Seasonal and diurnal variations of carbonyl compounds and air criteria pollutants in Monterrey, Mexico

CERÓN-BRETÓN J.G.[1] AND CERÓN-BRETÓN, R.M.[1]
[1]Research Center on Environmental Sciences (CICA)
Autonomous University of Carmen (UNACAR)
Av. Abasolo s/n Col, Renovación, 2da. Sección, C.P. 24180, Ciudad del Carmen, Campeche
MEXICO
jceron@pampano.unacar.mx http://www.unacar.mx

Abstract: - Carbonyl compounds levels (formaldehyde and acetaldehyde) were measured in an urban site located in Monterrey Mexico using an active sampling during winter and spring, 2013. A total of 39 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). CO, O_3, NO, NO_2, NOx, and SO_2 were measured by automatic analyzers during the sampling period. Formaldehyde was found to be the most abundant carbonyl. Both carbonyls showed clear diurnal and seasonal patterns. Formaldehyde mean concentrations were 35.74 + 4.37, and 33.67 + 3.92 for spring and winter, respectively. Whereas, acetaldehyde mean concentrations were 25.68 + 2.18, and 28.31 +7.91 for spring and autumn, respectively. Levels of carbonyls were higher when wind blew from WSW, where heavy traffic avenues, a railway and electric power companies are located. These sources could influence the levels of carbonyls measured in this study.

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

1 Introduction

Carbonyl compounds are key components of photo chemically generated air pollution [1-2]. These compounds have both, primary sources (directly emitted) and secondary sources (formed from photochemical reactions in the atmosphere). The main primary sources of carbonyls include motor vehicles exhaust, burning biomass, industrial activities and area sources. Other important characteristic is that carbonyl compounds play an important role in atmospheric chemistry due to their participation in photochemical air pollution constituting photo-oxidation products of gas-phase hydrocarbons in sunlight [3-6]. As they are the major source of free radicals in the troposphere, they are the main ozone; peroxyacyl nitrates (PANs) and secondary organic aerosols (SOA) precursors [7].

Considering the important roles of carbonyls in atmospheric chemistry, and their negative impact on human health (some carbonyls such as formaldehyde, acetaldehyde and acrolein are suspected to be carcinogenic and mutagenic to humans [8]), the concentration of atmospheric carbonyls and their variability can be an effective indicator reflecting the status of local photochemical activity and air pollution.

In Mexico, standard values for formaldehyde and acetaldehyde concentrations have not been established, therefore, monitoring of their levels in the ambient air is of fundamental importance in assessing their role in photochemical activity and it may help in the development of local control strategies for these pollutants and tropospheric ozone.

Even many investigations about carbonyls levels have been conducted in some cities in Mexico [10-12], there are not still enough reports about theses pollutants in sites located at the northeast of the country. Most of the studies have been focused on the central part of Mexico and there is not enough information about other big cities like Monterrey, Nuevo Leon [27-31]. Monterrey is known to be 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 km2 and it is located within the Metropolitan Area of Monterrey (MAM).

In this study, the major objective was to recognize the pollution levels of carbonyls in an urban site located in Monterrey, Nuevo Leon, Mexico. In addition, we investigated the relations

among carbonyl compounds and other criteria air pollutants and meteorological parameters using a principal component analysis (PCA) in order to try to infer their possible sources.

2 Methodology

2.1 Sampling Site Location

Monterrey is the most populated city in Nuevo León State. In 2010, it was reported a population of 1, 135, 512 inhabitants for this municipality. This city is one of the most developed urban areas in Mexico being a business, industrial and economic center. Monterrey has a semi-arid warm climate (Bsh) according to the Köppen climatic classification modified by García [9]. 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. 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 Monterrey (25° 43' 30" N; 100° 18' 48" 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.

