

Measurement of Carbonyls and its relation with Criteria Pollutants (O_3 , NO, NO_2 , NO_x , CO and SO_2) in an Urban Site within the Metropolitan Area of Monterrey, in Nuevo León, México

Facundo-Torres D.M., Ramírez-Lara E., Cerón-Bretón J.G., Cerón-Bretón R.M., Gracia-Vásquez Y., Miranda-Guardiola R. And Rivera De La Rosa J.

Abstract— C_1 - C_4 carbonyls concentrations were measured at one site located within the Metropolitan Area of Monterrey (MAM) in Nuevo León México during spring and summer, 2011. Formaldehyde, acetaldehyde and acetone were found to be the most abundant carbonyls, with formaldehyde showing the highest levels during spring, while acetaldehyde was in summer. Concentrations showed a clear diurnal pattern with the highest values in the morning and decreasing during the afternoon period. Mean concentrations for formaldehyde, acetaldehyde and acetone were a 61.7 and 20.4 $\mu\text{g m}^{-3}$, 32.4 and 34.8 $\mu\text{g m}^{-3}$ and 21.1 and 26.6 $\mu\text{g m}^{-3}$, spring and summer respectively. The strong correlation between C_1 - C_2 with CO, NO and NO_2 indicated a common origin for these compounds. This was supported by a factor analysis which showed high loading on C_1 - C_2 with these criteria pollutants. The influence of local meteorological conditions and the 24 h back air masses trajectories showed that the sources contributing to the carbonyl levels were located at the NE of the sampling site where there are important industrial sources. The C_1/C_2 ratios varied from 0.72 to 1.89, which can be considered typical of an urban area. From the PCA Analysis it was evident that the carbonyls measured had mixed sources (vehicular, industrial sources and photochemical activity).

D.M. Facundo-Torres is with The Autonomous University of León, U.A.N.L., México. Chemistry Sciences Faculty. Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451. México; email: qfbmaribel@hotmail.com .

E. Ramírez-Lara is with The Autonomous University of León, U.A.N.L., México. Chemistry Sciences Faculty. Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451. México;

J.G. Cerón-Bretón is with the Autonomous University of Carmen City. Chemistry Faculty. Calle 56 No. 4 Esq. Ave. Concordia, Col. Benito Juárez, C.P. 24180, Cd. Del Carmen, Campeche, México (52-938-3826514) fax: 52-938-3826514; e-mail: jceron@ pampano.unacar.mx.

R.M. Cerón-Bretón is with the Autonomous University of Carmen City. Chemistry Faculty. Calle 56 No. 4 Esq. Ave. Concordia, Col. Benito Juárez, C.P. 24180, Cd. Del Carmen, Campeche, México; e-mail: rceron@ pampano.unacar.mx.

Y. Gracia Vásquez is with The Autonomous University of León, U.A.N.L., México. Chemistry Sciences Faculty. Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451. México.

R. Miranda Guardiola is with The Autonomous University of León, U.A.N.L., México. Chemistry Sciences Faculty. Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451. México.

J. Rivera de la Rosa is The Autonomous University of León, U.A.N.L., México. Chemistry Sciences Faculty. Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451. México.

