



# ANALYSIS OF THE CORRELATIONS BETWEEN NO, NO<sub>2</sub> AND O<sub>3</sub> CONCENTRATIONS IN CAMPO GRANDE – MS, BRAZIL

Amaury de Souza,<sup>[a]</sup> Flavio Aristone,<sup>[a]</sup> Ujjwal Kumar,<sup>[b]</sup> E. Kovač -Andrić<sup>[c]</sup>  
Milica Arsić<sup>[d]</sup> Priscilla Ikefuti<sup>[e]</sup> and Ismail Sabbah<sup>[f]</sup>

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Ozone (O<sub>3</sub>) is a secondary gaseous pollutant in the urban environment, and its variation correlates well with nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>). Continuous monitoring has been done in the Campo Grande city urban area, using ozone 49C and NO-NO<sub>2</sub>-NO<sub>x</sub> 42CTL gas analyzers. The results show that the maximum concentrations of O<sub>3</sub> and oxidant (O<sub>x</sub> = O<sub>3</sub> + NO<sub>2</sub>) in Campo Grande often appear in the early afternoon around 15:00 hours. The daily variation of NO concentrations shows a very clear cycle with two peaks, one appearing around 07:00 a.m. and the other at 11:00 p.m. At the lowest level, NO<sub>2</sub> is the main component of NO<sub>x</sub>, while NO dominates the higher mixing ratio. It is also shown that the level of O<sub>x</sub> is composed of two factors: the regional and the local contributions. The former is affected by the regional O<sub>3</sub> level, while the latter is effectively correlated with the primary pollution level. The daily variation also appears in the concentrations of oxidant components.

## \* Corresponding Authors

E-Mail: amaury.de@uol.com.br

- [a] Author Address line 1<sup>1</sup> Federal University of Mato Grosso do Sul, C.P. 549, 79070-900 Campo Grande, MS – Brazil
- [b] SENR - School of Environment & Natural Resource, Doon University, Dehradun, India
- [c] University of Osijek, Osijek Department of Chemistry Croatia
- [d] University of Belgrade, Technical faculty in Bor, Serbia
- [e] Federal University of South Border, campus Erechim, Geography Department, Brazil.
- [f] Department of Natural Sciences College of Health Sciences, Kuwait

have been systematically realized by different researchers,<sup>8-12</sup> Furthermore, modeling of urban atmospheric dispersion has been applied to exploit results of Campo Grande climate effects.<sup>13-14</sup> It has been developed, recently, the first version of a CO and NO<sub>x</sub> inventory of emissions.<sup>8</sup>

In the present study, the values of environmental concentration of O<sub>3</sub>, NO, NO<sub>2</sub> and NO<sub>x</sub>, continually measured in the city of Campo Grande, are used to investigate, for the first time for this town, the concentration of oxidizers (O<sub>x</sub>, O<sub>3</sub> and NO<sub>2</sub>) along with NO<sub>x</sub>. This analysis shall contribute to a better understanding of atmospheric sources of O<sub>x</sub> for this specific urban area. The relationships that were found to describe the concentrations of O<sub>3</sub>, NO and NO<sub>2</sub> are in agreement with the current knowledge of their chemical coupling.

## INTRODUCTION

One of the main problems caused by air pollution in urban areas is the presence of photochemical oxidizers. Among these, ozone (O<sub>3</sub>) and nitrogen dioxide (NO<sub>2</sub>) are particularly important since they are susceptible of provoking adverse effects on human health (OMS, 2000). The formation of ozone at ground level depends on the intensity of the solar radiation, the absolute concentration of NO<sub>x</sub> and the VOCs (Volatile Organic Compounds), and the ratio between NO<sub>x</sub> and VOCs.

Various observations have shown that, in shiny days, the ozone concentration increases with the growing intensities of solar radiation and temperature. The concentration of photochemical oxidizers may be reduced throughout the control of their precursors, which are nitrogen oxides NO<sub>x</sub> (NO and NO<sub>2</sub>) and VOCs.<sup>2-4</sup> It is necessary, hence, to search for a complete comprehension of the relationships involving concentrations of O<sub>3</sub>, NO and NO<sub>2</sub> under different atmospheric conditions. Different authors,<sup>5-7</sup> studied the relationship between the environmental levels of O<sub>3</sub>, NO and NO<sub>2</sub> to improve the comprehension of their chemical coupling.

