Levels of carbonyls, CO, O_3, NO, NO_2, NO_x and SO_2 in ambient air of Monterrey, Mexico during winter 2013

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Abstract: - Atmospheric levels of formaldehyde and acetaldehyde were measured in an urban site located in Monterrey Mexico using an active sampling during winter 2013. 2 h-samples were collected using DNPH-cartridges at 09:00 h, 12:00 h and 15:00 h, and then analyzed using high performance liquid chromatography with ultraviolet detector (HPLC-UV). Criteria pollutants (CO, O_3, NO, NO_2, NO_x, and SO_2) were measured by automatic analyzers. Mean formaldehyde levels were higher than acetaldehyde levels. Both carbonyls showed a clear diurnal pattern. Formaldehyde levels were higher during the morning sampling (37.815 ppbv) and acetaldehyde showed the highest levels during the afternoon sampling (39.186 ppbv). Levels of carbonyls were higher when wind blew from WSW, a heavy traffic avenue, a railway and electric power companies are located in this direction. The result of principal component analysis (PCA) suggests that the primary pollution sources at Monterrey were vehicle exhausts (gasoline and diesel engines). CO, NO, NO_2, NOx and formaldehyde were probable ozone precursors during the morning sampling and relative humidity had a washout effect on NO, NO_2, O_3, NO_x levels during the midday and afternoon sampling periods.

Key-Words: - Carbonyls, ozone, criteria pollutants, air pollution, Monterrey, COVs

1 Introduction

Carbonyl compounds are ubiquitous components of the atmosphere and play an important role in atmospheric chemistry [1]. These compounds are the main organic compounds involved in photochemical air pollution constituting photo-oxidation products of gas-phase hydrocarbons in sunlight [2-4], are the major source of free radicals, and are the precursors to ozone, peroxyacyl nitrates (PANs) and secondary organic aerosols (SOA) [5].

Monitoring carbonyls in the ambient air is of fundamental importance in assessing the significance of photochemical activity and understanding the oxidation mechanisms of atmospheric volatile organic compounds (VOCs). Other important characteristic of these compounds is the fact that some carbonyls such as formaldehyde, acetaldehyde and acrolein are suspected to be carcinogenic and mutagenic to humans [6]. In Mexico most of the studies about the spatial and temporal levels of carbonyls have been focused to Mexico City [7-9] and there is not enough information about other big cities in Mexico like Monterrey, Nuevo Leon. Monterrey is the third largest city in Mexico, where important urban and industrial activities are carried out. This city is located at 25°40'N and 100°18' W at 537 masl and covering an area of 580.5 km^2. Monterrey is one of the 12 municipalities of the Metropolitan Area of Monterrey and it is a high profile center of education, tourism and business with a population of 4,000,000 habitants.

The objectives of this work were: 1) to quantify the atmospheric concentrations of formaldehyde and acetaldehyde in an urban site in Monterrey, Nuevo León, Mexico during winter 2013, and 2) to identify potential sources using principal component analysis from their relation with other criteria pollutants and meteorological parameters.

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2 Methodology

2.1 Sampling Site Location

Monterrey has a humid subtropical climate. Its weather is hot in the summer (temperature reaches 35 °C in August), though reasonably pleasant in spring and autumn. The average temperature in winter is 8 °C. Rainfall is scarce, but more prominent during May to September. Humidity in winter can be high, although without showers. Snowfall is a very rare event. The annual average precipitation is 615 mm. The weather patterns over the area are influenced by frontal systems coming from the north of the continent. The specific sampling site was located in the facilities of the Chemistry Faculty, Postgrade Division of the Universidad Autonoma de Nuevo León within the MAM in the municipality of San Nicolás de los Garza (25° 44' 42" N; 100° 15' 17" W), at 500 masl (Fig. 1).

The site was located within an industrial, residential, educational and commercial area where also there are three avenues of high vehicular traffic.