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I. INTRODUCTION

OZONE is considered as a strong oxidant commonly present in urban areas atmosphere and it has long been a serious problem in the world. O_3 is a secondary air pollutant; so, it is not emitted directly, but formed from photochemical interactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) [1,2,3,4,5]. VOCs group includes compounds like non-methane hydrocarbons (NMHCs) and carbonyls, which are important constituents of urban atmospheres. VOCs are emitted from both anthropogenic and biogenic source. Carbonyls are sources of free radicals and precursors of carboxylic acids, O_3 and peroxyacetyl nitrates (PAN) [6], and they have received much attention for decades due to the fact that they are important precursors to photochemical smog and their possibilities of causing adverse effects health. Formaldehyde, acetaldehyde and acetone are the most important carbonyl compounds present in urban atmosphere and hydrocarbons oxidation is the main secondary source of these compounds. Carbonyls have primary sources like combustion engines, landfills, wastewater surface, petrochemical and chemical industry, steel industry and indoor pollutants [7]. Life times of formaldehyde and acetaldehyde in the troposphere are short (they have been estimated to be in the order of few hours in the summer) [8] and they can be transported over few kilometres from their origin, while acetone has a long chemical lifetime (estimated to be weeks) it possible to accumulate in the atmosphere. Some carbonyls are known to be toxic, mutagenic and/or carcinogenic [9]. Formaldehyde has been classified as carcinogenic by the IARC [10]. Ambient air concentrations of carbonyls in urban areas have been reported for several authors around the world [3,7,8]. However, in México, most of the studies about carbonyls have been focused to México City and its Metropolitan Area [11, 12, 13, 14,15,16] and very few information has been registered about other important urban and industrialized areas.

At the northeast of the country, it is located an important industrial area named Metropolitan Area of Monterrey (MAM), where important industrial activities are carried out and few studies about carbonyls in ambient air have been reported for this area [17]. The main municipality within this area is Monterrey City, which is the third largest city in México and is located in Nuevo León State (at 25°40'N latitude and 100°18'W longitude), with an average altitude of 537 m above sea level, and with an area of 580.5 km² (Fig 1).

MAM is constituted by 12 cities or municipalities (Apodaca, Escobedo, García, Guadalupe, Cadereyta, Juárez, Salinas Victoria, San Nicolás de los Garza, San Pedro Garza García, Santa Catarina, Monterrey and Santiago). This area is considered a high profile center of education, tourism and business with a population of 4 000 000 habitants with 85 % in urban area.



Fig.1. Sampling Site Location.

This study is focused on San Nicolás de los Garza located at the over the north of the MAM where industrial activities and vehicular fleet are common potential pollution sources. More than 60% of total emissions of NO_x, CO, HC and Pb are due vehicular fleet, and 92% of SO₂ emissions are due industrial activities [18]. This study reports carbonyls concentrations and its relation with criteria air pollutants (O₃, NO, NO₂, NO_x, CO and SO₂) during spring and summer-2011 in one site located within the MAM in Nuevo León.

A correlation analysis between carbonyls and criteria air pollutants was made and supported by a principal compound analysis (PCA). In addition, the influence of local meteorological conditions was studied by meteorological parameters measurements and the probable origin of carbonyls measured was inferred from the 24 h air mass trajectories calculated for the studied period using the HYSPLIT model from NOAA, in order to identify the possible sources

contributing to the carbonyl levels during the study period in this area.

II. MATERIALS AND METHODS

A. Sampling Site Location

MAM 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 Facultad de Ingeniería Mecánica y Eléctrica of the Universidad Autónoma de Nuevo León within the MAM in the municipality of San Nicolás de los Garza (25° 43' 30" N; 100° 18' 48" W) (Fig. 1). The site was located within an industrial, residential, educational and commercial area where also there are three avenues of high vehicular traffic.

B. Sampling Method

Ninety two samples were collected during spring 2011 (from March 27 to May 16) and summer 2011 (from August 08 to September 23). Formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde 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 4h intervals (day and afternoon), from 8:00 to 12:00 and from 15:00 to 19:00. An ozone scrubber was connected to the upstream end of the cartridge to avoid degradation of hydrazone derivatives [19]. Each cartridge was immediately sealed with teflon caps, then wrapped in aluminum foil and stored in the refrigerated (4 °C) before being analyzed.

C. 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 [20].

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, acetaldehyde, acetone, propionaldehyde and butyraldehyde derivatives were 0.09, 0.25, 0.78, 0.26 and 0.17 $\mu\text{g m}^{-3}$, respectively, according to Miller and Miller [21] 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.

D. 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 27 to May 16, 2011 (spring) and from August 08 to September 23, 2011 (summer), using a portable meteorological station model Davis Vantage Pro II and wind roses were constructed for each day using the software WRPLOT (Lakes Environmental) [22].