There is not an official network for air quality monitoring installed in the city of Campo Grande. Nonetheless, some studies and campaigns of weather and climate monitoring

## MATERIALS AND METHODS

### Studied and observational data

Campo Grande is the capital city of South Mato Grosso (MS) state, located in the southern of Brazil Midwest region, sited in the center of the state. Geographically the city is near to the Brazilian border with Paraguay and Bolivia. It is located at 20°26'34'' South latitude and 54°38'47'' West longitude. It occupies a total area of 8,096.051 km<sup>2</sup> or 3,126 mi<sup>2</sup>, representing 2.26% of the total state area, within 860,000 inhabitants (2016) and a corresponding HDI of 0.78. The urban area is approximately 154.45 km<sup>2</sup> or 60 mi<sup>2</sup>, where tropical climate and dry seasons predominate, with two defined seasons: warm and humid in summer, and less rainy and mild temperatures in winter. During the months of the winter, the temperature can drop considerably, arriving in certain occasions to the thermal sensation of 0°C or 32°F with occasional and light freezing. The year average precipitation is 1,534 millimeters, with small up or down variations. The main pollution problems in the city are attributed to the traffic of vehicles, to the raise of building

activities, to the presence of dumping grounds, to the use of small power generators running on oil to supply the lack of electric grid power, and to the induced fire outbreak used to clean up local terrains.

### Ensemble of observational data

The air quality and meteorological variables are monitored by an automatic station operated by the Institute of Physics of the Federal University of South Mato Grosso (UFMS). This station is located on the University campus, 8 km or 5 miles to the west of downtown. The main sources of pollution in that area are the building activities; therefore, there are no significant precursor sources of ozone identified close to the region. The ozone levels of Campo Grande area are stored in a regular database since 2004. The equipment of measurement was installed at the top of a tower from where air samples are extracted throughout vertical pipes that are placed approximately 2 meters above the ground level. The concentrations values for O<sub>3</sub>, NO<sub>x</sub>, NO and NO<sub>2</sub>, the ultraviolet (UV) radiation and other meteorological features, such as the air temperature, relative humidity, wind speed and direction are values measured systematically.

The concentrations of pollutants NO, NO<sub>2</sub>, NO<sub>x</sub> (NO+NO<sub>2</sub>) and O<sub>3</sub>, were measured continuously during a one-year period (2015). The equipments used for measurements included a nitrogen oxide analyzer (AC31M—using chemiluminescence method), an ozone analyzer (O341M—LCD/UV Photometry). All equipments were made by Environnement S.A.

## RESULTS AND DISCUSSIONS

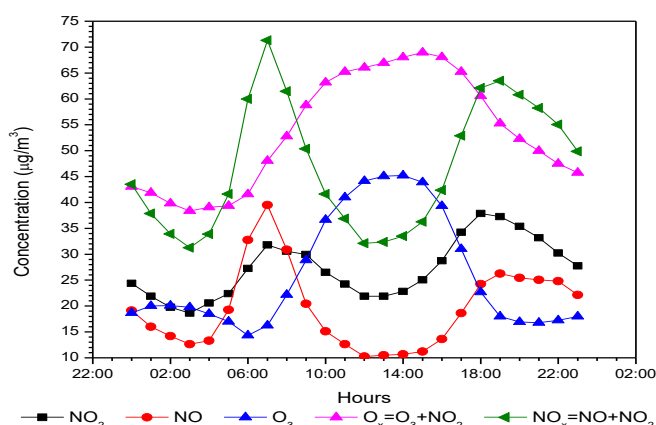
### Hourly variation of O<sub>3</sub>, NO, NO<sub>2</sub>, and NO<sub>x</sub> concentrations

The average per day variation observed for the NO, NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> concentrations are exhibited in figure 1. The daily cycle of ozone concentration reaches a peak during the middle day and presents smaller concentrations during the night. The ozone concentration slowly increases after the first rays of sun shining, getting to its maximum value during the daylight period, after which it starts to decrease slowly until the next morning.

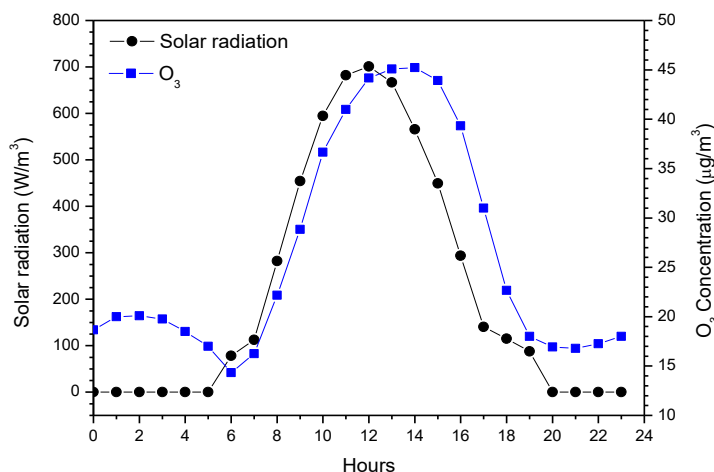
The variation pattern of the average concentration of gases was well defined during the analyzed period, and the pronounced peak of the concentration of NO in the first hour of the morning was due to photolysis of the nocturnal NO<sub>2</sub> accumulated after sunset ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ ), both for NO and O<sub>3</sub> values are minimal at this time (Figure 01). After sunset, a concentration of NO increases slowly. This occurred because of the variation of the emission of NO due to the change of temperature and humidity<sup>16</sup>. Other mechanisms of heterogeneous reactions during day and night may be important, although few known, such as the influence of humidity, temperature and precipitation<sup>17</sup>. The NO<sub>2</sub> (Figure 1) clearly shows that not only the lowest concentration values occur around midday, but also the lower variability in this time, which can be explained by Figure 02, where they have a mean daily value higher global solar radiation and NO photolysis, which reaches maximum values and lower zenith angle. This causes a greater

penetration of the solar rays (<400 nm), responsible for the photolysis of the NO<sub>2</sub>, since, due to the strong UV radiation, has high photochemical activity, in addition, there is the later oxidation of NO<sub>2</sub> by part of the hydroxyl radical (OH) ( $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ ), which is the main mechanism of NO<sub>x</sub> loss<sup>18</sup>.

