



Time-series analysis of surface ozone and nitrogen oxides concentrations in an urban area at Brazil

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ABSTRACT

The purpose of the present work was to study the concentration variations in O₃, NO, NO₂, NO_x over a 4-year period (2006–2009), using the Kolmogorov–Zurbenko filter. Data were decomposed into seasonal and trend components. Seasonal component of the time-series analysis (2006–2009) of NO and NO_x in Canoas and Esteio showed values above average during the cold seasons, while O₃ showed an opposite pattern. The trend component was marked by the decrease of NO₂ at Canoas and the increase of NO at Esteio, thus revealing their variation (NO and NO_x) due to local emissions. Furthermore, evaluations of the mean daily concentrations of NO, NO_x, NO₂, O₃, PM₁₀ and CO, and correlations of these pollutants with meteorological parameters (ambient temperature, wind velocity, solar radiation and relative humidity) allowed the confirmation of the influence of mobile sources in the study area.

Keywords: Nitrogen oxides, ozone, traffic air pollution



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1. Introduction

Air pollution caused by photochemical oxidants, especially in urban areas, has risen in later years (Notario et al., 2012), mainly by vehicular fleet increase. Tropospheric ozone (O₃) is formed by a series of complex photochemical reactions between nitrogen oxides (NO_x=NO+NO₂) and volatile organic compounds (VOCs) in the presence of sunlight (Finlayson–Pitts and Pitts, 2000). NO_x is a reactive pollutant and its major effects on O₃ are limited to its proximity to emission sources (Uherek et al., 2010). The O₃ formation by reactions involving the catalytic action of NO_x on the oxidation of CO is also possible (Seinfeld and Pandis, 2006). CO is emitted directly from the fuel combustion and therefore makes some contribution to tropospheric O₃ production in the boundary layer (Jenkin and Clernitshaw, 2000). NO_x emitted by heavy vehicles produce five times the amount of NO_x by mass of burnt fuel compared to gasoline vehicles (Kirchstetter et al., 1998). Also, the addition of biodiesel in diesel can slightly increase NO_x emissions (Coronado et al., 2009).

Due to the chemical coupling of surface O₃ and NO_x, the response to NO_x emissions reductions is remarkably not linear and any resultant reduction in the level of nitrogen dioxide (NO₂) is invariably accompanied by an increase in the atmospheric concentration of O₃ (Mazzeo et al., 2005).

Although elevated O₃ concentrations had been registered in cities, the highest values normally occur at downwind locations, due to the transport of precursors. Depending on weather condi-

tions, O₃ precursors can be transported over long distances and originate O₃ formation in locations far from their sources (Castell–Balaguer et al., 2012). Stedman (2004) studied the influence of the decrease in CO and NO_x concentrations; however O₃ concentrations seem to be steady or even increased in the last few years.

Several studies highlight the importance of meteorological factors in O₃ formation and transport (Millan et al., 2000; Thompson et al., 2001). The studies have shown O₃ concentrations increase with high temperatures and solar radiation intensities (Garcia et al., 2005; Castell et al., 2008; Teixeira et al., 2009; Han et al., 2011; Castell–Balaguer et al., 2012). Other authors, such as Pudasainee et al. (2006), reported that daily variations of ground-level O₃ occur more frequently in the spring and summer than in the winter. Teixeira et al. (2009) reported seasonal variations of surface ozone in the same study area during one year period (in 2006), with maximum O₃ concentration during summer and spring.

The Kolmogorov–Zurbenko (KZ) filter developed by Rao and Zurbenko (1994), used in the present study, has been widely used for treating ozone data, since other statistical methods are poorly developed for situations of O₃ changes due to meteorological variations larger in magnitude than those induced by emissions (Rao et al., 1997). The KZ filter is a good method to separate O₃ time series effectively into their various spectral components (Kang et al., 2013). Some studies, such as Dallarosa et al. (2007), Teixeira et al. (2009), Meira et al. (2009), and Cuchiara and Carvalho (2012), did not have their results filtered to remove the seasonal

component of temporal variability in order to examine the data and detect changes in the emission of O₃ and their precursors.

Thus, the purpose of the present study was to study the variations in O₃, NO, NO₂, NO_x concentrations over a 4-year period (2006–2009). The data were decomposed into their seasonal and trend components by applying the Kolmogorov–Zurbenko filter. Moreover, meteorological parameters (ambient temperature, wind velocity, solar radiation, and relative humidity) were correlated with O₃, NO, NO₂, NO_x, PM₁₀ and CO concentrations. Also, the mean daily variation of the concentration of those pollutants was also calculated.

2. Methodology

2.1. Study area

The chosen region for this study was the metropolitan area of Porto Alegre (MAPA). It is located in the eastern part of Rio Grande do Sul state at south Brazil, and has a total area of 84 764 km². This area is represented by a stretch of 32 counties (SEPLAG, 2011) and is the most urbanized region of Rio Grande do Sul state. The air quality in the MAPA is under direct influence of industrial activities and, especially, emissions from mobile sources which account for about 40% of emissions in the state (Teixeira et al., 2010). Additional details and explanations of the samplings sites locations are shown in Figure 1.

The study area has a strong influence of light and heavy-duty vehicles, with daily traffic congestions, and also because of the proximity of the BR–116 highway. The different industrial typologies include several stationary sources such as an oil refinery, steel mills that uses natural gas, and coal-fired power

plants, as reported in Teixeira et al. (2010; 2012). Sampling sites were Canoas and Esteio in the study area.

Due to its location, winter in the MAPA is strongly influenced by cold air masses migrating from Polar Regions. The seasons are well defined and the rain is evenly distributed all over the year. According to Koppen’s international system of climate classification, the climate type of the study area is a humid subtropical climate (Cfa) with well distributed rain all over the year, and an average temperature above 22.0 °C during the warmest month of the year. The prevailing wind direction is SE, followed by NE (EMBRAPA, 2003). The average annual speed of wind is 2.2 m s⁻¹ (INMET, 2009). In the cold seasons, there is less dispersion of pollutants due to lower wind speeds, higher incidence of calm winds, and greater variability in wind direction, associated with a lower thickness of the mixing layer (due to migration of polar air masses over the region). In warm seasons, the dispersion is favored by higher wind speeds, lower incidence of calm winds, and increased thickness of the mixing layer (Teixeira et al., 2012). During the day, the wind reaches its lowest speed at dawn and early morning, and highest speeds in the late afternoon, between 5:00–7:00 p.m. This pattern is related to energy availability at the surface (sensible heat) during the day, intensifying local and mesoscale atmospheric circulations. The prevailing wind results from interactions of mesoscale phenomena, especially sea/land breezes (from the Atlantic Ocean and the Patos Lagoon) and valley/mountain breezes (from the nearby Serra Geral Mountains located to the north of the MAPA). Details about the annual average and maximum per day of the meteorological variables ambient temperature, relative humidity, rainfall, number of days with rainfall ≥1 mm, wind speed, and pressure by season: summer (Jan/Feb/Mar), autumn (Apr/May/Jun), winter (Jul/Aug/Sep), and spring (Oct/Nov/Dec) for the sampling period (2006–2009) of the present study can be found in Table 1.