24 hr back air masses trajectories were calculated for the studied period using HYSPLIT model from the NOAA (National Oceanic Administration Agency, USA) [23] 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 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.

E. 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 [24].

III. RESULTS AND DISCUSSION

A. Diurnal Variation and meteorological influence

Ambient concentrations of carbonyl C_1 – C_4 were measured in 92 samples from spring (March 27 to May 16) and summer 2011 (August 08 to September 23). Formaldehyde (FA) was the most abundant carbonyl, followed by acetaldehyde (AA) and acetone (ACE).

The concentration of propionaldehyde and butyraldehyde were below of the detection limit. Diurnal variation of the carbonyls concentrations are shown in Tables I and II.

Table I. Concentrations of carbonyl compounds ($\mu\text{g m}^{-3}$) at MAM in spring 2011.

| Carbonyl | Mean Concentrations | Mean Concentrations |
|--------------|---------------------|---------------------|
| | Morning | Afternoon |
| Formaldehyde | 75.4± 33.2 | 47.6±15.3 |
| Acetaldehyde | 39.9 ± 52.3 | 27.3±44.5 |
| Acetone | 24.2 ±12.1 | 16.1 ±8.2 |

Table II. Concentrations of carbonyl compounds ($\mu\text{g m}^{-3}$) at MAM in summer 2011.

| Carbonyl | Mean Concentrations | Mean Concentrations |
|--------------|---------------------|---------------------|
| | Morning | Afternoon |
| Formaldehyde | 26.8± 16.5 | 13.9±5.90 |
| Acetaldehyde | 34.4 ± 26.7 | 35.1±53.9 |
| Acetone | 30.0 ±12.9 | 23.4 ±9.2 |

Higher concentrations were observed in the morning, in spring, formaldehyde had the highest average concentration whit 75.4 $\mu\text{g m}^{-3}$, while in summer was acetaldehyde whit 34.4 $\mu\text{g m}^{-3}$ and acetone shown an increase during the summer, these levels probably due to higher traffic volumes and industrial activity around the sampling site. Motor vehicles exhaust is expected to be most important source of carbonyls in cities [25].

Low levels of carbonyls during the afternoon were probably due to photolysis and reactions with OH radicals [26]. Comparing with other sites, the carbonyl levels are higher than those reported in Shanghai [26], México City [16], and Bangkok [27].

Fig. 2 shows the ambient mixing ratio of carbonyl measured at MAM during spring and summer, 2011. Formaldehyde was the most abundant carbonyl in ambient air during spring, the presence of forests fires and road surfacing near the sampling site possibly influenced at high concentrations of formaldehyde during this season. Acetaldehyde presented a slight increase in the concentration during the summer.

There was an episode with a maximum concentration for acetaldehyde of 268.8 $\mu\text{g m}^{-3}$, observed during a rainy day characterized by a high traffic intensity condition, favoring acetaldehyde production. During the same day, formaldehyde concentrations showed a minimum value of 4.80 $\mu\text{g m}^{-3}$ probably due to the fact that formaldehyde is more soluble in water than acetaldehyde, and for this reason, HCHO is incorporated into clouds and rain in a greater degree than

acetaldehyde [28]. Other factors influencing carbonyls concentration were variability and intensity of emission sources.