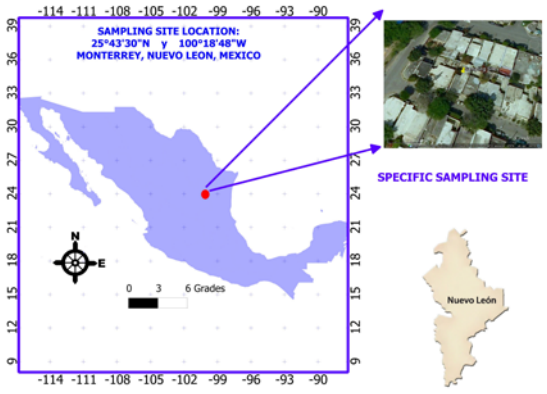


Figure 1. Sampling Site Location.

2.2 Sampling Method

A total of 39 samples were collected during winter 2013 (from March 4 to March 12) and spring 2013 (from April 26 to May 17). Formaldehyde (FA), and acetaldehyde (AA) were measured in ambient air. Samples of air were collected with 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 [13]. 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 [14]. 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 FA and AA were 0.09, and 0.25 µg m-3, respectively, according to Miller and Miller [15] 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 the 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) and from April 26 to May 17, 2013 (spring) using a portable meteorological station model Davis Vantage Pro II and wind roses were constructed for each day using the software WRPLOT (Lakes Environmental) [16].
24 hr back air masses trajectories were calculated for the studied period using HYSPLIT model from the NOAA (National Oceanic Administration

Agency, USA) [17] 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.

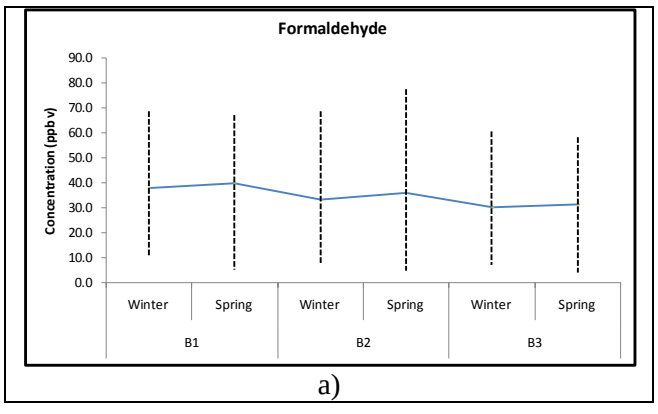
2.5 Correlation and Principal Component Analysis (PCA)

Spearman rank was applied to all data collected at the sampling site. A Principal Component Analysis (PCA) was applied in order to assess the relationships among carbonyls concentrations, meteorological parameters and criteria air pollutants using the XLSTAT software [18].

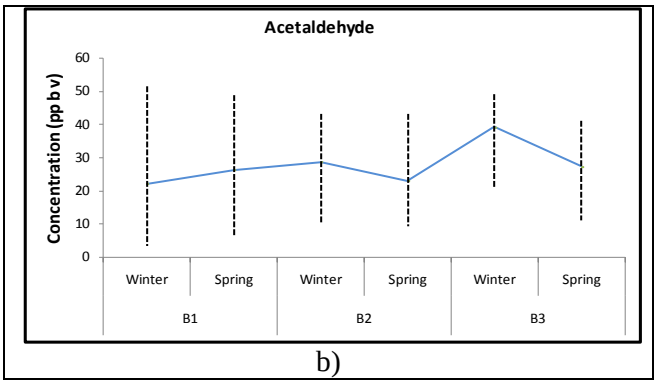
3 Results

3.1 Diurnal Variation

Ambient concentrations of carbonyl C_1 –C_2 were measured in eighteen samples during winter 2013 (from March 4 to March 12) and in twenty one samples during spring 2013 (from April 26 to May 17). Formaldehyde (FA) was the most abundant carbonyl, followed by acetaldehyde (AA). 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 Fig. 2.



a)



b)