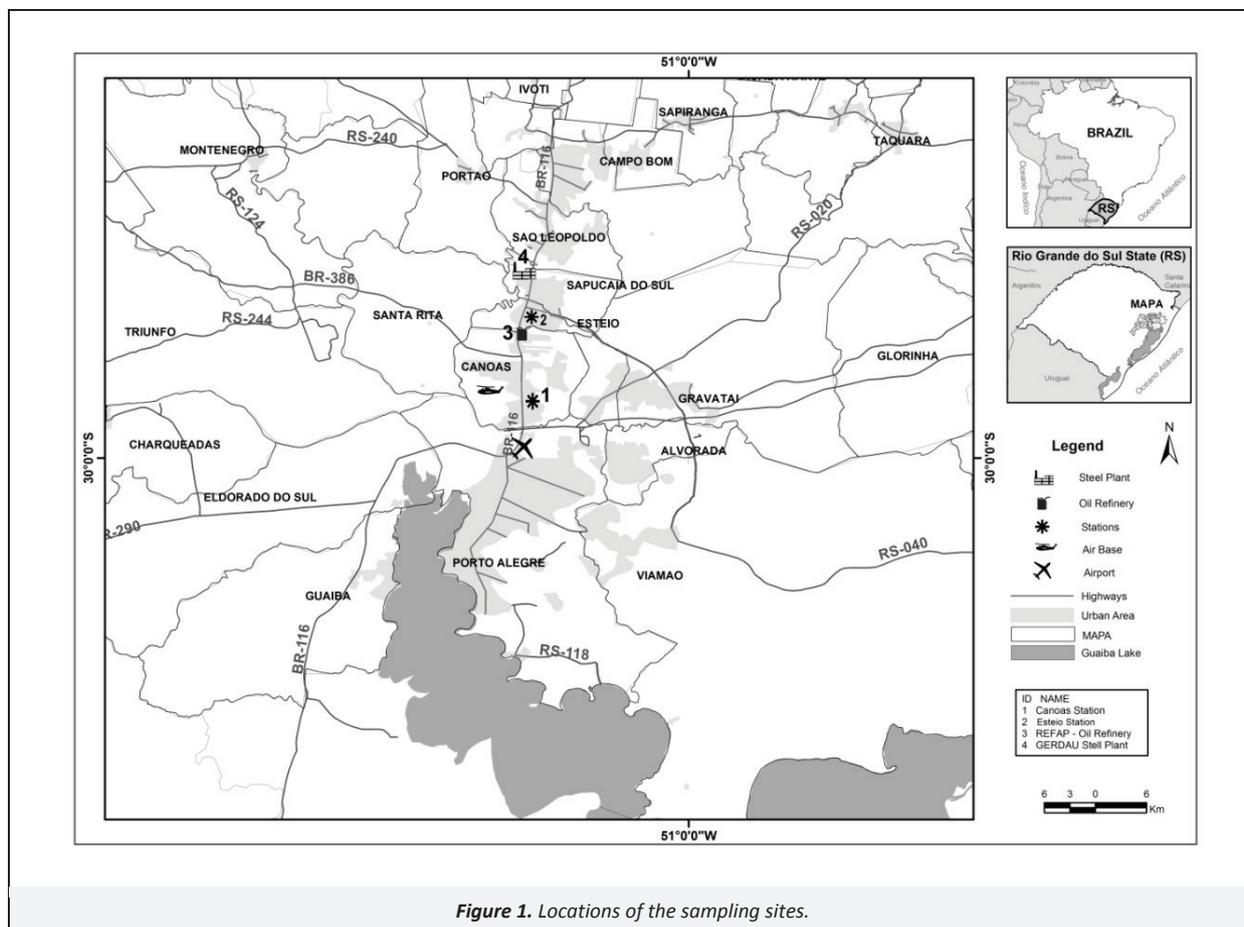


Figure 1. Locations of the sampling sites.

Table 1. Meteorological data for the sampling period (2006–2009)

Parameter	Unit	Summer	Autumn	Winter	Spring
Ambient temperature	°C	24.2	17.0	15.5	21.6
Maximum daily temperature	°C	30.1	23.3	20.4	26.2
Minimum daily temperature	°C	20.3	14.3	11.4	16.6
Relative Humidity	%	72.7	77.1	76.8	72.5
Maximum daily relative humidity	%	89.1	89.6	90.8	89.3
Minimum daily relative humidity	%	48.2	55.4	55.9	49.8
Precipitation ^a	mm	320	339	444	376
Number days with precipitation ^b	days	28.0	23.0	28.0	26.0
Wind speed	m s ⁻¹	1.7	1.3	1.6	1.8
Pressure	hPa	1 007	1 012	1 013	1 008

Source: Instituto Nacional de Meteorología – INMET

^a Precipitation average of the stations in the study period

^b Number of days per season in the study period

During the period of study (2006–2009), the average rainfall in winter was 444.2 mm year⁻¹, 28% higher than in summer (320.4 mm year⁻¹). The wind speed was higher in spring and lower in autumn, with the average rate slightly lower than the climatological normals. The atmospheric pressure was higher in autumn and winter, with values slightly below the climatological normals.

Average temperatures (Table 1) showed behavior similar to the climatological normals. Temperatures (average, maximum and minimum) in the summer were about 9–10 °C higher than those in the winter. Average maximum daily temperature in the summer was 30.7 °C and in the winter 20.4 °C, while the average minimum daily temperature in the summer was 20.3 °C and 11.4 °C in the winter. This same range between the daily maximum and minimum temperatures was observed in all seasons. The relative humidity was slightly below the climatological normals, and did not show much variation among the different seasons. However, the variation between the daily averages of maximum and minimum relative humidity was 46% in the summer and 38% in the winter.