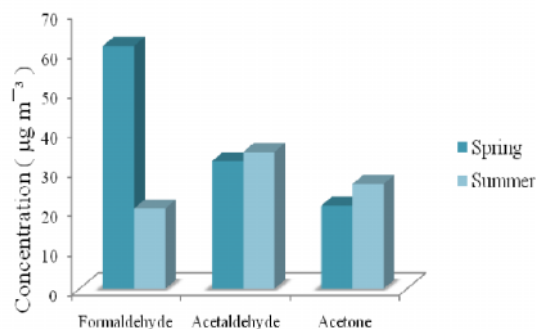


Fig. 2. Average concentration of carbonyls compounds in MAM

B. Carbonyls, criteria pollutants and meteorological conditions

The measurement period was characterized by clear skies, warm weather and absence of precipitation during the spring. During summer, in August 26th, an event of precipitation was observed. In MAM, during spring, the temperature was ranged from 16 to 41 °C, the relative humidity varied from 4.7 to 91 %; and during summer, temperatures varied from 21.6 to 38.0 °C, and the relative humidity varied from 14 to 84 %. For both seasonal periods, the range of wind speed was from 0.0 to 5.9 m s⁻¹. During spring the winds prevailing direction was from East-Northeast (27 %) and during summer wind was blowing from East (48 %) most of the time. 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). May 16 th was a day peak for carbonyl compounds, in the morning (FA: 35.5 µg m⁻³ y AA: 192.8 µg m⁻³) with prevailing winds from E-NE (low speed: 0.0 -1.3 m s⁻¹). These wind conditions probably contributed to increase the carbonyls concentration in the site. During afternoon, wind speed increased (1.3 - 3.1 m s⁻¹) and blew from East, helping to the dispersion of pollutants from the area which is highly industrial (Fig. 3). Relative humidity were high (average: 87.3 %) and the temperature varied between 17.3 to 21.6 °C. Lü et al., 2010 [29] reported that relative higher humidity might favors urban photochemistry and it could probably be the reason of carbonyl compounds concentrations increases.

Summer conditions were similar to the spring, the highest total concentration was observed at August 26th (481.2 µg m⁻³), high humidity, low winds speed during the morning, increased in the afternoon, prevailing northeast winds and temperature between 24.2 to 28.1 °C. The criteria contaminants (CO, NO and NO₂) shown high values at early morning and late afternoon, while the ozone concentration always peak at 12:00 to 14:00 h in the afternoon (Fig. 4 and

Fig. 5). During the morning, heavy traffic intensity and congestion accompanied with low winds speed increased the concentration of CO, NO and NO₂, while in the midday low concentrations were observed. Khoder, 2009 [30] reported that lower concentrations of NO and NO₂ during midday could be due to the high dispersion and high dilution conditions under the effect of high temperature.

Concentrations of ozone increase in the midday due high temperatures and higher solar radiation favoring photochemical reactions resulting in higher levels of ozone. Levels of SO₂ presented a slight increase (spring day average: 7.32 ppb; summer day average: 4.09 ppb) during the afternoon in both periods of sampling (spring afternoon average: 7.73 ppb; summer afternoon average: 4.51), these concentrations were influenced by wind direction, higher concentrations were observed when the winds blew from E and NE.

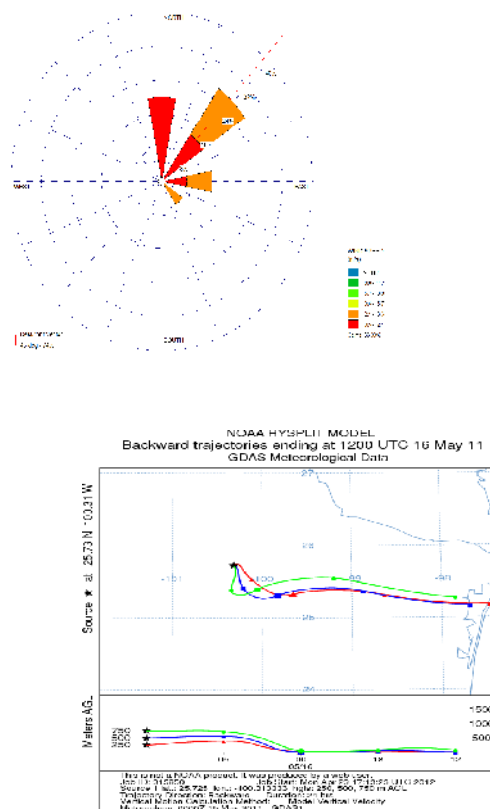


Figure 3. Wind rose plot and 24 h back air mass trajectory for May 16 in the MAM.