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 clear diurnal and seasonal patterns. During winter, the highest FA mean concentrations were found in the morning sampling period (B1) followed by the midday sampling period (B2) and having the lowest levels during the afternoon sampling period (B3). AA had the highest mean levels during the afternoons in winter season (B3), decreasing during the midday (B2) and having the lowest values of concentrations during the mornings (B1). On the other hand, during the spring season, FA had the same behavior than that showed during the winter season. AA meanwhile presented the highest values during the afternoon sampling period (B3) and the lowest concentrations during the midday (B2). 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 FA during the afternoon were probably due to photolysis and reactions with OH radicals [19]. Mean concentrations for AA were higher during the winter. Since photochemical activity decreases during winter time, it seems to be that the main source of this carbonyl was vehicular exhaust emissions. Comparing with other sites, the carbonyl levels are higher than those reported in Shanghai [19], México City [12], and Bangkok [20].

3.2 Meteorological influence

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).

During winter 2013, the wind prevailing direction was from WSW most of the time (60 %). 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. 3.

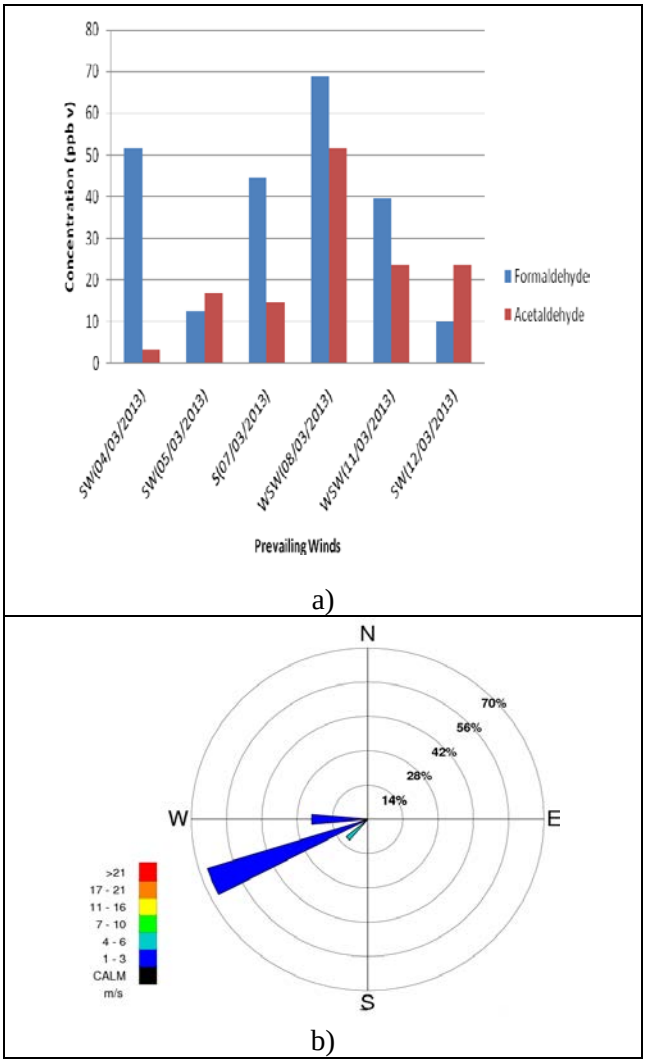


Figure 3. Meteorological influence on carbonyl levels (a) and a wind rose for an air pollution episode in March 8, 2013(b).

During spring 2013, the wind prevailing direction was from SW most of the time (65%). In April 26 there was a peak for FA (67.09 ppbv) during the morning sampling when wind blew from W (1-3 m/s). The highest concentrations for both carbonyls were found when the wind was blowing from SW. There was an air pollution episode in April 29 when wind blew from SW with concentration values of 58.29 ppbv for FA (during B1 sampling period) and 48.8 ppbv, 43.03 ppbv and 41.07 ppbv for AA during the B1, B2, and B3, sampling periods, respectively. Wind roses for air pollution episodes during spring 2013 are presented in Fig. 4.