2.2. Sampling and calibration

The pollutants NO, NO₂, NO_x (NO+NO₂), O₃, and CO were measured continuously during a 4–year period (2006–2009). The equipments used for measurements included a nitrogen oxide analyzer (AC31M–using chemiluminescence method), an ozone analyzer (O341M–LCD/UV Photometry), a carbon monoxide analyzer (CO11M–using infrared absorption), and a PM₁₀ analyzer (MP101M–using beta radiation method). All equipments were made by Environnement S.A. Air temperature (°C), relative humidity (%), solar radiation (W m⁻²), wind direction (°) and wind speed (m s⁻¹) were measured continuously by a weather station, at 15–min intervals, using a thermo hygrometer, a global radiometer, and an anemometer. All the analyzers were located in Canoas and Esteio, the sampling sites of the study area (Figure 1).

In order to have a good quality control of the data, monthly calibrations were performed in these analyzers. For the AC31M and CO11M, calibration gases with uncertainty <3% were used, together with the MGC 101 multicalibrator (Multigas Multi–Point Calibrator). The calibrations of the O341M analyzer were done with an ozone generator present in the MGC. For the MP101M, it was used a reference gauge provided by the manufacturer.

2.3. KZ filter

The KZ filter treatment was applied to the 15–min data to analyze the temporal series for the period 2006–2009. This filter was proposed by Kolmogorov and formally defined by Zurbenko (1986). It can be written as:

$$KZ_{m,p}[X(t)] = \sum_{s=-\frac{p(m-1)}{2}}^{\frac{p(m-1)}{2}} \frac{a_s}{m^p} X(t + S) \tag{1}$$

where, $X(t)$ corresponds to the time series, t is a position in the time series and a_s corresponds to the coefficients of the polynomial $(1+z+z^2+\dots+z^{m-1})^p$.

The KZ filter can also be defined as p –times iterations of a moving average [Equation (2)] with window length m .

$$MA = \sum_{s=-(m-1)/2}^{(m-1)/2} \frac{X(t + S)}{m} \tag{2}$$

The KZ filter is a low–pass filter, removing high frequency variations in the time series. The effective width (P) of this filter depends of the number of iterations (p) and window size (m), estimated as $m \sqrt{p} \leq P$ (Milanchus et al., 1998).

The KZ filter is capable of separating out both trend and short–term variations in the time–series, and the seasonal component, too. The short–term component is attributable to weather and short–term fluctuations in precursor emissions, the seasonal component is a result of changes in the solar angle, and the trend–term results from changes in overall emissions, pollutant transport, climate, policy, and/or economics (Rao and Zurbenko, 1994; Wise and Comrie, 2005). The seasonal component reflects “normal” variations that recur every year to the same extent (OECD, 2007). It is also referred to as the seasonality of a time series.

The KZ filter is based on the Rao and Zurbenko (1994) statement that a time–series of atmospheric pollutants can be represented by:

$$A(t)=e(t)+S(t)+W(t) \tag{3}$$

where, $A(t)$, $e(t)$, $S(t)$ and $W(t)$ are the original time–series, the trend–term, the seasonal variation, and the short–term component, respectively. The sum of the trend–term and the seasonal variation corresponds to the baseline component.

In this work, we used a p value of 5 and an m value of 15 days for the baseline (Rao et al., 1997). To obtain the trend component, we used a value of $KZ_{(m,p)}$ equal to $KZ_{(365,3)}$ as used in Wise and Comrie (2005) for tropospheric ozone. By subtracting the value of $e(t)$ from baseline, the seasonal component $S(t)$ was obtained.

The KZ filter has several advantages because it can be applied directly to datasets that have missing values, without the need for special treatment for gaps. In the present study, the quantity of missing data corresponded to 7.4% of the database. Several authors such as Sebald et al. (2000), Wise and Comrie (2005), Papanastasiou et al. (2012), Kang et al. (2013) have used this type of filter.

2.4. Statistical analyses

With the 15-min data the mean hourly concentrations for NO/NO_x/NO₂/O₃ for each of the four seasons were calculated. Also, the mean daily variations of studied pollutants were calculated. Correlation analyses between hourly mean concentrations of O₃/NO/NO_x/OX/PM₁₀/CO and meteorological parameters were performed. A scatter plot of the variation of daily mean [NO₂]/[OX] as a function of NO_x was used to provide a better overview and interpretation of the relations between NO_x and the pollutants NO₂/NO_x/O₃.

3. Results and Discussion

3.1. Temporal-series variability of NO_x and O₃

The variability of atmospheric pollutant concentrations depends on specific emissions and general meteorological conditions. NO_x (NO₂+NO) is a primary contaminant and O₃ is a secondary contaminant that originates in the atmosphere through a set of complex reactions (Seinfeld and Pandis, 2006). Previous authors (Teixeira et al., 2009; Agudelo–Castaneda et al., 2013) studying surface O₃ in the MAPA have found that its concentrations are influenced by NO_x precursors and meteorological conditions (temperature and solar radiation). The present work examined time-series of atmospheric pollutant concentrations (NO, NO₂, NO_x and O₃) in a longer study period (4-years). The Kolmogorov–Zurbenko filter was employed to separate the seasonal component [*S(t)*] of the time-series and also to obtain the trend-term component [*e(t)*].

Figure 2a and 2b shows the trend-term of the time-series (2006–2009) for Canoas and Esteio regarding NO, NO₂, NO_x and O₃ concentrations [*e(t)*]. The trend was marked by two different situations: NO₂ decrease in Canoas and NO increase in Esteio. In Canoas (Figure 2a), NO_x concentrations were dominated by NO₂ concentrations, indicating a significant contribution of NO₂. Additionally, NO₂ and NO_x concentrations in Canoas (Figure 2a) show a decrease from 2007 to the end of the studied period. In Esteio (Figure 2b) was observed a similar behavior for NO₂, although was a minor decrease, possibly, due to the processes modifications of a refinery located in the study area. These modifications, such as equipment improvements and partial replacement of fuel oil by refinery gas, resulted in lower NO_x emissions from this stationary source. Also, in 2007 the frequency of wind speed <1 m s⁻² was higher (frequency: 52.4%) than in 2006. Thus, lower wind speeds may have increased the influence of local emission sources.

Elevated NO_x and NO concentrations were observed in Esteio (Figure 2b), in all the studied period. Moreover, this site showed higher NO concentrations than Canoas, which can be attributed to their stronger vehicular influence, characterized by heavy-duty fleet, in Esteio. This vehicular influence in the study area, especially of diesel-fueled vehicles, was evidenced in previous studies (Teixeira et al., 2008; Teixeira et al., 2009; Feltes et al., 2010; Teixeira et al., 2011; Teixeira et al., 2012; Agudelo–Castaneda et al., 2013).