The levels of NO<sub>2</sub> observed in the atmosphere showed a general tendency in which they tend to decrease in the period of the day of greatest insolation and to grow at the end of the day (Figure 1). This fact suggests that the photochemical processes are the main mechanisms to remove NO<sub>2</sub> from the atmosphere with formation of by-products. The model that best explains this fact is the consumption of NO<sub>2</sub> by direct photochemical reactions generating ozone. The formed O<sub>3</sub> reacts with water vapor and generates HO radicals, this radical is the main chemical species involved in the NO<sub>2</sub> consumption, with the production of HNO<sub>3</sub>, the reaction of formation of nitric acid is significant in the region under study, mainly due to the conditions Favorable conditions of insolation during a large part of the year, the presence of oxidants in the atmosphere is determinant for the formation of NO<sub>2</sub> in the atmosphere, from the NO emitted by the combustion processes. The production of NO<sub>2</sub> occurs mainly by the reaction of NO with O<sub>3</sub><sup>19-20</sup>.



**Figure 1.** Average of measured values for a daily period of NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub> and O<sub>x</sub> concentrations. The interval between measurements equals 1 hour.



**Figure 2.** Average concentrations of O<sub>3</sub> and UV irradiance for the studied period.

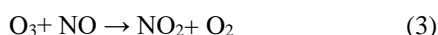
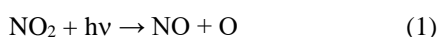
Such a variation is due mainly to the photochemical formation and meteorological conditions. The effect of the increasing solar radiation that occurs between 08:00 and 14:00 / 15:00, along with the height of the mixture layer entails the reduction of NO<sub>x</sub> concentration and a raising in the concentration of O<sub>3</sub>. The simultaneous measurement of O<sub>3</sub> and UV during the daylight period (from 07:00 to 19:00, see Figure 2) shows that the concentration of O<sub>3</sub> is strongly correlated to the UV irradiance (W/m<sup>2</sup>). The daily cycles of O<sub>3</sub> and UV flux are similar, with the maximum O<sub>3</sub> occurring at 14:00, i.e., approximately 1 or 2 hours after the maximum UV flux. The statistical analysis reveals that the correlation between O<sub>3</sub> concentration and UV is significant with a correlation coefficient (*R*) of 0.79.

While O<sub>3</sub> and a large percentage of NO<sub>2</sub> are secondary contaminants, NO is a primary contaminant, formed through a complex set of chemical reactions. At 07:00, the sun light begins to induce a series of photochemical reactions. NO is converted in NO<sub>2</sub> through a reaction with O<sub>3</sub>. During the shining hours, NO<sub>2</sub> has converted again into NO because of photolysis, which induces the regeneration of O<sub>3</sub>.

Another factor influencing the atmospheric pollutant concentrations is the height of the mixture layer over the city. In a shiny day, pollutants are diluted when the mixture layer increases during the day and stays limited to the inside of NPBL during the night. Emitted pollutants, like NO, are kept underneath such an inversion, and it can cause an increase of the hourly average concentration of NO<sub>x</sub> overnight.

### Chemistry of O<sub>3</sub>, NO and NO<sub>2</sub>

The basic chemistry that leads to the production and destruction of ozone has been detailed elsewhere.<sup>26</sup>



where

M represents a molecule absorbing the excess of vibrational energy and thus stabilizing the O<sub>3</sub> molecule that has been formed, normally it is N<sub>2</sub> or O<sub>2</sub>;

*hν* represents the photon energy, with a 424 nm wavelength; and

O is an active monoatomic molecule of oxygen.

These equations form a cycle free of liquid chemistry, i.e., the global effect of reaction (2) is the opposite of reaction (1). Such reactions represent, therefore, a closed system for which the components NO<sub>x</sub> (NO and NO<sub>2</sub>) and O<sub>x</sub> (O<sub>3</sub> and O<sub>2</sub>) are referred separately. Along the daytime, concentrations of NO, NO<sub>2</sub> and O<sub>3</sub> remain typically balanced during a period of a few minutes. Such a situation

is known as a photocatalytic state. The concentrations of NO, NO<sub>2</sub> and O<sub>3</sub> are related through the following equation:

$$\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} = \frac{t_2}{k_2}$$

where

*t*<sub>2</sub> is the NO<sub>2</sub> photolysis rate, and

*k*<sub>1</sub> is the coefficient of reaction between NO and O<sub>3</sub>.