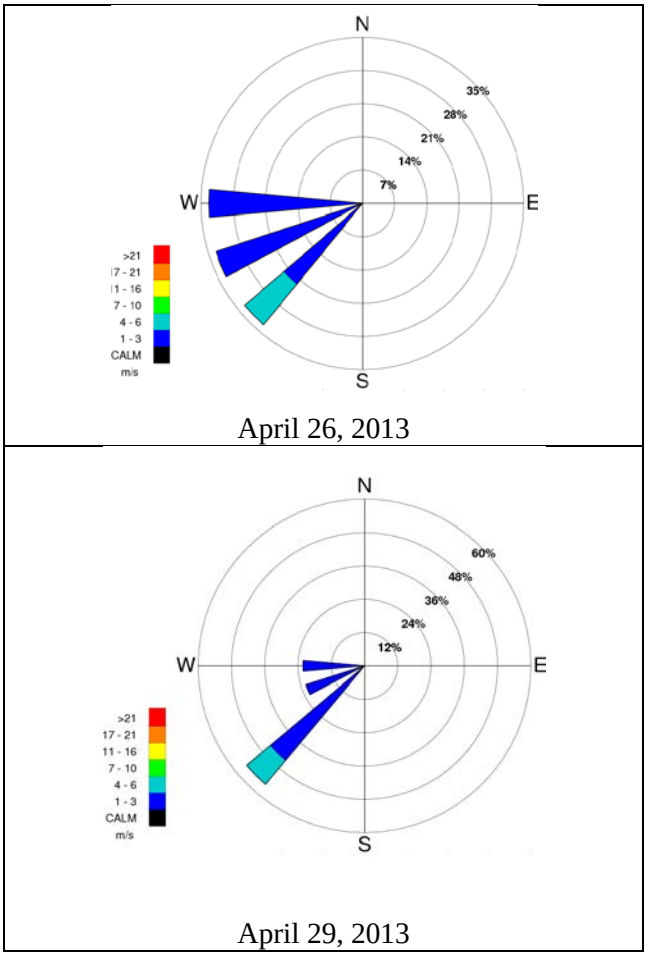


Figure 4. Wind roses for air pollution episodes during spring season.

A heavy traffic avenue, a railway and electric power companies and Santa Catarina municipality are located at SW of the sampling site. Therefore, sources located in this direction could influence carbonyl levels.

3.3 Criteria Air Pollutants Levels

Levels of NO, NO_2, NOx, O_3 and SO_2 expressed as ppb can be observed in Fig. 5. Even all criteria air pollutants were lower than maximum permissible values established by the Mexican Standards, it can be observed that ozone levels were the highest observed during the studied period. Levels of NO, NO_2, NOx, O_3 and SO_2 expressed as ppb can be

observed in Fig. 5. Whereas, CO concentrations expressed in ppm can be observed in Fig. 6.

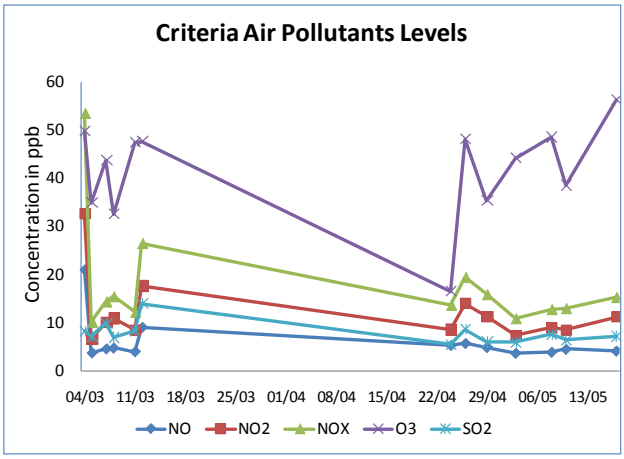


Figure 5. Levels of NO, NO_2, NO_x, O_3 and SO_2 during the whole sampling period.