The O₃ trend-term of the sampling sites showed a different behavior (Figure 2a and 2b). Figure 2a showed increased levels of O₃ concentration since 2007 in Canoas, probably due to decreased levels of NO and, consequently, a lower O₃ consumption,

producing an accumulation of tropospheric O₃. In Esteio (Figure 2b), a different behavior was observed, a decreased O₃ concentration since 2007. As explained above, Esteio had increased NO and NO_x concentrations levels that may cause an O₃ reduction. In a NO_x-limited atmosphere (with high NO_x concentrations) O₃ may depend on the overall level of NO_x (Seinfeld and Pandis, 2006). Also, O₃ ambient concentration is strongly influenced by diurnal fluctuation of NO₂ and the ratio of NO₂ to NO (Sebald et al., 2000).

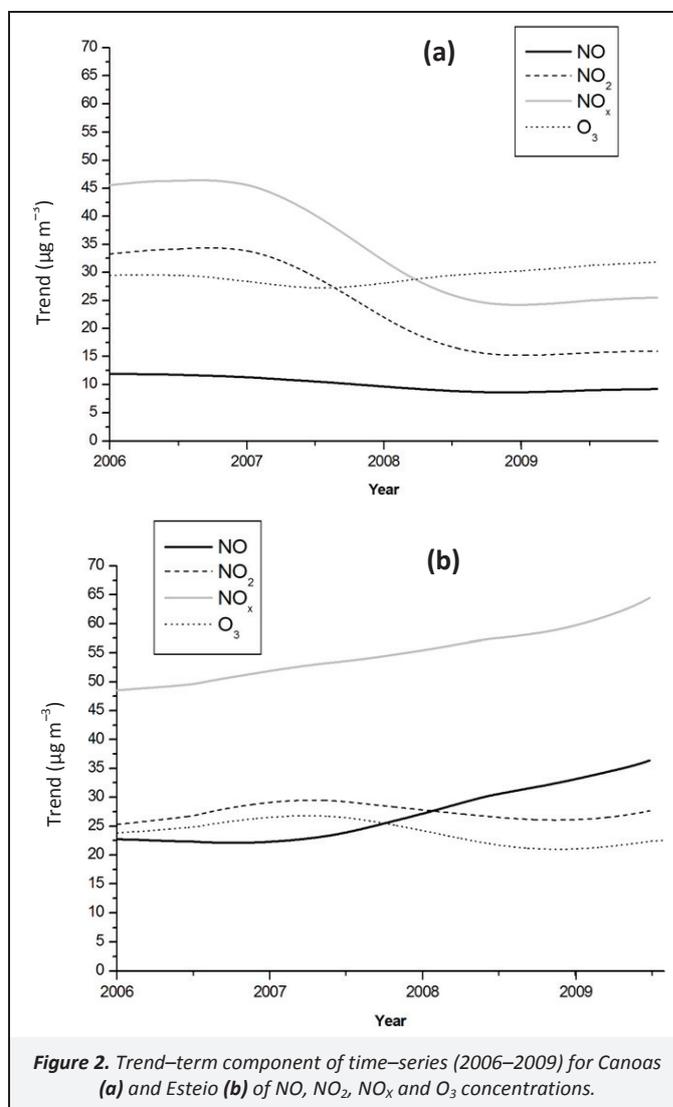


Figure 2. Trend-term component of time-series (2006–2009) for Canoas (a) and Esteio (b) of NO, NO₂, NO_x and O₃ concentrations.

Figure 3a and 3b shows the seasonal component of the time-series (2006–2009) of NO, NO₂, NO_x and O₃ concentrations for Canoas and Esteio. Overall, it can be observed that at both sites the values of NO, NO₂ and NO_x were above average from May to October of each year. These months corresponded to the colder seasons of the year: winter and autumn (Figure 3a and 3b). Below average values of these pollutants (NO, NO₂, NO_x) were observed between November and February, which corresponded to the warmer seasons of the year: spring and summer. O₃ (Figure 3a and 3b) showed an opposite behavior, with concentrations below average in the colder months (winter and autumn) and above average in the warmer months (spring and summer).

The seasonal variation of these pollutants may be better assessed in the Figure 4. Figure 4 shows the mean concentration of NO, NO_x, NO₂ and O₃, in winter, spring, summer, and autumn in Canoas and Esteio. In general, levels of nitrogen oxides (NO, NO₂, NO_x) concentrations in the cold seasons (autumn and winter) and of O₃ in the warm seasons (summer and spring) were higher.

Greater O₃ concentrations during spring and summer were due to favorable temperature and abundance of solar radiation, thus promoting photochemical reactions. The lower O₃ concentrations during the colder months may be attributed to the presence of higher concentrations of NO, NO₂ and NO_x and to specific weather conditions such as lower solar radiation, lower mixing layer, and to weak winds (Notario et al., 2012). In these colder days, the photochemical formation of O₃ is inhibited by the lack of intense solar radiation (Sadanaga et al., 2008; Geddes et al., 2009).

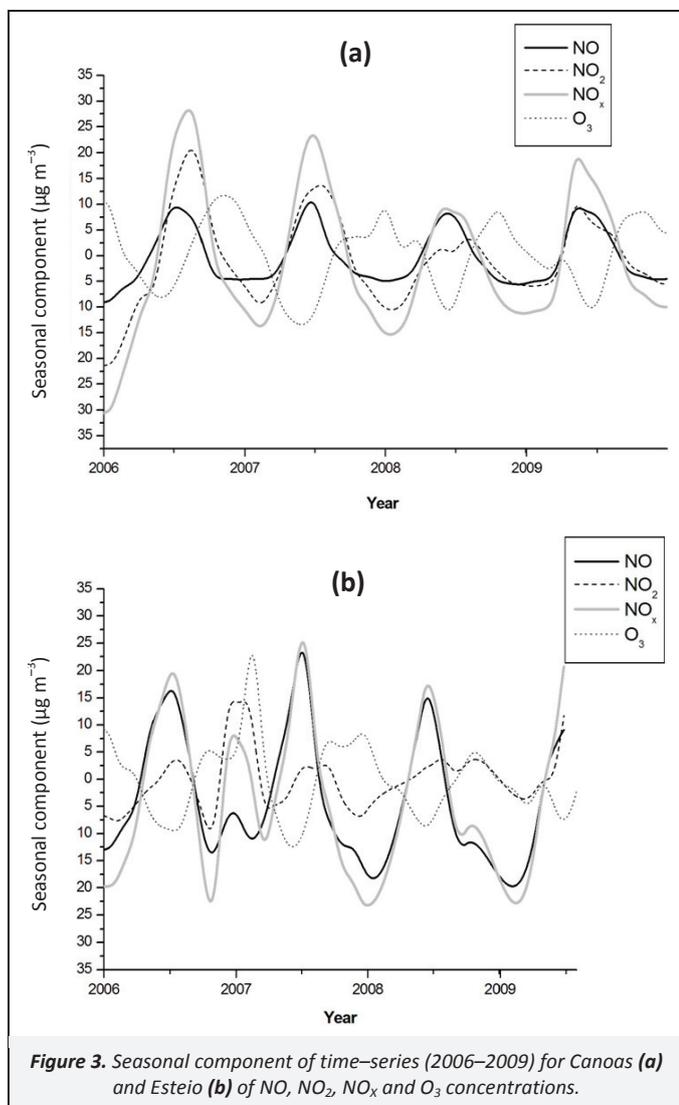


Figure 3. Seasonal component of time-series (2006–2009) for Canoas (a) and Esteio (b) of NO, NO₂, NO_x and O₃ concentrations.

