Temporal variations of SO$_2$ in an urban environment

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ABSTRACT

Sulfur dioxide (SO₂) is considered the most widespread pollutant that threatens human and environmental health. Seasonal variation revealed higher levels of SO₂ on cold days. The variations of the day revealed a higher concentration of SO₂ indicating traffic influence, especially during peak hours. The analysis of hourly/daily/annual means identified an increasing trend in SO₂ concentrations, implying that emission control systems and the technological improvement of engines and fuels were not sufficient and, therefore, points to the need for better subsidy mechanisms for the control of pollutants and effective emission reduction strategies, environmental agencies, should prioritize considering local realities.

Keywords: Sulfur dioxide, Air pollution, Statistical analysis

1. INTRODUCTION

Sulfur dioxide (SO₂) is an atmospheric pollutant whose emission an urban environment has been associated with industrial processes and burning of fossil fuels. Its presence contributes to the formation of sulfuric acid and sulfate-containing aerosols, removed from the atmosphere by both dry deposition and wet deposition (rainwater) [Wayne, 1991; Seinfeld and Pandis, 2006; Souza et al., 2017].

As a type of important air pollutants, SO₂ critically affects the global environment, climate change and public health. SO₂ has become one of the most popular research topics in recent decades to examine its changes in some of the most polluted regions of the world [M. Chin, R. Rood, S. J. Lin et al., 2000; B. Denby, I. Sundvor, M. Cassiani et al., 2010; V. E. Fioletv, C.A. Mclinden, N. Krotkov, M. D. Moran, and K. Yang, 2011; C. Lee, R. V. Martin, A. Van Donkelaar et al., 2011; Z. Klimont, S. J. Smith, and J. Cofala, 2013; J. L. Hand, B.A. Schichtel, W. C. Malm et al., 2012; N. Theys, I. De Smedt, J. Gent et al., 2015; H. He, K. Y. Vinnikov, C. Li et al., 2016]. In addition, SO₂ is the pollutant most closely associated with development in industrialization and urbanization economy, recognized as a primary combustion product of fossil fuels, such as coal, fuel oil, gasoline and diesel (Yang et al., 2017).

Drastic environmental measures have been implemented in recent years to reduce SO₂ emissions, especially from major industrial sources. However, it has not shown significant reductions in some countries due to the burning of a large amount of fossil fuels resulting in significant emissions of SO₂ (Meng et al., 2010), with the corresponding direct impact on the population. These impacts occur in places with stationary sources, high vehicular traffic; especially in urban areas, such as the region of Campo Grande, MS. Although vehicles have been shown to be the main contributors to SO₂ emissions, stationary sources located in the Campo Grande region, oil refinery, thermo-electric and coal-fired power plants are probably related to SO₂ emission levels.

This evidence has led to the development and implementation of numerous legislation regulating different aspects of air pollution, such as air quality limit values and guide values for SO₂. In particular, the EU Council Directive for SO₂ (89/427 / EEC) implemented in 1993 specified that the annual average value should not exceed 80 mmg/m² with an associated value for suspended particulates of 150 mg/m³ and that the daily average value of 250 mmg/m² for SO₂ should not be exceeded for more than three consecutive days (EU, 1989). Other stricter directives, 1999/30 / EC and 2008/50 / EC (EU, 2008), have amended Directive 89/427/EEC (EU, 1999).

While USEPA, 2008 and 2012 recommend values of 75 ppb and 0.5 ppb for primary and secondary standards respectively. Brazilian legislation, on the other hand, is less demanding recommending an average annual concentration of 80 μg / m³ of air and an average concentration of 24 hours of 365 μg / m³ of air, which cannot be exceeded more than once a year.

Several studies have shown the correlation between SO₂ concentration and meteorological parameters (Landim et al, 2018) (Luvsana et al., 2012), (Akpinar et al., 2008) (Bridgman et al., 2002), ([Et al., 2010], [Wang et al., 2011], [Afan et al., 2008]). Sulfur dioxide enters the atmosphere through a series of anthropic activities and natural phenomena. Large quantities are released directly into the troposphere, resulting from the burning of fossil fuels, and to a certain extent by the oxidation of organic matter in the soil and by the burning of biomass (Eisinger and Burrows, 1998).

The purpose of the present work was to evaluate the seasonal and temporal variability of SO₂ in 2016.