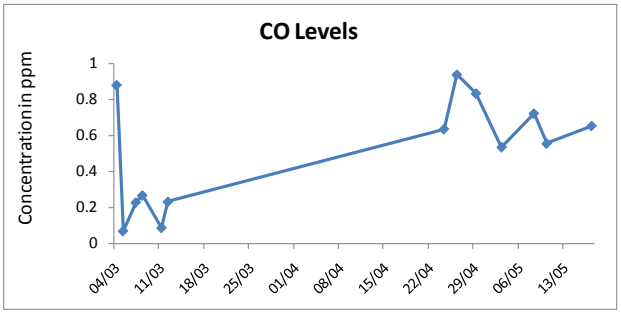


Figure 6. Levels of CO during the whole sampling period.

3.4 Formaldehyde/Acetaldehyde 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 **[**19]. Tables 1 and 2 show formaldehyde and acetaldehyde (FA/AA) ratios for winter and spring season, respectively. In this study, the average FA/AA concentration ratio was 1.87, which is higher, than the studies reported in Guangzhou, China 0.97 [22], Athens, Greece 1.27 [3], Shanghai, China 1.58 [23] and Mexico City (range = 0.77–1.19) [11]. Our values can be considered within the range of values for urban areas.

Table 1. Formaldehyde/Acetaldehyde ratio for winter season

FA/AA RATIO		
B1 (09:00-11:00 h)	B2 (12:00-14:00 H)	B3 (15:00-17:00 H)
4.05	1.47	6.66

Table 2. Formaldehyde/Acetaldehyde ratio for spring season

FA/AA RATIO		
B1 (09:00-11:00 h)	B2 (12:00-14:00 H)	B3 (15:00-17:00 H)
4.73	1.32	0.66

3.5 Correlation of carbonyls with criteria air pollutants and meteorological parameters

To investigate the factors affecting the carbonyls levels in the study area, correlation analysis was carried out using air quality data. The air quality data of criteria pollutants as SO_2, NO, NO_2, NOx, O_3 and CO were obtained from the SIMA air monitoring network. The results of correlation analysis (AS Pearson coefficients) are shown in Tables 3-5 and 6-8, for winter and spring seasons, respectively.

Table 3. Pearson correlation matrix for the morning sampling period (B1): Winter season.

	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**

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 CO, NO, NO_2, NO_x and FA, indicating that all these compounds could act as ozone precursors. AA showed moderate negative correlations with CO, NO, NO_2, NO_x and $_{SO2}$, indicating that this carbonyl had an important participation in the secondary pollutants formation.

Table 4. Pearson correlation matrix for the midday sampling period (B2): Winter season.

	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 the midday and afternoon sampling periods (B2 and B3) a good correlation between CO and FA was found. Morknoy and collaborators [20] 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 moderate (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 NO_x had a good correlation indicating that all these compounds could be originated in common sources (combustion of fossil fuel). FA and AA had different sources (r = 0.390). A good correlation between FA and CO indicated that FA was produced primarily from vehicular exhaust. Whereas, a good correlation between AA and SO_2 (r = 0.965) indicated that this carbonyl was more associated to industrial emissions. During the afternoon sampling period (Table 5), FA and AA correlated positively in a significant way with CO, NO, NO_x 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 5. Pearson correlation matrix for the afternoon sampling period (B3): Winter season.

	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**

During the morning sampling period in spring season (B1), high correlations among CO, NO, NO_2, NO_x and SO_2 were found indicating that these pollutants were largely associated to combustion related sources (Table 6). High negative correlations between FA and O3 and AA and O_3 were found (r = - 0.818 and r = -0.939, respectively). These results are evidence that both measured carbonyls contributed in a significant way to the instantaneous production rate of O_3. Both carbonyls had a good correlation between each other and they did not present a good correlation with air pollutants associated to vehicular emissions. Therefore, they probably were associated with fugitive emissions instead of combustion related sources during this period.