3.2. Daily variations

Figure 5 shows the daily variation of the hourly mean concentrations of NO, NO₂, NO_x, OX, CO, and O₃ from 2006 to 2009 for Canoas and Esteio. NO₂ and O₃ can be observed together as OX (OX=NO₂+O₃), i.e., the total amount of photochemical oxidants. In fact, OX represents better, as it is less sensitive to emissions and its uncertainties. OX is not influenced by the rapid photo-stationary balance between NO, NO₂, and O₃ (Monteiro et al., 2005). In both sites, OX concentration incremented slowly after sunrise (Figure 5), reached a maximum during the day (Canoas: 74.23 µg m⁻³; Esteio: 70.64 µg m⁻³), and decreased until the next morning. OX concentration increase is due to photochemical O₃ formation. Some authors (Han et al., 2011) have reported that OX variation during daytime and nighttime would be expected, if the photochemical processes have an influence on OX levels in polluted areas. The variation of surface O₃, within a day, may be

helpful in delineating the processes responsible for O₃ formation at a particular location (Singla et al., 2011).

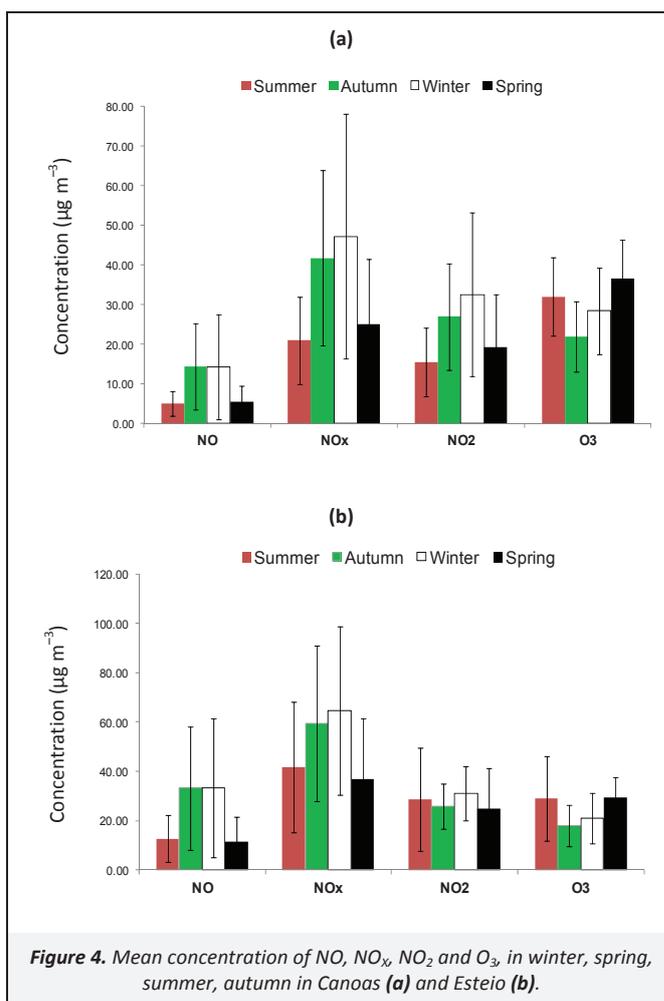


Figure 4. Mean concentration of NO, NO_x, NO₂ and O₃, in winter, spring, summer, autumn in Canoas (a) and Esteio (b).

It may be seen in Figure 5, that NO as well as CO increase at 6:00 at both sites, along with an increase in emissions from motor vehicles or, possibly, industrial activities, showing their highest concentrations at 8:00. As explained before, the two sites (Canoas and Esteio) of the study area has a strong vehicular influence, especially Esteio. Hence, NO mainly emitted by vehicle exhausts is present in elevated concentrations. NO (see Figure 5) showed morning peak values of 28.51 µg m⁻³ in Canoas and 74.54 µg m⁻³ in Esteio, at 8:00. NO₂ peak concentrations were 32.25 µg m⁻³ and 35.06 µg m⁻³ in Canoas and Esteio, respectively, at 10:00. There is a displacement of about 2 h in the morning between NO and NO₂ peaks (Figure 5). In the morning, NO₂ is produced by oxidation of NO (Jenkin and Clemitshaw, 2000), as NO may be converted in NO₂ in the presence of peroxi radicals (Dallarosa et al., 2007). CO showed peak values of 0.60 ppm at Canoas and 0.74 ppm at Esteio in the morning, and 0.66 ppm (Canoas) and 0.82 ppm (Esteio) in the late afternoon (18:00) during the rush hour. At night, concentrations of NO, NO₂ and CO exhibited a slight increase caused by the rise of vehicular traffic during the rush hour (18:00) and the influence of the stability of the nocturnal boundary layer. At this time, NO₂ reached peaks at 18:00 (36.18 µg m⁻³) and 20:00 (30.91 µg m⁻³) for Esteio and Canoas, respectively. These concentrations were similar to the peaks exhibited in the morning. Jenkin and Clemitshaw (2000) reported that at night the OH radical can be ignored since it is produced mainly from the photolysis of stable molecules. Therefore, NO₂ cannot be photolyzed to regenerate NO, or removed by reaction with OH, which will react with O₃ to form NO₃, thereby removing O₃.