C. Formaldehyde/Acetaldehyde ratio

Table III 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 [31]. A high FA/AA ratio may reflect the local generation of natural reactive hydrocarbons, whose oxidation yields more formaldehyde than acetaldehyde [26]. In this study, the average FA/AA concentration ratio was 1.89 in spring, which is higher, than the studies reported in Guangzhou, China 0.97 [29], Athens, Greece 1.27 [32], Shanghai, China 1.58 [33] and Mexico City (range = 0.77 –

1.19) [15]. During summer concentration ratio was 0.72, Martinis and collaborators [34] reported FA/AA ratio was 0.63 in Brazil, using fuels containing ethanol. Our values can be considered within the range of values for urban areas.

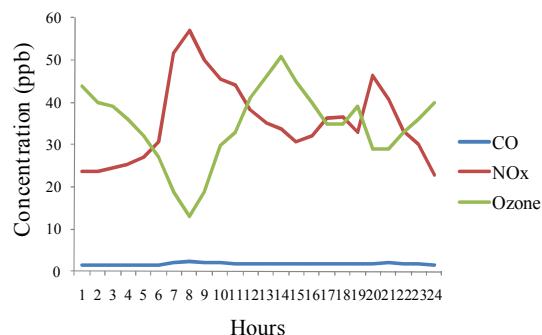


Figure 4. Diurnal variation in CO, NO_x and O₃ concentrations during the spring (May 16, 2011).

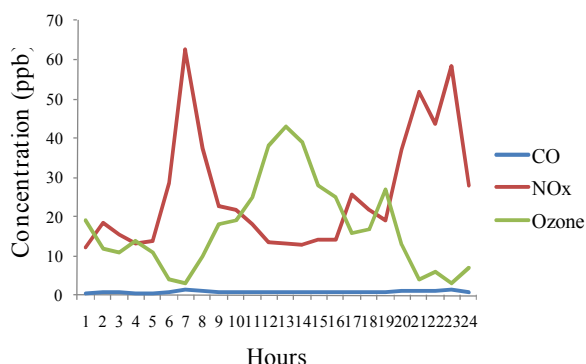


Figure 5. Diurnal variation in CO, NO_x and O₃ concentrations during the summer (August 26, 2011).

Table III. Diurnal variation of FA/AA ratio.

| | | Mean Value FA/AA ratio | | |
|-------|--------|------------------------------|--------------------------------|---------|
| | | Morning 08:00- 12:00 h | Afternoon 15:00- 19:00 h | Average |
| FA/AA | Spring | 2.05 | 1.74 | 1.895 |
| | Summer | 0.84 | 0.59 | 0.72 |

Note: FA: Fomaldehyde; AA: Acetaldehyde

D. Role of carbonyls in the photochemical reactivities and O₃ formation

Carbonyl compounds are common constituents of urban atmospheres [15] and they have received attention due to the fact that they are ozone. Ozone is formed from photochemical interaction of volatile organic compounds and oxides of nitrogen (NO_x) [6]. To estimate the photochemical production

of ozone from carbonyl compounds reaction whit OH radicals and production potential of O₃, the propene-equivalent and the Maxima Incremental Reactivity (MIR) are calculated [6,35]. The propene-equivalent of specie (j) is defined as:

$$\text{Prop-Equiv} = \text{Conc. (j)} \times K_{\text{OH}}(\text{j}) / K_{\text{OH}}(\text{propene})$$

Where Conc. (j) is the concentration of specie (j) expressed in $\mu\text{g m}^{-3}$, $K_{\text{OH}}(\text{j})$ and $K_{\text{OH}}(\text{propene})$ are rate constant for the reaction between specie j or propene and OH. Prop-Equiv (j) is measure of the concentration of specie j on an OH-reactivity-based scale normalized to the reactivity of propene, the MIR coefficient (dimensionless, gram of ozone produced per gram of specie j) [6]. Aldehydes, specially acetaldehyde and formaldehyde have high potential of ozone formation and have great influence on ozone levels in urban atmosphere [32]. Tables IV and V show that acetaldehyde was the main contributor to the Prop-Equiv concentration followed by formaldehyde and acetone.