The variation of *t*<sub>2</sub>/*k*<sub>1</sub> average value along the time was obtained using the observed measurements of NO, NO<sub>2</sub> and O<sub>3</sub> is exhibited in Figure 3. The average value of *t*<sub>2</sub>/*k*<sub>1</sub> is 16.9, with a minimum of 11.9 and maximum of 22.4 μg m<sup>-3</sup>. The maximum value occurs typically at 08:00 hours.

The *k*<sub>1</sub> coefficient varies as a function of temperature (*T*). Sienfeld and Pandis,<sup>27</sup> proposed the following equation for *k*<sub>1</sub>:

$$k_1 (1 / (\text{ppm min})) = 3.23 \times 10^3 \exp\left(\frac{-1430}{T}\right) \quad (4)$$

As expected, the variation of *k*<sub>1</sub> is similar to the variation of the average air temperature.

Figure 4 presents the variation of daily concentration of O<sub>3</sub> as a function of the ratio [NO<sub>2</sub>]/[NO], sampled hourly. The level of O<sub>3</sub> increases with the raise of [NO<sub>2</sub>]/[NO]. According to Figure 4, the concentration of O<sub>3</sub> increases rapidly for small values of [NO<sub>2</sub>]/[NO]. For levels that are more elevated, the concentration of O<sub>3</sub> gets close to reach a photocatalytic state, when it remains relatively stable. In our study, we adjust these data to a polynomial function of ln([NO<sub>2</sub>]/[NO]) that can be used to predict the concentration of O<sub>3</sub> during the day:

$$[\text{O}] = 20.82 + 14.22 \ln\left[\frac{\text{NO}_2}{\text{NO}}\right] (R^2 = 38.34\%) \quad (5)$$

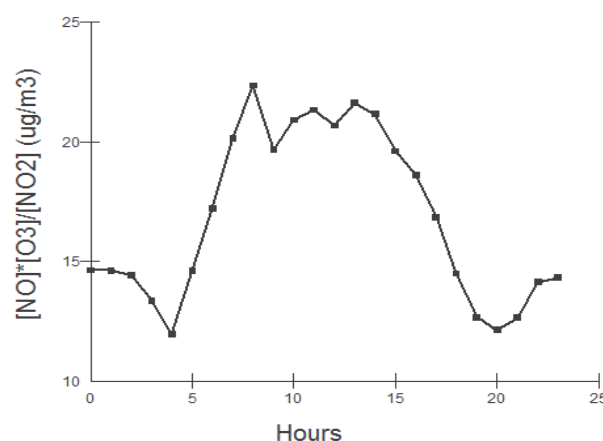
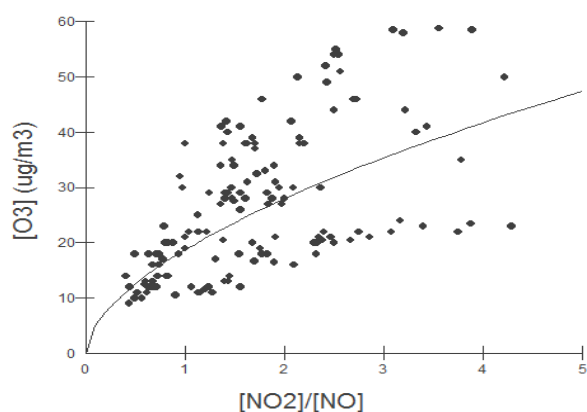


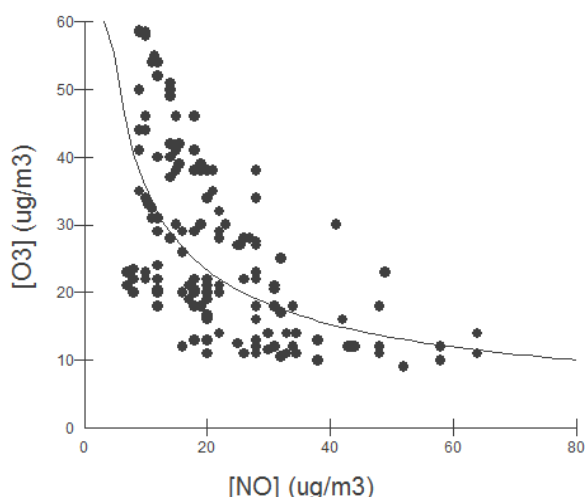
Figure 3. Daily variation of *t*<sub>2</sub>/*k*<sub>1</sub> (μg m<sup>-3</sup>) average values