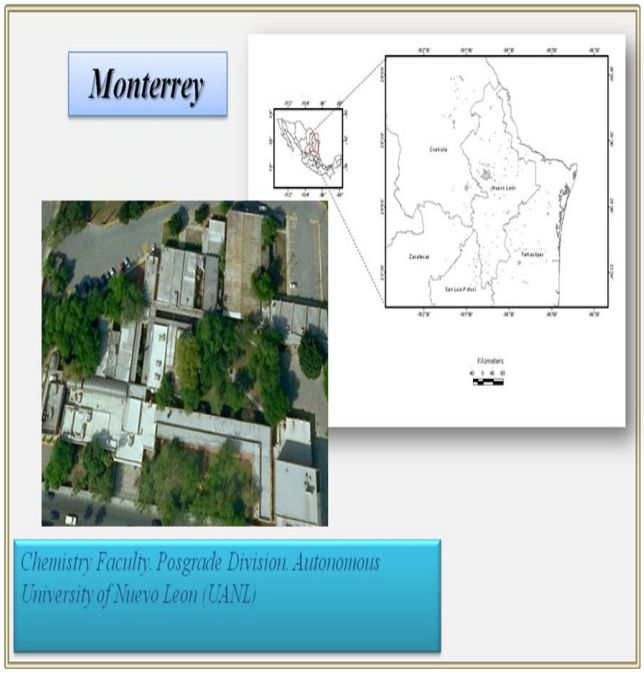

Figure 1. Sampling Site Location.

2.2 Sampling Method

Samples were collected during winter 2013 (from March 4 to March 12). Formaldehyde, and acetaldehyde were measured in ambient air. Samples of air were collected with a Sep-Pak DNPH-Silica cartridges (Waters, Milford, USA). The downstream end of the cartridge was connected to a calibrated flow meter. Ambient air was passed through the cartridge at a flow rate of 700 ml min-1 at 2h intervals (morning, midday and afternoon), from 9:00h to 11:00 h, from 12:00 h to 14:00 h, and from 15:00 h to 17:00 h. An ozone scrubber was connected to the upstream end of the cartridge to avoid degradation of hydrazone derivatives [10]. Each cartridge was immediately sealed with Teflon ® caps, then wrapped in aluminum foil and stored in the refrigerated (4 °C) before being analyzed.

2.3 Analytical Method

Cartridges were eluted with 5 ml of HPLC grade acetonitrile, and 20 µl aliquots were injected into an Agilent 1100 instrument coupled to an UV detector at 360 nm. The analytical conditions were as follows: a Zorbax ODS column (250 mm x 2.6µm DI), water/acetonitrile 45/55 v/v as a mobile phase and a flow rate of 1 ml min-1. Calibration was done by direct injection of standard mixtures with known amounts of solid hydrazones dissolved in acetonitrile according to the EPA Method TO-11 A [11]. Cartridge laboratory blanks and cartridge field controls were analyzed to determine background levels of DNPH derivatives and found values for field were similar to those of the laboratory blanks.

The analytical detection limits for formaldehyde and Acetaldehyde were 0.09, and 0.25 µg m-3, respectively, according to Miller and Miller [12] for a sampling volume of 168 l. Cartridge efficiency was determined by connecting two cartridges in series. Values of >95% were obtained for all carbonyls using the sampling conditions described above.

2.4 Monitoring of meteorological parameters and criteria air pollutants

Wind conditions (direction and speed), relative humidity, temperature, solar radiation and barometric pressure were monitored from March 4 to March 12, 2013 (winter) using a portable meteorological station model Davis Vantage Pro II and wind roses were constructed for each day using the software WRPLOT (Lakes Environmental) [13]. 24 hr back air masses trajectories were calculated for the studied period using HYSPLIT model from the NOAA (National Oceanic Administration Agency, USA) [14] in order to identify the probable origin of the air masses.

Criteria Air Pollutants (O_3, NO, NO_2, NO_x, CO and SO_2) were obtained from the Integrated System of Environmental Monitoring of the MAM (SIMA), specifically from the Northeast Station, located in the Laboral Unity District in San Nicolás de los

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Garza, N.L. at 25° 44' 42 "N and 100° 15' 17" W at 500 m above sea level, within an area with high density of population. All criteria pollutants were determined using automatic analyzers API Teledyne.