Table IV. OH reactivity of carbonyls.

| Carbonyl | $10^{12} \times K_{\text{OH}}^*$ | ppbC | | Prop-Equiv | |
|----------|----------------------------------|--------|--------|------------|--------|
| | | spring | summer | spring | summer |
| FA | 9.37 | 50.3 | 16.6 | 17.9 | 5.92 |
| AA | 15.0 | 36.0 | 41.4 | 20.5 | 23.6 |
| ACE | 0.17 | 26.6 | 33.7 | 0.17 | 0.22 |

*Rate constant of carbonyl compound react with OH at 298 K ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)

Table V. Estimated average values of ozone production from carbonyl compounds.

| Carbonyl | MIR* | $\mu\text{g/m}^3$ | | Ozone formation ($\mu\text{g/m}^3$) | |
|----------|------|-------------------|--------|--|--------|
| | | spring | summer | spring | summer |
| FA | 8.80 | 61.7 | 20.4 | 542.96 | 179.4 |
| AA | 5.50 | 32.3 | 34.8 | 177.65 | 191.2 |
| ACE | 0.56 | 21.1 | 26.6 | 11.8 | 14.9 |

* MIR denote maximum incremental reactivity (gO_3/gVOCs)

During spring, ozone formation was more influenced by formaldehyde while during summer, acetaldehyde contributed in a major degree to ozone formation. Values obtained for Ozone formation potential were higher than cities like Guangzhou, China [29], but were lower than those reported for Beijing, China during an ozone episode [6].

E. Correlation of carbonyl compounds with criteria pollutants

Pearson correlation was applied in order to know the correlation between carbonyls concentration with criteria pollutants. In spring, during the morning, formaldehyde and

CO showed a high correlation ($r = 0.858$) ($p < 0.05$), which indicates that the formaldehyde was probably emitted from vehicular sources. Morknoy and collaborators [27] reported good correlations between formaldehyde-CO ($r = 0.796$), this relations indicate a strong influence of vehicular sources. Formaldehyde - NO₂ correlations were good ($r = 0.743$) ($p < 0.05$), indicating that these compounds had sources in common, probably combustions process at high temperatures.

In the afternoon, formaldehyde showed a high correlation with SO₂ ($r = 0.761$) ($p < 0.05$), which is a common tracer of industrial activities, indicating that formaldehyde in this period was influenced by industrial sources. Acetaldehyde showed a moderate negative correlation ($r = -0.474$) ($p < 0.05$), with O₃ indicating that probably this carbonyl contributed to O₃ formation during this period. Acetone showed for both sampling periods (morning and afternoon) low correlations with criteria pollutants. During summer, formaldehyde-acetone and formaldehyde-acetaldehyde showed good correlations ($r = 0.665$; $r = 0.600$, respectively) ($p < 0.05$) indicating that these compounds probably had common sources. Acetone-CO correlation was good ($r = 0.629$) ($p < 0.05$), indicating that vehicular traffic could influence the levels of this carbonyl during the morning. In the afternoon, acetone-O₃ showed a good correlation ($r = 0.512$) ($p < 0.05$), which indicate that this carbonyl could be originated from photochemical reactions. Low correlations among carbonyls compounds and criteria pollutants were probably due to strong variability and intensity of the sources, photochemical reactions and meteorological conditions.

F. 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. Table VI and Table VII show the result of the PCA analysis in spring. During the morning, two factors from the PCA were enough to explain 60.6 % of the total compounds carbonyl and criteria pollutants, while in the afternoon three factors were required to explain the 84.8 % of the total variance.

The first principal component was identified to account 35.3 % (morning) of the total variance, this included formaldehyde, acetone, CO, NO₂ and SO₂. This factor indicates that probably formaldehyde and acetone were related to CO and NO₂ due to the influence of vehicular exhaust and incomplete combustion processes. These carbonyls had mixed sources and were related to SO₂, which is emitted mainly from industrial activities.