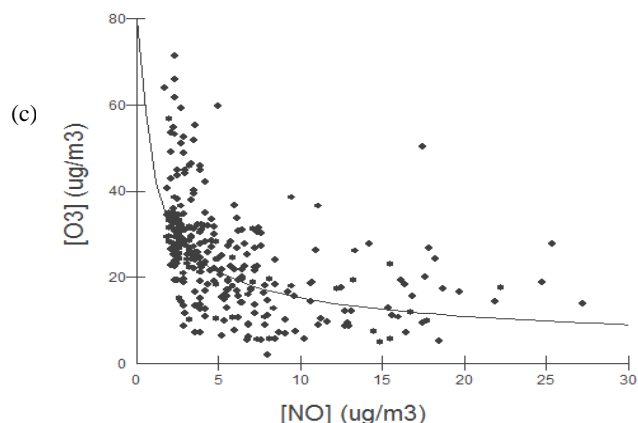
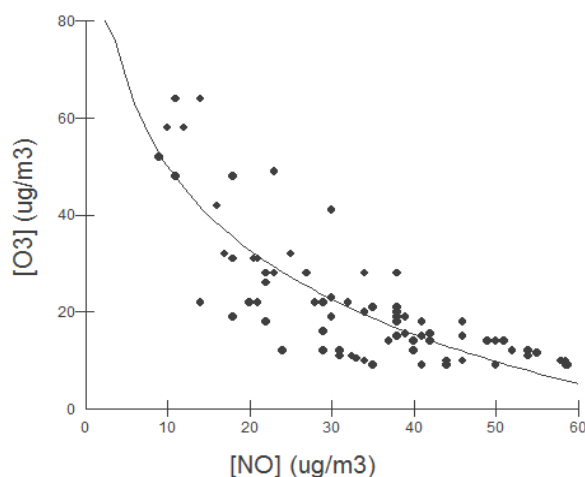
**Figure 4.** Variation of O<sub>3</sub> as a function of the [NO<sub>2</sub>]/[NO] ratio.

The comparison between the average concentrations of NO and O<sub>3</sub> is exposed in Figure 5; the measurements have been taken at one-hour intervals. Three periods have been used for purpose of comparison: the whole day:  $Y=71.25-15.93\ln[\text{NO}]$ ;  $R^2=36.8\%$ . Daylight (from 06:00 to 18:00):  $Y=107.98-25.10\ln[\text{NO}]$ ;  $R^2=67.96\%$  and nighttime shift (from 18:00 to 06:00):  $Y=75.40-18.20\ln[\text{NO}]$ ;  $R^2=33.26\%$ .

(a)



(b)



**Figure 5.** Variation of average values of O<sub>3</sub> plotted along with NO. (a) for the entire day; (b) for the daytime; (c) for the nighttime.

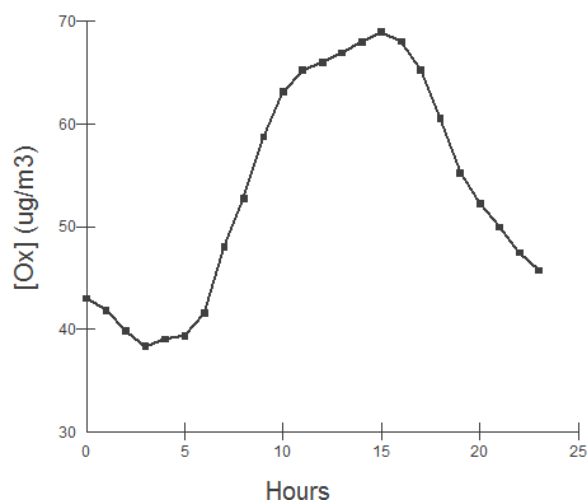
The average concentration of O<sub>3</sub> decreases when the concentration of NO increases. Comparing the values of average concentrations of NO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub>, the following characteristics can be observed:

- ✓ The average concentration (1 hour) of O<sub>3</sub> decreases along with the increase of NO<sub>x</sub>, while the levels of NO and NO<sub>2</sub> increase with NO<sub>x</sub>;
- ✓ The largest concentrations of NO<sub>2</sub>, NO and O<sub>3</sub> observed during the day are 48, 64 and 58.8 μg m<sup>-3</sup>, respectively;
- ✓ The largest concentrations of NO<sub>2</sub>, NO and O<sub>3</sub> observed during the night are 49.50, 48 and 39 μg m<sup>-3</sup>, respectively;
- ✓ The numbers presented on items b) and c) below confirm that the larger daily average concentrations (1 hour) of NO<sub>2</sub> and O<sub>3</sub> are higher during the daylight period than those measured during the night time. However, the highest average (1 hour) concentrations of NO and NO<sub>x</sub> observed during the full period considered for this study have occurred during the night time.