2.5. Correlation and Principal Component Analysis (PCA)

Spearman rank was applied to all data collected at the sampling site. To assess the relationships between concentrations of the carbonyls studied and meteorological parameters and criteria air pollutants measured, factor analysis (Principal Component Analysis) was applied using the software XLSTAT [15].

3 Results

3.1 Diurnal variation

Ambient concentrations of carbonyl C_1 –C_2 were measured in eighteen samples during winter 2013 (March 4 to March 12). Formaldehyde was the most abundant carbonyl, followed by acetaldehyde. The concentration of acetone, propionaldehyde and butyraldehyde were below of the detection limit. Diurnal variation for formaldehyde and acetaldehyde and descriptive statistics are shown in Table I and Fig. 2.

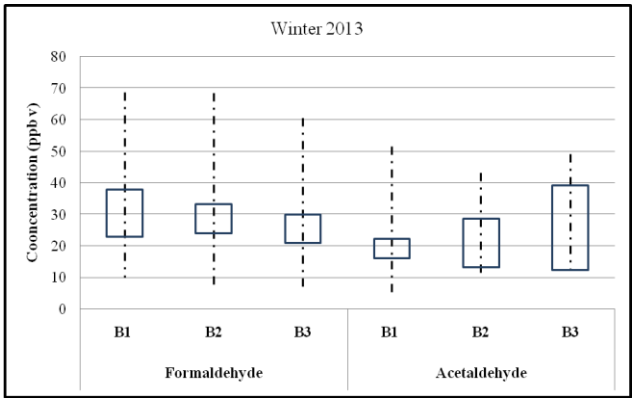

Figure 2. Diurnal variation for measured carbonyls during winter 2013: B1 (09:00-11:00 h), B2 (12:00-14:00 h) and B3 (15:00-17:00 h).

Both measured carbonyls showed a clear diurnal pattern. The highest mean concentrations were found for formaldehyde during the morning sampling period (B1) followed by the midday sampling period (B2) and having the lowest levels during the afternoon sampling period (B3). Acetaldehyde had the highest mean levels during the afternoons, decreasing during the midday and having the lowest values of concentrations during the mornings. This difference in diurnal variation of both carbonyls may be an indicative that these compounds had different sources during the present study. Low levels of formaldehyde during the afternoon were probably due to photolysis and reactions with OH radicals [16]. Comparing with other sites, the carbonyl levels are higher than those reported in Shanghai [16], México City [9], and Bangkok [17].

Table I. Parametric statistics for the measured carbonyls during winter 2013: B1 (09:00-11:00 h), B2 (12:00-14:00 h) and B3 (15:00-17:00 h).

	Formaldehyde (FA)			Acetaldehyde (AA)		
Parametric Statistics	B1	B2	B3	B1	B2	B3
Mean	37.82	33.17	30.03	22.23	28.65	39.19
Maximum	68.73	68.50	60.45	51.46	43.08	49.13
Minimum	9.97	7.36	7.14	3.51	10.48	20.89
Standard Deviation	22.82	23.92	20.97	16.10	13.35	12.47
Q1	19.34	13.12	11.85	15.13	18.44	31.50
Q3	49.75	46.79	41.13	23.47	36.52	47.21

3.2 Meteorological influence

During winter 2013, the wind prevailing direction was from WSW most of the time (60 %). Wind rose analysis was used to determine the prevailing conditions during the sampling campaign and to identify the probable sources using the Software WRPLOT View (Lakes Environmental). In March 8 there was a peak for carbonyl compounds, during the morning (FA: 68.72 ppbv and AA: 51.45 ppbv) with prevailing winds from W-SW (low speed: 1-3 ms^{-1}) and during the afternoon (FA: 51.45 ppbv). These wind conditions probably contributed to increase the carbonyls concentration in this site. Acetaldehyde showed peaks in concentration in March 12 during midday (with a value of 43.083 ppbv when wind blew from SW at 4-6 ms^{-1}), and in March 7 during the afternoon sampling period (with a value of 49.12 ppbv when wind blew from S at 1-3 ms^{-1}.Meteorological influence and a wind rose for one of these air pollution episodes can be observed in Fig. 2. A heavy traffic avenue, a railway and

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electric power companies and Santa Catarina municipality are located at SW of the sampling site, whereas, Monterrey municipality is located at S of this site.