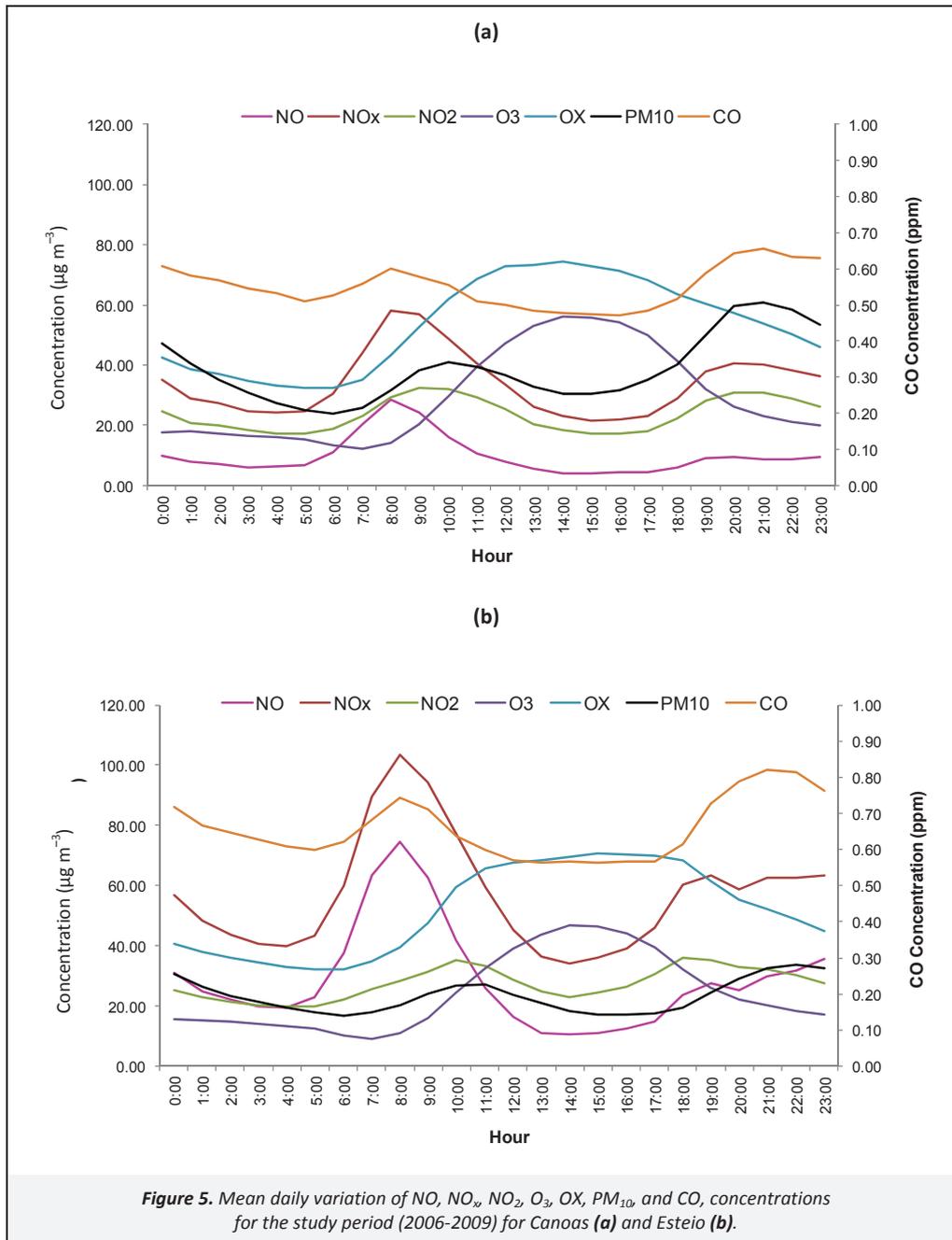


Figure 5. Mean daily variation of NO, NO_x, NO₂, O₃, OX, PM₁₀, and CO, concentrations for the study period (2006–2009) for Canoas (a) and Esteio (b).

Likewise, Figure 5 exhibits an increase in O₃ concentrations during the day, beginning at 8:00 and reaching its maximum at 14:00 in Canoas (55.96 $\mu\text{g m}^{-3}$) and Esteio (46.71 $\mu\text{g m}^{-3}$). NO is converted to NO₂ via reaction with O₃, and during daytime hours NO₂ is converted back to NO as a result of photolysis, which leads to the regeneration of O₃ (Han et al., 2011). Han et al. (2011) reported similar results, where O₃ in urban atmospheres reached peaks during the day, usually at 14:00–15:00, when there is a maximum in the intensity of solar radiation and temperature. This increase is probably marked by photolysis of NO₂, and expansion of the height of the boundary layer during the day, that can result in the mixing of O₃ due to thermal stratification and heat transfer by convection to the surface from air at higher altitudes (Swamy, et al., 2012). After reaching the peak concentration at 14:00, O₃ concentration reduces slowly due to the decrease in photochemical activity. The pattern observed in the present study is in agreement with previous works done in the same study area (Agudelo-Castaneda et al., 2013).

Canoas O₃ concentrations (see Figure 5) are slightly higher than in Esteio, probably because concentrations of O₃ precursors (NO, NO_x) in Canoas are lower. As explained above, Canoas has less traffic influence than Esteio. Also, Esteio is located downstream of the prevailing winds of Alberto Pasqualini oil refinery (Teixeira et al., 2009; 2012).

OX concentrations in Canoas and Esteio (Figure 5) were marked by NO₂ concentrations, especially in the early morning hours when concentrations raised mainly due to increase of vehicular traffic. Higher OX concentrations occurred in the afternoon, thus revealing an influence of photochemical processes (Han et al., 2011; Notario et al., 2012). At night, OX decreases due to the absence of solar radiation. This lack of radiation hinders the formation of NO₂ and O₃ by photolytic reactions, as well as the reactions of NO₂ with NO₃, and of NO₂ with O₃ (Jenkin and Clemitshaw, 2000).

The daily CO concentrations (Figure 5) exhibited a similar behavior for the two studied sites, indicating influence of gasoline–fueled vehicles. CO concentration increased between 6:00 and 9:00; also in the late afternoon (18:00) during the rush hour extending into the night. Even after the CO decrease (after 20:00), this and other pollutants maintain high concentrations during the night due to the formation of the nocturnal boundary layer (NBL) near the surface, trapping these pollutants in the lower troposphere. The observed behavior of NO and CO (increase of emissions at 6:00 at both sites) is characteristic of urban areas with the influence of mobile sources (Raga et al., 2001).

The data reported in the present study are consistent with those of several studies (Park et al., 2008; Hagler et al., 2009; Teixeira et al., 2009; Carslaw et al., 2011), which report the influence of vehicle emissions in the concentration increase of some pollutants, mainly nitrogen oxide and CO.