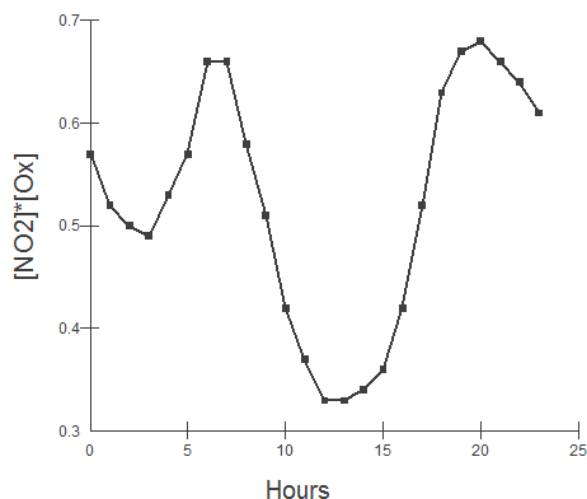
#### Diurnal variation of O<sub>x</sub>

The difference between the diurnal and nocturnal O<sub>x</sub> behavior shall be expected if the photochemical processes have any influence on the O<sub>x</sub> levels in polluted areas. Figure 6 shows the daily variation of the average concentration value of O<sub>x</sub> taken at intervals of 1 hour. The concentration of O<sub>x</sub>, likewise the variation of O<sub>3</sub> concentration, exhibits a peak at noon and lower concentrations during the night. The concentration of O<sub>x</sub> slowly increases after the sun rises, attaining a maximum value during the day and, in the sequence, decreases until the next morning. This is due to the photochemical formation of O<sub>3</sub>. Figure 7 shows the daily variation of NO<sub>2</sub>/O<sub>x</sub>.

The differences on the partition of NO<sub>2</sub> and O<sub>3</sub> can be related to the rate of chemical processes or with the available time for them to occur.



**Figure 6.** Daily variation of O<sub>x</sub> average values.



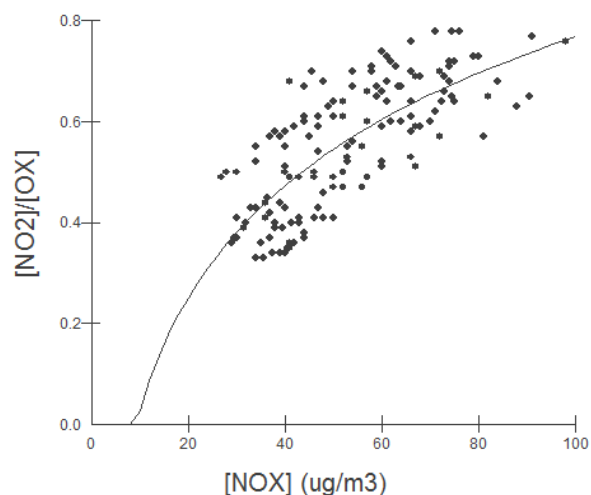
**Figure 7.** Daily variation of NO<sub>2</sub>/O<sub>x</sub> average values.

#### Variation of NO<sub>2</sub>/O<sub>x</sub> daily values with NO<sub>x</sub>

Figure 8 shows the adjusted expression of [NO<sub>2</sub>] / [O<sub>x</sub>] as function of [NO<sub>x</sub>]:  $Y = 0.71 + 0.33 * \ln [NO_x]$ ; with a correlation coefficient of  $R^2 = 55.2\%$ . The data show that, for lower values of the relation [NO<sub>2</sub>] / [O<sub>x</sub>] there are low NO<sub>x</sub> values, implying that at these times, O<sub>x</sub> concentrations are predominantly marked by high concentrations of O<sub>3</sub>. In addition, with increasing NO<sub>x</sub> concentrations, a large part of the concentration is in the form of NO<sub>2</sub>. The high values of [NO<sub>2</sub>] / [O<sub>x</sub>] can also be explained by the oxidation process of NO to NO<sub>2</sub> with concentrations of NO marked mainly by NO<sub>2</sub> concentration.

#### Correlation between concentrations of NO, NO<sub>2</sub> with NO<sub>x</sub>

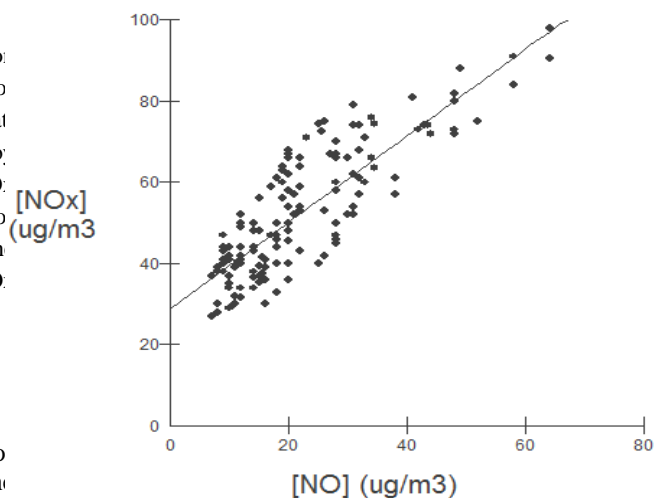
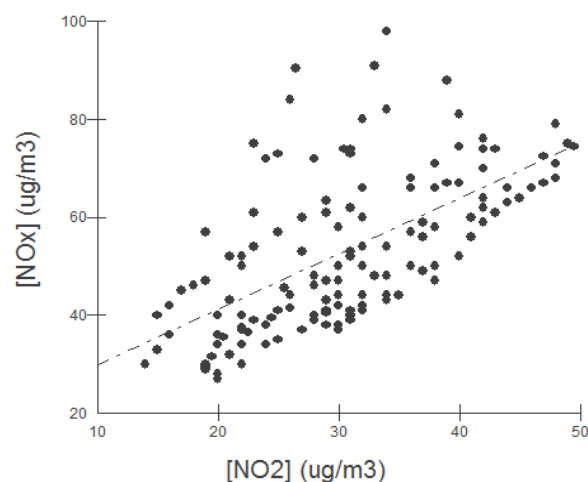
Figure 9 exhibits both variation of NO<sub>x</sub> as a function of NO and NO<sub>2</sub> for the average data observed with the sampling interval of 1 hour. The straight lines are, respectively: a)  $Y = 18.54 + 1.14[NO_2]$ ;  $R^2 = 28.44\%$ ; b)  $Y = 28.93 + 1.07[NO]$ ;  $R^2 = 70.176\%$ .