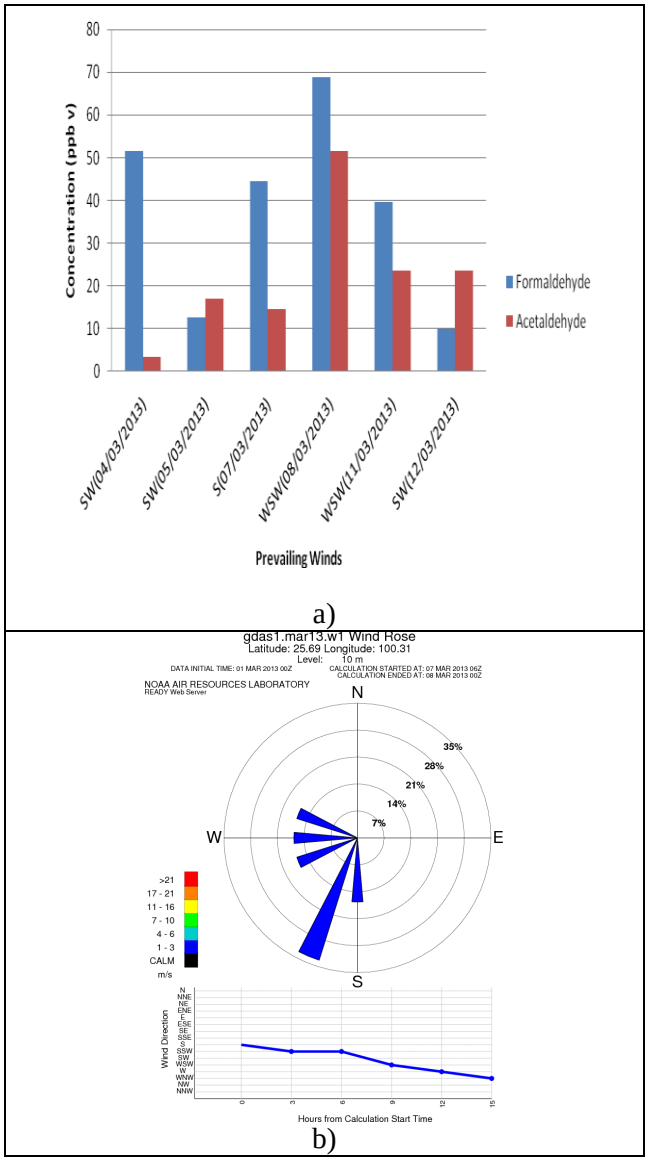

Figure 2. Meteorological influence on carbonyl levels (a) and a wind rose for an air pollution episode in March 8, 2013(b).

3.3 Formaldehyde/Acetaldehyde ratio

Table II shows formaldehyde and acetaldehyde (FA/AA) ratio. The FA/AA ratios vary from 1 to 2 for urban areas to about 10 for forested rural areas [24]. A high FA/AA ratio may reflect the local generation of natural reactive hydrocarbons, whose oxidation yields more formaldehyde than acetaldehyde [16]. In this study, the average FA/AA concentration ratio was 2.0625, which is higher, than the studies reported in Guangzhou, China 0.97 [19], Athens, Greece 1.27 [1], Shanghai, China 1.58 [20] and Mexico City (range = 0.77– 1.19) [8]. Our values can be considered within the range of values for urban areas.

Table II. Formaldehyde/Acetaldehyde ratio

FA/AA RATIO		
B1 (09:00-11:00 h)	B2 (12:00-14:00 H)	B3 (15:00-17:00 H)
4.051	1.474	6.661

3.4 Correlation of carbonyls with criteria air pollutants and meteorological parameters

Pearson correlation was applied in order to know the correlation between carbonyls concentration with criteria pollutants. Pearson correlation matrixes for the three sampling periods are showed in Tables III-V.