2. MATERIAL AND METHODS

Study area and observational data

Campo Grande is the capital of the state of Mato Grosso do Sul (MS), is located in the center of the state, south of the Center-West region of Brazil. Geographically, the municipality of Campo Grande is located near the borders of Brazil with Paraguay and Bolivia. It
is located in the latitude of 20°26'34" South and longitude of 54°38'47" West. It occupies a total area of 8,096,051 km², which corresponds to 2.26% of the total area of the State. The urban area totals 154,45 km². The main pollution problems in the city are attributed to vehicular traffic, the rate of increase in construction activity, garbage deposits, the use of small power generators used to supply the lack of electricity, and intentional cleaning of land.

**Observational Dataset**

Data were collected by continuous air monitoring stations on the campus of the Federal University of Mato Grosso do Sul (UFMS) in Campo Grande (Figure 1). These facilities provide measurements of hourly concentrations of pollutants such as SO₂, and also provide measurements of weather variables, such as air temperature, wind speed, wind direction, and relative air humidity. The data analyzed were obtained during the period of one year in 2016.

Atmospheric SO₂ was measured using automated sequential analyzers using the ultraviolet fluorescence radiation technique, model AF21M from Environnement S.A and model AF22M from Environnement S.A Table 1.

**Table 1** Instrumentation used to measure atmospheric pollutants and meteorological parameters during the year 2016 in Campo Grande

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model of the instrument</th>
<th>Detector</th>
<th>PA Equivalent Method Number</th>
<th>error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Thermo Environmental 43 C</td>
<td>Fluorescence</td>
<td>EQSA-0486-060</td>
<td>1 ppb</td>
</tr>
<tr>
<td>WS</td>
<td>Met One 010C</td>
<td>Anemometer</td>
<td>n.a.</td>
<td>1%</td>
</tr>
<tr>
<td>WD</td>
<td>Met One 020C</td>
<td>Potentiometer</td>
<td>n.a.</td>
<td>3°</td>
</tr>
<tr>
<td>T</td>
<td>Met One 060A</td>
<td>Multi-stage thermistor</td>
<td>n.a.</td>
<td>0.5 °C</td>
</tr>
<tr>
<td>AP</td>
<td>Met One 090D</td>
<td>Barometric sensor</td>
<td>n.a.</td>
<td>1.35 mbar</td>
</tr>
<tr>
<td>RH</td>
<td>Met One 083E</td>
<td>Capacitance sensor</td>
<td>n.a.</td>
<td>2%</td>
</tr>
<tr>
<td>SR</td>
<td>Met One 095</td>
<td>Pyranometer</td>
<td>n.a.</td>
<td>1%</td>
</tr>
</tbody>
</table>

**Figure 1** Location of the Municipality of Campo Grande in the State of Mato Grosso do Sul, and the continuous air monitoring station located on the campus of the Federal University of Mato Grosso do Sul, Campo Grande, MS.

**Data Analyses**

The relationship between SO₂ concentration and meteorological parameters is evaluated using (a) Pearson’s correlation and then (b) multiple linear regression analysis for the 2016 period. The Pearson correlation that reflects the degree of linear relationship between two variables and ranging from +1, which is a perfect positive linear relationship between two variables to -1, between the
mean daily concentrations of SO\textsubscript{2} and meteorological parameters including wind speed, temperature and relative humidity. A general linear regression model has the following regression equation:

\[ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_k X_k + \epsilon, \]

where \( k \) is the number of variables, \( X \) are regressors, \( \beta \) are the estimators, and \( \epsilon \) is the standard error.

The values of the constants and the coefficients are determined by the least squares method, which minimizes the error. SO\textsubscript{2} is considered as dependent variable (\( Y_i \)) as meteorological parameters, such as wind speed (\( x_1 \)), temperature (\( x_2 \)), relative humidity (\( x_3 \)), wind directions are considered as independent variables. A commonly used measure of the fit of a linear model is \( R^2 \). This is the ratio the total variability in the dependent variables that is explained by the regression equation. A significance level of 0.05 with bilateral distribution was used to determine statistical significance in our models (Cuhadaroglu and Demirci, 1997).

**Statistical Analyses**

Statistical analyses consisted of the calculation of the position and dispersion measures of the variables (hourly, monthly and annual averages), line graphs elaboration, moving average filtering, principal component analysis (PCA), cluster analysis and correlation coefficient of Pearson.

The ACP is a multivariate data reduction technique in which the main objective is to construct a linear combination of the original variables, generating new orthogonal components that represent and capture the variability of the original set of variables. This method was used to reduce the number of variables, generating new components by capturing the dependencies between the variables (Johnson; Wichern, 2002; Mingoti, 2005), thus seeking a natural relationship, with independence or dependency analysis, between variables.