**Figure 8.** Daily variation of NO<sub>2</sub>/O<sub>x</sub> average values as a function of NO<sub>x</sub> level.

When our data were adjusted to a linear function, the obtained correlation was weak.

(a)

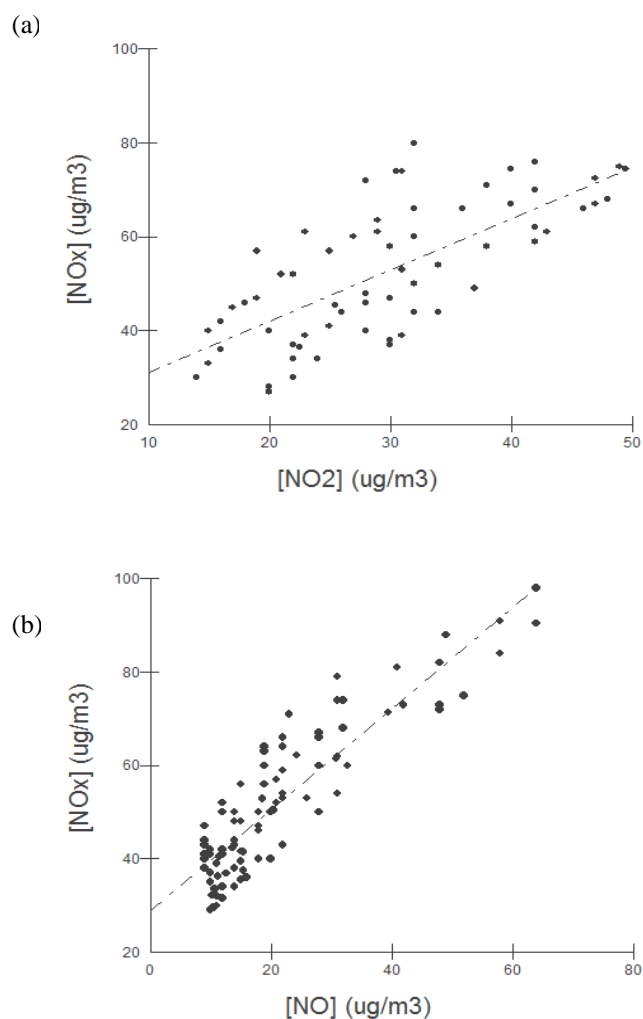


**Figure 9.** The average values of NO<sub>x</sub> plotted as a function of (a) NO<sub>2</sub> and (b) NO.

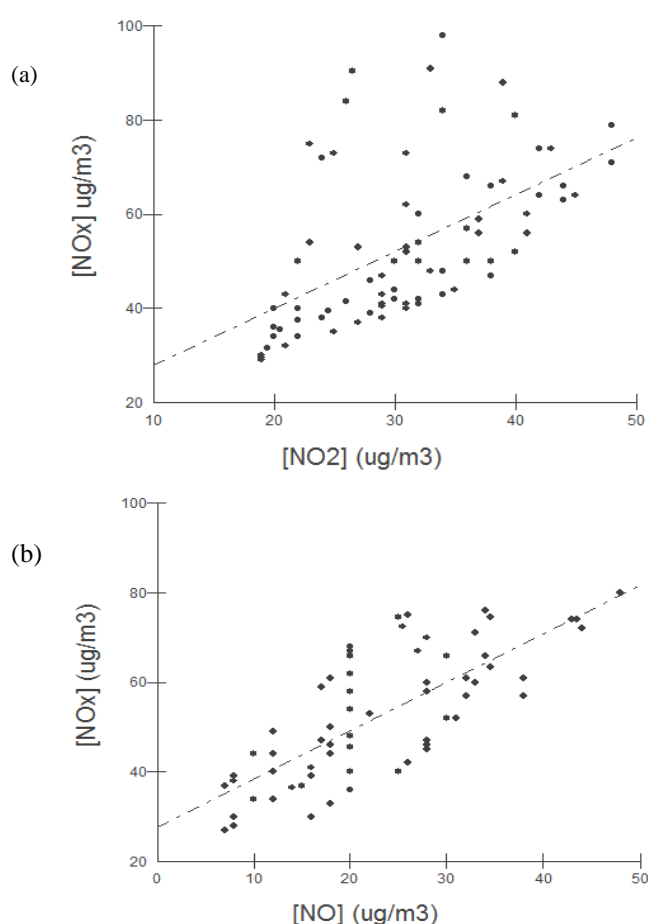


However, better results were obtained when the observed data are split into diurnal and nocturnal periods. In Figure 11 the observed data values for the diurnal period are exhibited and the respective relations obtained are: a)  $Y=15.98+1.10[\text{NO}_2]$ ;  $R^2=31\%$ , and b)  $Y=29.78+1.06[\text{NO}]$ ;  $R^2=79.1\%$ . In Figure 12, the measured data for the nocturnal period are exhibited and the relations obtained are: a)  $Y=20.37+1.09[\text{NO}_2]$ ;  $R^2=51.9\%$  and  $Y=27.73+1.08[\text{NO}]$ ;  $R^2=56.47$ . These results lead to the following conclusions: during the daytime, the linear correlation between NO<sub>x</sub> and NO<sub>2</sub> is quite good, while for the nighttime the correlation between concentrations of NO<sub>x</sub> and NO is very strong.

The variations of diurnal and nocturnal values of O<sub>3</sub> concentrations as a function of NO<sub>x</sub> level are represented in Figure 12. The total value of O<sub>x</sub> raised with NO<sub>x</sub>, and the data have been linearly adjusted. Due to the influence of photochemical reactions on the O<sub>3</sub> formation, differences between values and linearly adjusted equations of day and night have been found. It is noticeable that the total local O<sub>x</sub> has a contribution independent of NO<sub>x</sub> and another one that is dependent. The first part is a regional contribution comparable to the regional level of O<sub>3</sub>, while the last term is a local contribution effectively correlated to the level of primary pollution. It has been verified that the dependent local contribution of NO<sub>x</sub> to O<sub>x</sub> during the night is 37% lower than during the day.



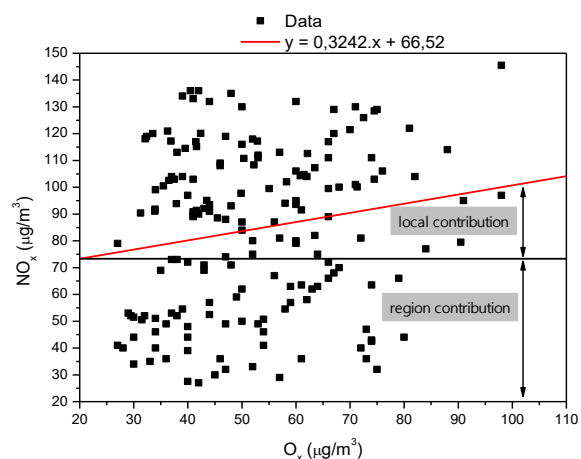
