Monte Pío is not presented because the results did not match those obtained with direct field observations. Possibly, this due to a combination of meteorological phenomena, specifically a strong wind from the south-southeast, locally known as ''surada'', whose first signs appeared around 09:00 hours on March 5, when a strong wind began blowing from the southeast; and a cold front from the north (''norte" from the Gulf of México), which began being more notorious at around 19:00 h on March 6, 2003, when the sky turned cloudy. Although no field meteorological information was obtained, the presence of a cold front that swept the Gulf of México coast was detected by the meteorological observatory of the Centro de Previsión del Golfo de México of the Obsercatorio Meteorológico Nacional in the coastal city of Veracruz on March 4, 2003, when a counter-clockwise shift of the wind direction from the east to the north was observed from around 3:00 to 4:10 h. The wind direction remained roughly from the North until 12:10 h, when it began shifting clockwise from the north to the east until 15:00 h. These meteorological phenomena represented a unique opportunity to relate carbonyl concentrations to meteorological parameters, and because of this, these sampling sites are discussed in detail in the next paragraph, based on field observations focusing special attention on the results obtained during the onset of the ''surada'' and the ''norte''.

Although there are no meteorological stations available at the sampling sites of this study, an interesting phenomenon could be observed: formaldehyde, acetaldehyde and acetone concentrations increased significantly in the Biology Station and only formaldehyde concentration increased significantly in Monte Pío (Table 8), between 07:00 and 11:00 h, precisely when a strong wind from the southeast began blowing. This fact is consistent with the localization of polluting sources in relation to Monte Pío and the Biology Station. Oil refineries and industrial complexes in Veracruz and Tabasco states are scattered southeast of these sites. It seems clear that the strong winds from the southeast transported air pollutants from these polluting sources to the sampling sites. However, it was not possible to know whether the tropical forest, which lies south and southeast of the sampling sites, contributed to some of the observed increase in carbonyl concentrations. Carbonyl concentrations were also high from 11:00 to 19:00 h coinciding with the fact that the wind from the southeast kept on blowing. It is important to notice that the concentration of carbonyls started to decrease between 19:00 h on March 5 and 07:00 h on March 6, when the wind from the south-southeast reached its maximum speed, possibly due to a dilution effect. Then, winds from the North (from the sea) began blowing as a result of a cold front whose effects were clearly notorious during afternoon hours, as it was afore mentioned, made carbonyl concentration decrease further. After the cold front passage, carbonyl concentrations did not change significantly, except formaldehyde concentration, which decreased significantly at Monte Pío and the Biology Station. This could be due to the shorter lifetime of formaldehyde. The strong wind from the south and the cold front observed on March 5 and 6, and on March 6 and 7, respectively, were meteorological phenomena that help to identify emissions of polluting sources situated south-southeast of Monte Pío and the Biology Station, as the main origin of the carbonyl concentration levels observed at these sites.

On the other side, the results observed at Rancho Viejo also suggest that anthropogenic contribution to carbonyl levels was the most important source. The fact that carbonyl concentrations

Table 8. Hourly variation of carbonyl concentrations (μg m^{-3}) in Monte Pío (MP) and Biology Station (BS).

Sampling date	Sampling time interval h	Formaldehyde		Acetaldehyde		Acetone	
		MP	BS	MP	BS	MP	BS
March 3, 2003	11:00-19:00	2.29	1.36	1.39	0.63	3.01	0.21
March 3-4, 2003	19:00-07:00	1.28	0.28	1.10	0.27	0.24	0.14
March 4, 2003	07:00-11:00	1.83	0.93	1.12	0.52	0.83	0.28
March 4, 2003	11:00-19:00	1.89	1.26	0.77	0.83	0.52	0.26
Mach 4-5, 2003	19:00-07:00	1.10	0.88	0.76	0.70	0.17	0.31
March 5, 2003	07:00-11:00	3.10	2.40	1.15	1.06	2.30	3.01
March 5, 2003	11:00-19:00	3.14	3.66	1.08	2.59	1.45	1.78
March 5-6, 2003	19:00-07:00	2.32	2.64	0.63	2.11	1.04	1.04
March 6, 2003	07:00-11:00	2.20	2.15	1.26	2.95	2.68	2.63
March 6, 2003	11:00-19:00	2.25	2.09	1.04	3.33	1.26	1.97
March 6-7, 2003	19:00-07:00	1.72	0.74	0.76	2.84	0.31	0.40
March 7, 2003	07:00-11:00	1.79	2.29	0.95	5.18	1.40	1.66
March 7, 2003	11:00-19:00	1.67	1.15	0.92	1.67	1.59	1.02
March 7-8, 2003	19:00-07:00	1.15	0.33	1.22	1.24	0.74	0.02
March 8, 2003	07:00-11:00	1.68	0.93	1.39	1.30	2.25	1.52
Mean concentration		1.96	1.54	1.03	1.81	1.32	1.08
Standard deviation		0.61	0.96	0.23	1.35	0.90	0.97