Table 6. Factor loading estimated by PCA during the B1 sampling period (8:00 to 12:00 h)

| Air Pollutants | F1 | F2 |
|----------------|--------------|--------|
| FA | 0.891 | -0.276 |

| | | |
|--------------------|--------------|--------------|
| AA | -0.300 | 0.084 |
| ACE | 0.569 | 0.329 |
| CO | 0.781 | -0.471 |
| SO ₂ | 0.690 | 0.267 |
| NO | 0.067 | 0.985 |
| NO ₂ | 0.808 | -0.135 |
| NO _x | 0.403 | 0.881 |
| O ₃ | 0.245 | -0.187 |
| Initial Eigenvalue | 3.174 | 2.285 |
| % Variance | 35.262 | 25.390 |
| Cumulative % | 35.262 | 60.652 |

Table VII. Factor loading estimated by PCA during the B1 sampling period (15:00 to 19:00 h)

| Air Pollutants | F1 | F2 | F3 |
|--------------------|---------------|--------------|--------------|
| FA | -0.522 | 0.646 | 0.230 |
| AA | 0.270 | -0.453 | 0.661 |
| CO | -0.789 | -0.288 | 0.446 |
| SO ₂ | -0.802 | 0.491 | 0.127 |
| NO | 0.848 | 0.511 | 0.035 |
| NO ₂ | 0.102 | 0.355 | 0.847 |
| NO _x | 0.815 | 0.542 | 0.174 |
| O ₃ | -0.446 | 0.638 | -0.307 |
| Initial Eigenvalue | 3.204 | 2.035 | 1.548 |
| % Variance | 40.044 | 25.440 | 19.347 |
| Cumulative % | 40.044 | 65.484 | 84.831 |

In factor 2, during the morning, high loadings were obtained for NO and NO_x, this factor explained 25.4 %, and these factors represented 40 % of total variance. Formaldehyde, NO, NO_x and O₃ (Factor 2) represented 25.4 % of the variance during the afternoon; this results suggest that formaldehyde and NO_x interacting photochemically to produce ozone, it means that the sampling site was sensitive to the O₃ formation in both trajectories (COV's and NO_x). Factor 3 showed a moderate loading on acetaldehyde and NO₂ (19.3 % of the variance), indicating that probably the carbonyl formation was due to high temperatures combustion processes.

In summer, two PCA factor was enough to explain 70.7 % (Table VIII) of the total variance of carbonyl compounds and criteria pollutants. Factor 1 are integrated by acetone, NO_x and CO which indicates that there are emitted by vehicular emissions. Ozone and SO₂ (Factor 2) represented 30.2. % of the variance, this results suggest that SO₂ interacting photochemically to produce ozone.

Table VIII. Factor loading estimated by PCA during the B2 sampling period (8:00 to 12:00 h)

| Air Pollutants | F1 | F2 |
|--------------------|--------------|--------------|
| FA | 0.388 | -0.770 |
| AA | -0.018 | -0.686 |
| ACE | 0.617 | -0.350 |
| CO | 0.633 | -0.393 |
| SO ₂ | 0.187 | 0.899 |
| NO | 0.893 | -0.147 |
| NO ₂ | 0.884 | 0.320 |
| NO _x | 0.941 | 0.139 |
| O ₃ | 0.457 | 0.657 |
| Initial Eigenvalue | 3.641 | 2.724 |
| % Variance | 40.457 | 30.263 |
| Cumulative % | 40.457 | 70.721 |