Table III. Pearson correlation matrix for the morning sampling period (B1).

	CO	NO	NO2	O3	NOX	SO2	FA	AA
CO	**1**	0.990	0.986	-0.483	0.988	0.800	0.292	-0.547
NO	0.990	**1**	0.998	-0.478	0.999	0.862	0.168	-0.576
NO2	0.986	0.998	**1**	-0.484	1.000	0.884	0.179	-0.551
O3	-0.483	-0.478	-0.484	**1**	-0.482	-0.309	-0.418	-0.382
NOX	0.988	0.999	1.000	-0.482	**1**	0.874	0.174	-0.562
SO2	0.800	0.862	0.884	-0.309	0.874	**1**	-0.095	-0.515
FA	0.292	0.168	0.179	-0.418	0.174	-0.095	**1**	0.379
AA	-0.547	-0.576	-0.551	-0.382	-0.562	-0.515	0.379	**1**

Table IV. Pearson correlation matrix for the midday sampling period (B2).

	CO	NO	NO2	O3	NOX	SO2	FA	AA
CO	**1**	0.163	0.492	0.799	0.444	-0.268	0.756	0.268
NO	0.163	**1**	0.926	0.703	0.947	-0.021	-0.347	-0.191
NO2	0.492	0.926	**1**	0.903	0.998	-0.042	0.010	-0.159
O3	0.799	0.703	0.903	**1**	0.879	-0.051	0.306	-0.068
NOX	0.444	0.947	0.998	0.879	**1**	-0.042	-0.045	-0.163
SO2	-0.268	-0.021	-0.042	-0.051	-0.042	**1**	-0.359	-0.965
FA	0.756	-0.347	0.010	0.306	-0.045	-0.359	**1**	0.390
AA	0.268	-0.191	-0.159	-0.068	-0.163	-0.965	0.390	**1**

During morning sampling periods (B1), it was found a good correlation among CO and NO_x, SO_2, NO_2 and NO, which indicates that these compounds probably had sources in common related to vehicular traffic. O_3 correlated negatively with

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CO, NO, NO_2, NO_x and FA, indicating that all these compounds could be ozone precursors. During the midday and afternoon sampling periods (B2 and B3) a good correlation between CO and FA was found. Morknoy and collaborators [17] reported good correlations between formaldehyde-CO (r = 0.756 and r=0.915, respectively), this relations indicate a strong influence of vehicular sources. FA - NO correlation was good (r = 0.580) (p <0.05), during the midday, indicating that these compounds had sources in common, probably combustions process at high temperatures. NO, NO_2 and NOx had a good correlation indicating that all these compounds could be originated in common sources. During the afternoon sampling period, FA and AA correlated positively in a significant way with CO, NO, NOx and SO_2, indicating that carbonyls during this period could be originated from mixed sources (vehicular emissions, combustion sources at high temperatures and industrial sources).

Table V. Pearson correlation matrix for the afternoon sampling period (B3).

	CO	NO	NO2	O3	NOX	SO2	FA	AA
CO	**1**	0.841	0.571	0.203	0.636	-0.156	0.915	0.598
NO	0.841	**1**	0.779	0.569	0.838	0.395	0.580	0.879
NO2	0.571	0.779	**1**	0.914	0.995	0.347	0.451	0.483
O3	0.203	0.569	0.914	**1**	0.884	0.579	0.056	0.377
NOX	0.636	0.838	0.995	0.884	**1**	0.358	0.492	0.559
SO2	-0.156	0.395	0.347	0.579	0.358	**1**	-0.518	0.650
FA	0.915	0.580	0.451	0.056	0.492	-0.518	**1**	0.223
AA	0.598	0.879	0.483	0.377	0.559	0.650	0.223	**1**

3.5 Principal Component Analysis (PCA)

To assess the relationships between ambient carbonyl concentrations with criteria air pollutants, a factor analysis (Principal Component Analysis: PCA) was applied. Figures 3-5 show the result of the PCA analysis in winter 2013. During the morning, two factors from the PCA were enough to explain 85.48% of the total compounds carbonyl and criteria pollutants, while in the midday and during the afternoon 2 factors were to explain the 82.36 % and 79.12 % of the total variance, respectively.