Table 6. Pearson correlation matrix for the morning sampling period (B1): Spring season.

	CO	NO	NO2	NOX	O3	SO2	FA	AA
CO	**1**	**0.926**	**0.868**	**0.928**	0.010	**0.602**	0.420	0.260
NO	**0.926**	**1**	**0.788**	**0.896**	-0.057	**0.795**	**0.570**	0.319
NO2	**0.868**	**0.788**	**1**	**0.979**	0.414	**0.490**	-0.009	-0.151
NOX	**0.928**	**0.896**	**0.979**	**1**	0.288	**0.621**	0.176	-0.012
O3	0.010	-0.057	0.414	0.288	**1**	0.159	**-0.818**	**-0.939**
SO2	**0.602**	**0.795**	0.490	**0.621**	0.159	**1**	0.423	0.056
FA	0.420	**0.570**	-0.009	0.176	**-0.818**	0.423	**1**	**0.892**
AA	0.260	0.319	-0.151	-0.012	**-0.939**	0.056	**0.892**	**1**

Table 7. Pearson correlation matrix for the midday sampling period (B2): Spring season.

	CO	NO	NO2	NOX	O3	SO2	FA	AA
CO	**1**	-0.027	**0.888**	**0.849**	0.384	0.284	0.236	0.132
NO	-0.027	**1**	-0.040	0.255	**-0.853**	**-0.683**	0.154	0.364
NO2	**0.888**	-0.040	**1**	**0.956**	**0.502**	0.306	-0.139	0.317
NOX	**0.849**	0.255	**0.956**	**1**	0.238	0.099	-0.093	0.416
O3	0.384	**-0.853**	**0.502**	0.238	**1**	**0.840**	-0.196	-0.227
SO2	0.284	**-0.683**	0.306	0.099	**0.840**	**1**	0.199	**-0.553**
FA	0.236	0.154	-0.139	-0.093	-0.196	0.199	**1**	**-0.721**
AA	0.132	0.364	0.317	0.416	-0.227	-0.553	**-0.721**	**1**

In Table 7 it can be observed a good correlation among CO, NO_2 and NO_x (vehicle exhaust emissions). A strong negative correlation between O_3 and NO may be an evidence of large NO emissions in the vicinity having as a result the net conversion of O_3 to NO_2 according to the following reaction[25-26]:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

Ozone formation through photolysis of NO_2 during the midday sampling period in spring season was evidenced by a moderate correlation between O_3 and NO_2 (r = 0.502) according to the following reaction [25-26]:

$$NO_2 + hv \rightarrow NO + O \quad (2)$$
$$O + O_2 + M \rightarrow O_3 + M \quad (3)$$

AA correlated in negatively with FA (r = -0.721), indicating that FA was probably produced in secondary way from photolysis of AA according to the following reaction:

$$CH_3CHO \rightarrow CH_3 + HCO \quad (4)$$

During the afternoon sampling period in spring season, CO correlated positively with NO_2 and NO_x (Table 8), indicating that they probably had common sources (combustion related sources). CO correlated negatively in a moderate way with O_3 (r = -0.517) indicating that CO could act as ozone precursor according to the following reaction [25-26]:

$$CO + OH \xrightarrow{O2} HO_2+O_2 \quad (5)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (6)$$
$$NO_2 + hv \rightarrow NO + O \quad (7)$$
$$O + O_2 + M \rightarrow O_3 + M \quad (8)$$

NO_x was negatively correlated with O_3 (r = -0.868) being evidence that this pollutant could act as ozone precursor. FA and AA correlated in a significant way with CO (r = 0.749 and r = 0.789, respectively) indicating that both carbonyls could have their origin in vehicular sources.

Table 8. Pearson correlation matrix for the afternoon sampling period (B3): Spring season.