3.3. Association of NO, NO₂, NO_x, PM₁₀, CO, O₃, OX with meteorological parameters

Tables 2 and 3 show the correlation coefficients between hourly pollutant concentrations (NO, NO₂, NO_x, PM₁₀, CO, O₃, OX) and meteorological parameters, for Canoas and Esteio sites. Positive correlations (>0.5) were found between nitrogen oxides (NO, NO₂, NO_x) and CO, evidencing that these pollutants had the same source and confirming the influence of mobile sources. Nitrogen oxides (NO, NO₂, NO_x) presented a significant correlation with O₃ (<0.5), although inverse. These results are similar to those obtained by He and Lu (2012). For being a photochemical pollutant, O₃ also had a significant correlation with solar radiation and temperature, for both studied sites. These relationships of O₃ have also been reported in the studies of Teixeira et al. (2009) and Pudasainee et al. (2006). In addition, the results of the present study showed OX correlation with solar radiation and ambient temperature, indicating the influence of photochemical processes on this pollutant in urban areas (Han et al., 2011).

Table 2. Pearson correlation coefficients between hourly mean O₃, NO, NO_x, OX, PM₁₀ and CO concentrations and meteorological parameters (ambient temperature, wind velocity, solar radiation and relative humidity) of Canoas

	PM ₁₀	OX	NO	NO _x	NO ₂	O ₃	CO	W. V. ^a	S. R. ^b	A. T. ^c	R. H. ^d
PM ₁₀	1	0.120 ^e	0.194 ^e	0.270 ^e	0.269 ^e	-0.088 ^e	0.241 ^e	-0.030 ^e	-0.016 ^f	0.113 ^e	-0.108 ^e
OX		1	0.107 ^e	0.413 ^e	0.574 ^e	0.652 ^e	0.173 ^e	0.187 ^e	0.405 ^e	0.311 ^e	-0.532 ^e
NO			1	0.849 ^e	0.531 ^e	-0.364 ^e	0.419 ^e	-0.321 ^e	-0.081 ^e	-0.224 ^e	0.155 ^e
NO _x				1	0.899 ^e	-0.343 ^e	0.519 ^e	-0.345 ^e	-0.090 ^e	-0.186 ^e	0.111 ^e
NO ₂					1	-0.247 ^e	0.488 ^e	-0.278 ^e	-0.077 ^e	-0.112 ^e	0.048 ^e
O ₃						1	-0.256 ^e	0.413 ^e	0.558 ^e	0.486 ^e	-0.682 ^e
CO							1	-0.111 ^e	-0.103 ^e	-0.041 ^e	0.064 ^e
W. V. ^a								1	0.198 ^e	0.190 ^e	-0.299 ^e
S. R. ^b									1	0.570 ^e	-0.627 ^e
A. T. ^c										1	-0.481 ^e
R. H. ^d											1

^a Wind Velocity

^b Solar Radiation

^c Ambient Temperature

^d Relative Humidity

^e Correlation is significant at the 0.01 level (2-tailed)

^f Correlation is significant at the 0.05 level (2-tailed)

Table 3. Pearson correlation coefficients between hourly mean O₃, NO, NO_x, OX, PM₁₀ and CO concentrations and meteorological parameters (ambient temperature, wind velocity, solar radiation and relative humidity) of Esteio

	PM ₁₀	OX	NO	NO _x	NO ₂	O ₃	CO	W. V. ^a	S. R. ^b	A. T. ^c	R. H. ^d
PM ₁₀	1	0.134 ^e	0.388 ^e	0.431 ^e	0.299 ^e	-0.127 ^e	0.441 ^e	-0.070 ^e	-0.064 ^e	-0.002	-0.037 ^e
OX		1	-0.069 ^e	0.235 ^e	0.673 ^e	0.666 ^e	-0.100 ^e	0.127 ^e	0.373 ^e	0.286 ^e	-0.520 ^e
NO			1	0.913 ^e	0.312 ^e	-0.408 ^e	0.544 ^e	-0.332 ^e	-0.156 ^e	-0.296 ^e	0.218 ^e
NO _x				1	0.673 ^e	-0.362 ^e	0.523 ^e	-0.356 ^e	-0.151 ^e	-0.236 ^e	0.168 ^e
NO ₂					1	-0.104 ^e	0.225 ^e	-0.226 ^e	-0.062 ^e	0.027 ^e	-0.036 ^e
O ₃						1	-0.253 ^e	0.169 ^e	0.562 ^e	0.474 ^e	-0.622 ^e
CO							1	-0.150 ^e	-0.197 ^e	-0.151 ^e	0.188 ^e
W. V. ^a								1	0.058 ^e	0.307 ^e	-0.171 ^e
S. R. ^b									1	0.473 ^e	-0.596 ^e
A. T. ^c										1	-0.484 ^e
R. H. ^d											1

^a Wind Velocity

^b Solar Radiation

^c Ambient Temperature

^d Relative Humidity

^e Correlation is significant at the 0.01 level (2-tailed)

^f Correlation is significant at the 0.05 level (2-tailed)

Furthermore, the results showed a significant, although <0.5, correlation between CO and O₃. This is due to the fact that in the atmosphere, CO is a major sink of hydroxyl radicals (OH), which are mainly generated by O₃ (Teixeira et al., 2009). Particles (PM₁₀) and NO_x had a significant correlation (coefficient <0.5) indicating that various sources with different emission rates, such as particle resuspension and some stationary sources were the major sources of these pollutants in Canoas and Esteio.

In the present study, wind speed showed a significant correlation with O₃ and an inverse correlation with nitrogen oxides in Esteio and Canoas (Tables 2 and 3). This relationship is explained by the fact that a higher wind speed (except for the very strong winds) enhances the dispersion and mixing of these atmospheric pollutants emitted at closer sources (i.e., at highways and stationary sources), thus optimizing the O₃ formation from precursors. These data show agreement with other studies, e.g. Jones et al. (2010) and Guerra and Miranda (2011).

The correlations of nitrogen oxides (NO, NO₂, NO_x), PM₁₀ and CO with relative humidity (Tables 2 and 3) were significant at the 0.01 level. This can be attributed to the influence of the migration of new air masses over the study area (mainly polar air masses), which can bring clean atmospheric air and minimize the cumulative concentrations of these pollutants (background). These results are similar to those reported in other studies (Elminir, 2005; Mavroidis and Iliá, 2012).

Also, Tables 2 and 3 show the obtained negative correlation of O₃ with the relative humidity. This relationship can be explained by the fact that when relative humidity increases, the major photochemical paths for O₃ removal are reinforced (Reddy et al., 2012). However, high values of relative humidity may be associated with atmospheric instability and large cloud cover, which can slow down photochemical processes, with O₃ being

depleted by wet deposition (Nishanth et al., 2012). As well by the fact that both (O₃ and relative humidity) have an opposite behavior; relative humidity has its peak at night (with decreasing air temperature), while O₃ shows its minimum value due to the absence of solar radiation, and vice-versa. Agudelo–Castaneda et al. (2013) also reported this behavior. The work of Song et al. (2011) reported similar results, high relative humidity may retard the O₃ production to some extent.

