	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.

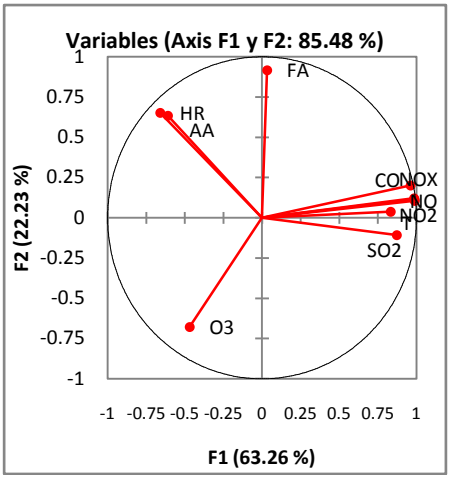

Figure 7. PCA Analysis for the morning sampling period (B1).

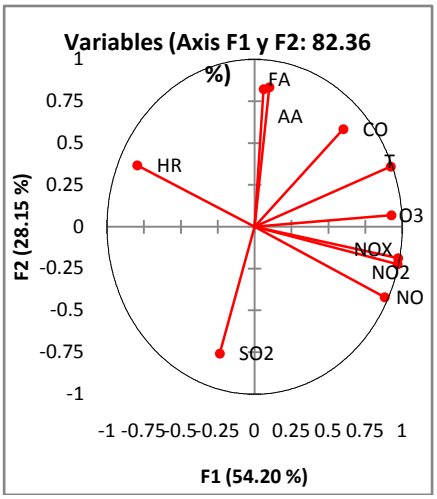

Figure 8. PCA Analysis for the midday sampling period (B2).

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.

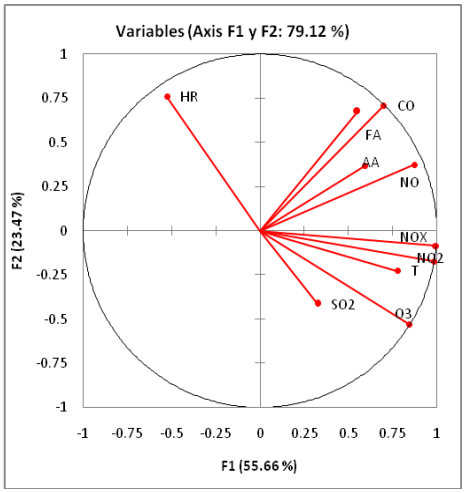

Figure 9. PCA Analysis for the afternoon sampling period (B3).

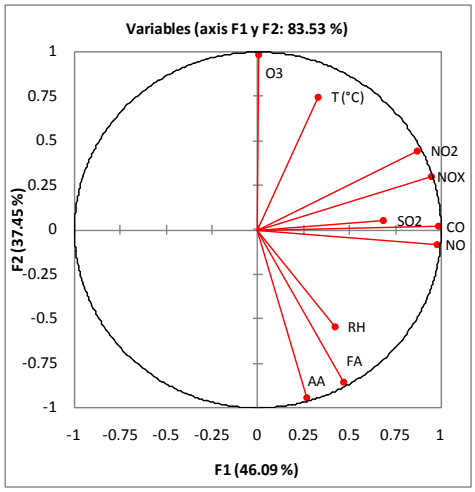

Figure 10. PCA Analysis for the morning sampling period (B1).

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.

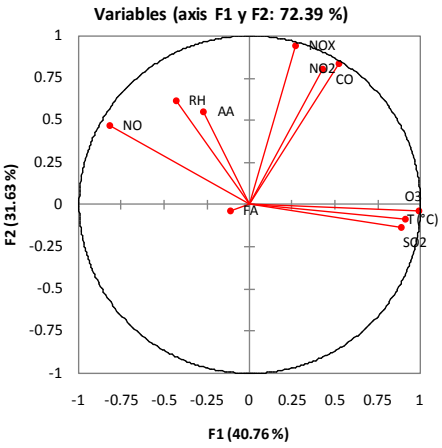

Figure 11. PCA Analysis for the midday sampling period (B2).

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.

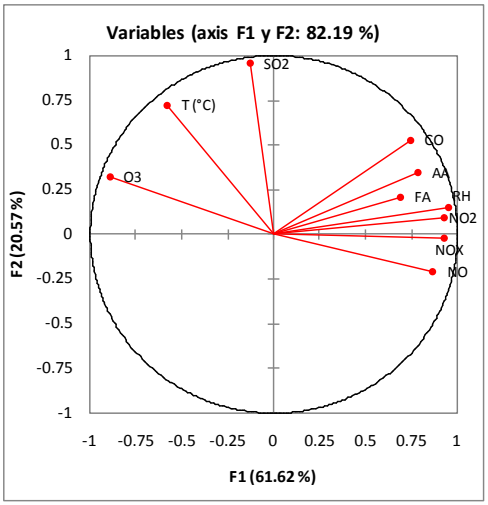

Figure 12. PCA Analysis for the afternoon sampling period (B3).

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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