	CO	NO	NO2	NOX	O3	SO2	FA	AA
CO	**1**	0.462	**0.598**	**0.550**	**-0.517**	0.355	**0.749**	**0.789**
NO	0.462	**1**	**0.845**	**0.942**	**-0.945**	-0.208	0.405	0.479
NO2	**0.598**	**0.845**	**1**	**0.974**	**-0.782**	0.008	**0.559**	**0.732**
NOX	**0.550**	**0.942**	**0.974**	**1**	**-0.868**	-0.062	**0.502**	**0.641**
O3	**-0.517**	**-0.945**	**-0.782**	-0.868	**1**	0.392	-0.415	**-0.587**
SO2	0.355	-0.208	0.008	-0.062	**0.392**	**1**	0.090	0.114
FA	**0.749**	0.405	**0.559**	**0.502**	-0.415	0.090	**1**	0.428
AA	**0.789**	0.479	**0.732**	**0.641**	**-0.587**	0.114	0.428	**1**

3.6 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 7-9 and figures 10-12 show the result of the PCA analysis in winter and spring, respectively, during 2013. During the morning, two factors from the PCA were enough to explain 85.48% of the total variance for the studied data set, while in the midday and during the afternoon 2 factors were to explain the 82.36 % and 79.12 % of the total variance, respectively.

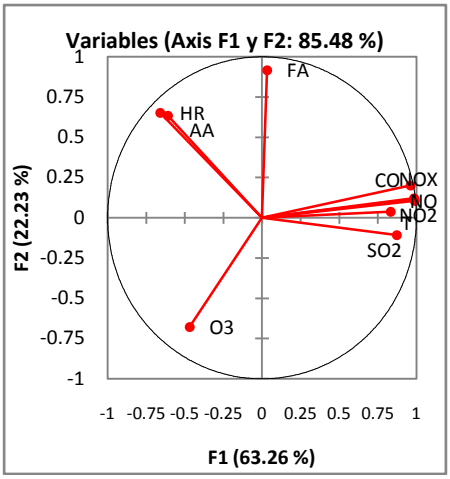


Figure 7. PCA Analysis for the morning sampling period (B1).

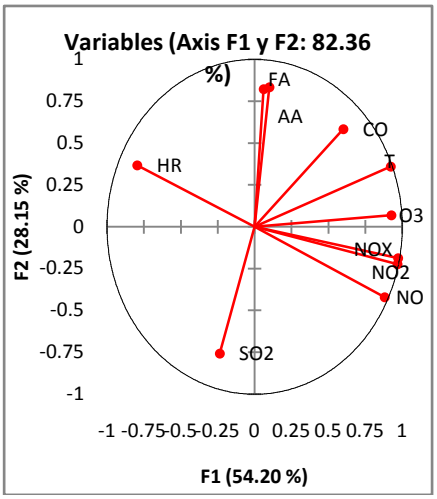


Figure 8. PCA Analysis for the midday sampling period (B2).

It can be observed that during winter period, FA probably had a different source than AA, whereas, NO, NO_2, NO_X 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 were more evident during the morning sampling period.

During the spring season, for the morning sampling period (B1) two factor were enough to explain 83.53% of the total variance in the data set. From

the biplot (Fig. 9) it can be observed that FA and AA had a strong correlation (indicating their common origin), whereas CO, NO, SO_2 could be grouped in a set of pollutants derived from combustion sources. Other group representing pollutants derived from photochemical activity could be indentified including NO_x and NO_2. O_3 showed a good relation with temperature. Relative humidity showed a negative correlation with almost all pollutants, indicating its influence on the wash-out processes to removal pollutants in the atmosphere.

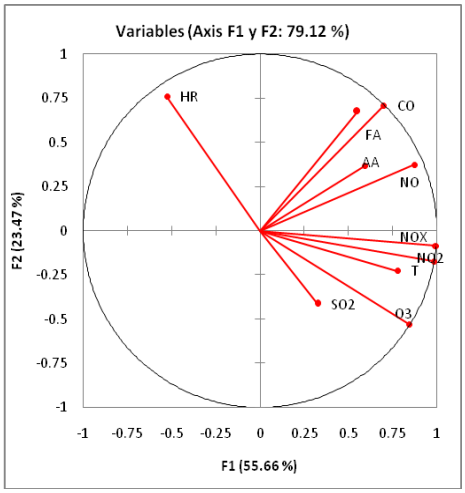


Figure 9. PCA Analysis for the afternoon sampling period (B3).