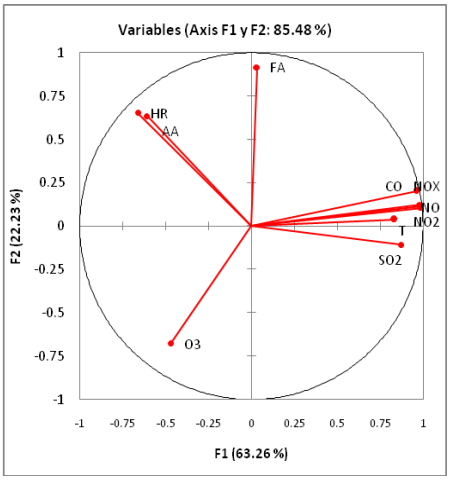

Figure 3. PCA Analysis for the morning sampling period (B1).

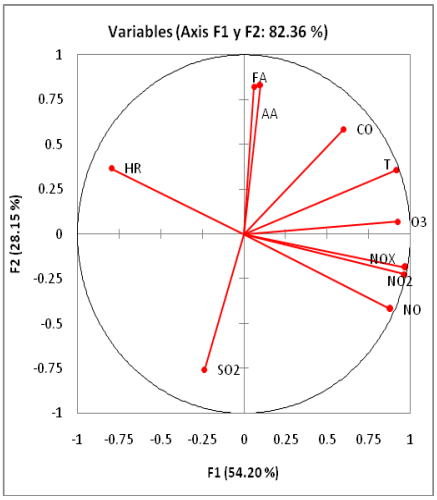

Figure 4. PCA Analysis for the midday sampling period (B2).

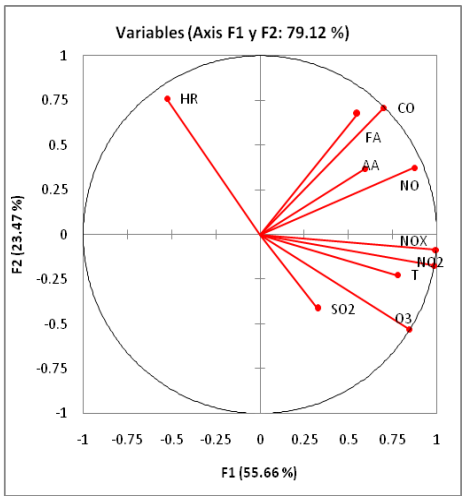

Figure 5. PCA Analysis for the midday sampling period (B2).

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It can be observed that during the studied period, FA probably had a different source than AA, whereas, NO, NO2, NOX and CO can be grouped as pollutants derived from vehicular emissions. The probable contribution of CO, NO, NO_2, NOx and FA to the ozone formation was more evident during the morning sampling period.

4 Conclusion

Carbonyl compounds measured during winter 2013 showed a strong diurnal pattern with higher concentrations for FA during the morning and decreasing during the afternoon. AA had a different behavior showing the highest levels during the afternoon and decreasing during the mornings. The most important carbonyl found in this site was formaldehyde followed by acetaldehyde. Pearson correlation analysis showed that carbonyls were influenced during the morning sampling period by vehicular emissions and incomplete combustion processes and during the afternoon, carbonyls levels could be influenced by industrial activities and high temperatures combustion processes. FA/AA ratio for this study showed values typical of urban areas. Finally, from the meteorological analysis we could observe that most of the time wind blew from WSW (from Santa Catarina municipality), where a heavy traffic avenue, a railway, electric power companies, the airport, gas-gasoline stations and some important industrial areas are located. These sources could influence the levels of carbonyls measured in this study.

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