**Figure 10.** The average values of NO<sub>x</sub> plotted as a function of (a) NO<sub>2</sub> and (b) NO for the daytime period.



**Figure 11.** The average values of NO<sub>x</sub> plotted as a function of (a) NO<sub>2</sub> and (b) NO for the nighttime period.

#### Local and regional contributions to the oxidant

However, the approximately  $75 \mu\text{g m}^{-3}$  regional contribution is almost equivalent during the day and night. The regional contribution to O<sub>3</sub> is consistent with the values observed by.<sup>5,7</sup> This result implies that the problem of air quality in Campo Grande is not just a local question, especially the street pollution, but also a regional issue of Campo Grande County. The territorial aspect observed for the analysis of O<sub>3</sub> pollution is consistent with the results reported by.<sup>5,24</sup>



**Figure 12.** Variation of daily average NO<sub>x</sub> concentration plotted as a function of O<sub>3</sub>.

## CONCLUSION

The present results indicate that the diurnal cycle of ozone concentration has a peak around noon and smaller nocturnal concentrations. The ozone concentration slowly increases after the sun rising, reaching a maximum value during the daytime and, in the sequence, decreases until the next morning. This is due to the photochemical formation of O<sub>3</sub>. The shape and amplitude of ozone cycles are strongly influenced by meteorological conditions (solar radiation) and by the prevailing levels of precursors (NO<sub>x</sub>). At the studied region, the daily cycle of NO concentration stem from vehicle emissions and its conversion to NO<sub>2</sub> has a huge impact on the daily cycle of ozone levels. A linear correlation between NO<sub>2</sub> and NO<sub>x</sub> has also been determined, as well as between NO and NO<sub>x</sub>, while a polynomial correlation between O<sub>3</sub> and NO<sub>2</sub>/NO has been found. These forms can be useful for the strategies of O<sub>3</sub> provision and efforts of air pollution control. The O<sub>x</sub> level is influenced by independent and dependent contributions of NO<sub>2</sub>. The first one is due to the regional concentration of O<sub>3</sub>, and the last one is correlated with the local level of primary pollution.

## ACKNOWLEDGEMENTS

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