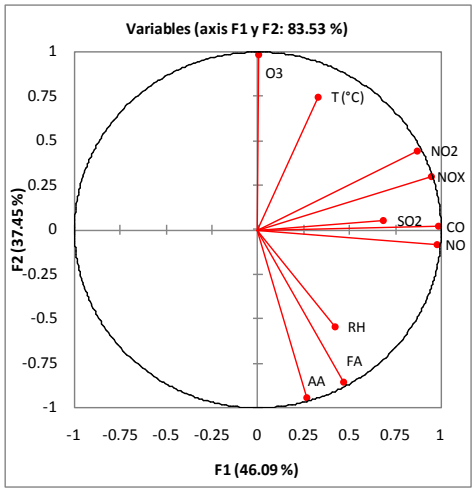


Figure 10. PCA Analysis for the morning sampling period (B1).

Two factors were necessary to explain 72.39% of the total variance for midday sampling period the data set. NO_x, CO and NO_2 could be grouped in a set of pollutants related to fossil fuels combustion. AA and FA showed a common origin and they could be grouped with NO, indicating, the influence of photochemical activity. O_3 could be related to temperature and SO_2.

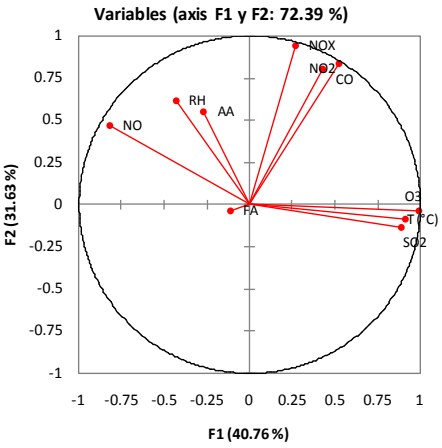


Figure 11. PCA Analysis for the midday sampling period (B2).

During the afternoon sampling period (B3) for the spring season, two factors were enough in order to explain 82.19 % of the total variance. FA and AA showed a probable origin in vehicular emissions showing a strong correlation with CO. NO_2, NO and NO_x could be indentified in a same group indicating that they probable had common sources. O_3 was correlated with temperature, indicating the photochemical origin of this oxidant.

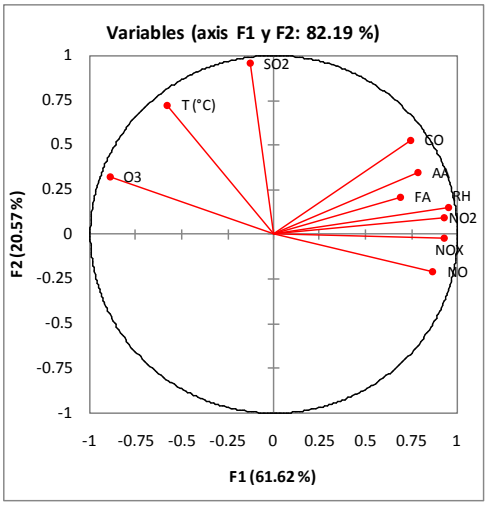


Figure 12. PCA Analysis for the afternoon sampling period (B3).

4 Conclusion

Carbonyl compounds measured during winter and spring 2013 showed strong diurnal patterns 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. Formaldehyde was found to be the most abundant carbonyl. Pearson correlation analysis showed that carbonyls had mixed sources and a complex behavior. They 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. From the PCA and Pearson correlation may be inferred that sometimes carbonyls could act as ozone precursors and during the spring season they could participate actively in secondary pollutants formation. 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 heavy traffic avenues, 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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