Nitrogen oxides (mainly NO₂) and PM₁₀ exhibited a negative and a positive correlation (<0.5) with temperature, respectively. CO also correlated with temperature. This relationship may be explained by the fact that NO_x and CO favor the O₃ production in the presence of sunlight and high temperatures (Jacob and Winner, 2009).

3.4. Relationship between NO₂, NO_x and OX

In some studies, analysis of the [NO₂]/[OX] ratio values have been used to explore the ground-level O₃ concentration variations and the relationship between OX and NO_x data (Clapp and Jenkin, 2001; Han et al., 2011). A photostationary state relationship exists between NO, NO₂ and O₃ (Clapp and Jenkin, 2001; Han et al., 2011). Based on this, it can be possible to infer an expected variation. Figure 6 shows the linear regression analysis with daily mean [NO₂]/[OX] ratio as a function of NO_x for the sampling sites (Canoas and Esteio). Data reveal that for lower values of the [NO₂]/[OX] ratio, there are low values of NO_x, implying that in these instants OX concentrations are predominantly marked by high O₃ concentrations. Also, with increasing NO_x concentrations, a great part of OX is in the form of NO₂. The high values of [NO₂]/[OX] can also be explained by the oxidation process of NO to NO₂ with concentrations of NO_x being marked mainly by the concentration of NO₂.

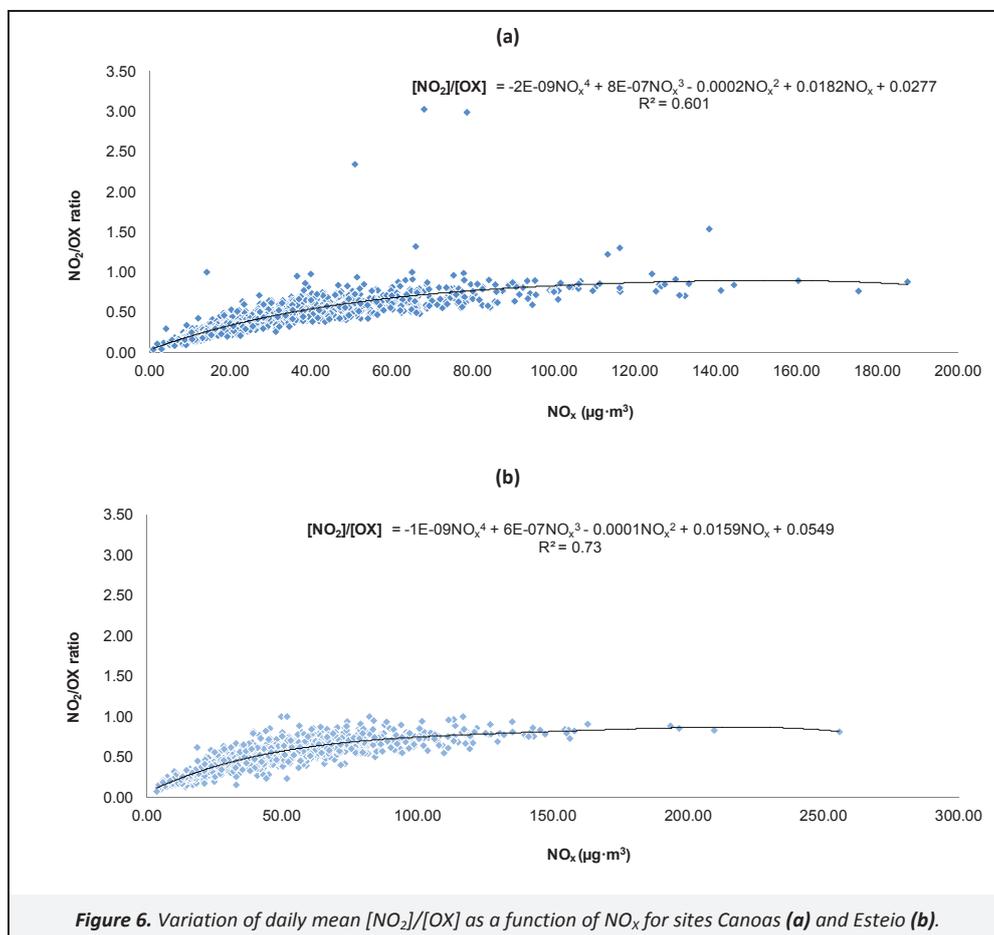


Figure 6. Variation of daily mean [NO₂]/[OX] as a function of NO_x for sites Canoas (a) and Esteio (b).

Similar equations and regression coefficients values were obtained for both sampling sites, despite the fact that Canoas had higher NO_x concentrations than Esteio. Equations showed intercept values of 0.0277 μg m⁻³ and 0.0549 μg m⁻³ for Canoas and Esteio, respectively. However, further studies should be conducted to understand the precise relationship between NO, NO₂ and O₃ and obtain fitted functions.

4. Conclusions

The Kolmogorov–Zurbenko filter proved to be a useful tool in the temporal analysis of O₃, NO, NO₂ and NO_x concentrations in Canoas and Esteio. By applying this filter, it was possible to decompose the time-series in the short-term, trend-term and seasonal component. The trend-term allowed analyzing the variation in the concentration of these pollutants due to local emissions. In this analysis, NO increased in Esteio due to a stronger vehicular influence (light and heavy-duty fleet, traffic congestion, and slow vehicle speed), being in accordance with works done in the study area. In general, trends for NO_x did not show significant changes in concentrations.

The seasonal component showed concentrations of NO, NO₂ and NO_x above average during the winter, due to adverse meteorological conditions, while O₃ concentrations were above average during the summer, due to increased photochemical activity.

Positive correlations (>0.5) between nitrogen oxides (NO, NO₂, NO_x) and CO indicate that these pollutants come from the same source, evidencing the influence of mobile sources in Esteio and Canoas.

PM₁₀ and NO_x showed a significant correlation, although with a coefficient <0.5, suggesting that resuspended particles and some stationary sources as major sources of these pollutants, at Canoas and Esteio.

In the correlation of NO₂/OX with NO_x it was observed that for low NO₂/OX values, there are low NO_x values, indicating that concentrations are predominantly marked by O₃. With high values of NO₂/OX, NO_x concentrations were marked mainly by NO₂ concentrations, which might be explained by the oxidation process of NO to NO₂.

The filter Kolmogorov–Zurbenko, the statistical technique, allowed the evaluation of the pollutant concentrations variations due to anthropogenic sources that are influencing the study area.

It is suggested that future studies should be conducted in order to understand precisely the relationship between NO, NO₂, O₃ and meteorological variables with associated emission sources.

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