Table IX. Factor loading estimated by PCA during the B2 sampling period (15:00 to 19:00 h)

| Air Pollutants | F1 | F2 |
|--------------------|--------------|--------------|
| FA | 0.768 | 0.502 |
| AA | -0.171 | -0.418 |
| ACE | 0.867 | 0.276 |
| CO | -0.072 | 0.891 |
| SO ₂ | 0.282 | -0.671 |
| NO | -0.066 | -0.131 |
| NO ₂ | 0.846 | -0.400 |
| NO _x | 0.809 | -0.420 |
| O ₃ | 0.519 | 0.436 |
| Initial Eigenvalue | 3.099 | 2.291 |
| % Variance | 34.437 | 25.459 |
| Cumulative % | 34.437 | 59.896 |

Table IX shows that during the afternoon two factors were required to explain the 59.9 % of the total variance. The first principal component was identified to account 34.4 % of the total variance, this included formaldehyde, acetone, NO, NO₂ and O₃, indicating that these carbonyls probably had their origins from photochemical reactions derived from an intense atmospheric chemistry. Formaldehyde and CO integrated a second factor with 25.5 % of total variance, indicating that this carbonyl could be produced from vehicular sources.

IV. CONCLUSION

Carbonyl compounds measured during spring and summer 2011 showed a strong diurnal pattern with higher concentrations during the morning and decreasing during the

afternoon. 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. During the spring, in the afternoon, formaldehyde and NO_x could interact photochemically to produce O₃, while in summer formaldehyde and acetone were probably originated from photochemical reactions. All these conclusions could be supported by the PCA analysis. FA/AA ratio for this study showed values typical of urban areas. Finally, we can conclude that this site was sensitive to the O₃ formation in both trajectories (COV's and NO_x) and carbonyl compounds had mixed sources. From the meteorological analysis we could observe that most of the time wind blowed from NE (from Apodaca municipality), where some important industrial areas are located. These sources could influence the levels of carbonyls measured in this study.

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Facundo-Torres D.M. Is currently finishing PhD studies on Sustainable Process in the Autonomous University of Nuevo León in Monterrey, México. She has carried out several studies focused on atmospheric pollution specially on atmospheric deposition measurement and analysis and organic volatile compounds in ambient air.

Ramírez- Lara E. Is Professor Researcher of the Chemistry Faculty of the Autonomous University of Nuevo León in Monterrey, Nuevo León, México. She has carried out several research projects on characterization of atmospheric deposition (dry and wet) and the trends of criteria pollutants and organic volatile compounds (carbonyls and aromatic hydrocarbons) in ambient air.

Cerón-Bretón J.G. Is a professor-researcher in the Chemistry Faculty of the Autonomous University of Carmen City since 2006, has a PhD degree in Earth Sciences from the Autonomous National University of México (UNAM) in 2005. She was carried out several projects on air pollution and its effects on ecosystems and she is author of numerous papers published in refereed journals dealing with the environment, air pollution and earth sciences areas. Dr. Cerón is a membership of the National System of Researchers of México named as Researcher level I since 2007 and she is the leader of the Academic Group in Chemical Engineering of the Chemistry Faculty in UNACAR.

Cerón-Bretón R.M. Is a professor-researcher in the Chemistry Faculty of the Autonomous University of Carmen City since 2002, has a PhD degree in Earth Sciences from the Autonomous National University of México (UNAM) in 2004. She was carried out several projects on air pollution and its effects on ecosystems and she is author of numerous papers published in refereed journals dealing with the environment, air pollution and earth sciences areas. Dr. Cerón is a membership of the National System of Researchers of México named as Researcher level I since 2006.

Gracia Vázquez Y. Is currently Postgrade Coordinator and Professor Researcher of the Chemistry Faculty of the Autonomous University of Nuevo León in Monterrey, Nuevo León, México. She has carried out several research projects on environmental pollution.

Miranda-Guardiola R. Is currently Professor Researcher of the Chemistry Faculty of the Autonomous University of Nuevo León in Monterrey, Nuevo León, México. She has carried out several research projects on environmental pollution.

Rivera de la Rosa, J. Is currently Professor Researcher of the Chemistry Faculty of the Autonomous University of Nuevo León in Monterrey, Nuevo León, México. She has carried out several research projects on environmental pollution.