observed at this site resembled those observed at Monte Pío and the Biology Station indicates that vegetation type did not seem to have any effect on carbonyl levels; Rancho Viejo is surrounded by coniferous forests, whereas Monte Pío and the Biology Station are surrounded by tropical forests. Consequently, it can be assumed that the transport of air pollutants from anthropogenic sources seems to be the main origin of carbonyl levels observed at all sampling sites. This was indeed expected because, despite Los Tuxtlas rain forest is a national park, it cannot be considered as a remote site since important industrial complexes and highways are relatively close. In other words, the observed carbonyls levels would have been significantly lower if Los Tuxtlas national park had lain in a remote region.

4. Conclusions

In this paper the results of measurements of C_1- C_4 carbonyls performed at different forested regions in México are presented. This data set represents the first measurements of these carbonyl compounds in rural sites in México. A marked diurnal variation of carbonyl concentrations was commonly observed because of the influence of meteorological conditions, photochemical activity and anthropogenic activities. Overall, formaldehyde and acetone were the most abundant of the

three measured carbonyls. The maximum concentrations were obtained from 07:00 to11:00 h and from 11:00 to 19:00 h for formaldehyde, acetaldehyde and acetone. Formaldehyde/acetaldehyde concentration ratios have been used as a measure of the impact of hydrocarbons emitted by anthropogenic sources on the photochemistry of a particular air mass. The relatively low mean ratios (1.31-2.90) of formaldehyde to acetaldehyde indicate that the anthropogenic contribution to carbonyl levels seemed to be more important than the biogenic contribution in these sites.

When winds blew from the northeast, carbonyl concentrations in Rancho Viejo and Temascaltepec were consistent with a significant anthropogenic contribution due to transport phenomena. When winds blew from the south-southwest, carbonyl concentrations in Cuetzalan were also consistent with a significant anthropogenic contribution due to transport. The concentrations of formaldehyde, acetaldehyde and acetone increased significantly in the Biology Station during the onset of strong winds from the south (locally known as ''surada''), whereas only the concentration of formaldehyde increased significantly in Monte Pío during this phenomenon. Unfortunately, not a satisfactory explanation could be found to this fact. Nevertheless, the results obtained in all the sampling stations suggest that the transport of pollutants from anthropogenic sources to forested regions seems to be the main origin of carbonyl levels observed in these regions. It was not possible to assess by how much forests contribute directly or indirectly, via photochemical reactions of natural hydrocarbons, to carbonyl levels observed in any of the sampling sites of this study.

The results obtained in this study should be taken as preliminary since further measurements of other carbonyls such as methyl vinyl ketone and methacrolein and hydrocarbons (biogenic and anthropogenic) and meteorological parameters at these sites could provide valuable information regarding the relative contribution of natural and anthropogenic hydrocarbons to local photochemical processes. The findings obtained in this study suggest that a network of simultaneously operated meteorological sampling stations should also be established along the Gulf of México coast and over the sea to provide valuable information on specific relative contributions of biogenic sources from forests and the sea, and of anthropogenic sources.

Relatively few measurements of carbonyls in clean air have been published and the results obtained display a considerable amount of uncertainty and it is difficult to interpret them when they are included in current photochemical models. For this reason, it is also necessary to carry out more measurements of the variations of carbonyls in the clean troposphere, which will reduce the uncertainties of hydrocarbon oxidation in models. However, carbonyls are also generated by anthropogenic processes leading to large local variations, which mask those carbonyls caused by natural production and destruction processes. Therefore, these measurements must be made also in background regions where the hydrocarbon precursors of carbonyls are expected to be homogeneously distributed and where the effects of transport of carbonyls from polluted areas are not considerable.

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