In addition, the ACP consists of calculating the eigenvalues and respective eigenvectors of an array of variances and covariates or a matrix of correlation coefficients between variables. The latter matrix is more adequate for the present study because of the units of unequal measures and the variance presents a great difference between the variables (Johnson; Wichern, 2002; Mingoti, 2005; Willks, 2006). Its application occurs through a linear transformation of “\( m \)” original variables into “\( n \)” new variables, so that the first new variable (1st component) is responsible for the largest variation in the data set, and so on, until that all the variation of the set has been captured (Mingoti, 2005; Willks, 2006).

**3. RESULTS**

In this study, we observed an increasing trend in hourly SO\textsubscript{2} levels over time in Campo Grande. These trends are not consistent with other published trends in SO\textsubscript{2} levels (Hecq et al., 1997, WHO, 2006, EEA, 2010, Aphekom Summary Report, 2011, US_EPA, 2012) and Anttila and Tuovinen (2010).

Cuhadaroglu and Demirci, 2018, analyzed trends in sulfur dioxide (SO\textsubscript{2}) concentrations in annual and winter periods (1990-2009) in Aegean, Denizli, Izmir, Afyon, Aydin, Kutahya, Manisa and Usak cities, using Spearman’s Mann-Kendall, Sen and Rho linear regression methods to evaluate the long-term increase or decrease in SO\textsubscript{2} concentration. Trend analyzes of linear regression analyzes showed that decreasing trends in SO\textsubscript{2} concentrations were observed in Izmir and Kutahya. According to the Mann-Kendall, Sen and Rho tests of Spearman, a downward trend was observed for the concentrations of SO\textsubscript{2} in Denizli. Constant reductions in SO\textsubscript{2} concentrations were determined in Izmir. Downward trend in SO\textsubscript{2} concentrations was observed in Afyon. The increase in the winter season trend of SO\textsubscript{2} concentrations was determined in Aydin. There was a downward trend in SO\textsubscript{2} concentrations in Kutahya. Decreasing tendency of SO\textsubscript{2} concentrations was observed in Manisa. The downward trend in annual SO\textsubscript{2} concentrations was determined in Usak. The probability distribution of the data was identified as lognormal according to the Kolmogrov-Smirnov and Anderson-Darling tests.

Some of the differences observed between cities may be due to the various EU legislation being implemented on different dates in their respective cities, such as the EU Integrated Pollution Prevention and Control Directive (EU, 1996), the multi-pollutant in Gothenburg. The 1999 Protocol to the LRTAP Convention (UNECE, 1999), the EU Directive on National Emissions (EU, 2001b) and the EU Council Directive 2001/80 / EC on the limitation of emissions from large combustion plants (EU, 2001a) may also have contributed to the differences between cities.
In Campo Grande, we observed a morning SO$_2$ peak (11:00 hours); we believe this reflects traffic-related pollution due to “rush hour”; and a nocturnal peak (22:00 hours) that possibly reflects a combination of traffic and domestic space heating. This common observation suggests that sources of combustion related to traffic and heating are boosting diurnal patterns. These bi-modal patterns, with a distinct peak the morning and evening, are similar to those reported by Zhao et al. (2009) for PM2.5 in Beijing and for NOx by Makra et al. (2010) in Szeged, Hungary, and Freiburg, Germany. Jo and Park (2005) reported that the maximum levels of SO$_2$ in Daegu, South Korea, coincided with morning and afternoon peak hours.

The late afternoon SO$_2$ levels observed in this study can be partially explained by the dilution of the ambient concentrations of SO$_2$ due to the growth at midday of the blend layer together with a reduced traffic density compared to the peak times. We believe that the differences in the dynamics of the boundary layers of the atmosphere, due to different climatic and geographical conditions. Clearly, there are likely to be other sources of combustion other than traffic that contribute to the observed SO$_2$ levels, such as industries (Figure 2 & 3).
Statistical evaluation and effect of meteorological factors on pollutant levels

Table 2 shows the descriptive analysis of the data

<table>
<thead>
<tr>
<th>Variable</th>
<th>Count</th>
<th>Mean</th>
<th>StDev</th>
<th>Minimum</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_2)</td>
<td>8758</td>
<td>16.884</td>
<td>18.506</td>
<td>0</td>
<td>1.3</td>
<td>46.6</td>
</tr>
<tr>
<td>T</td>
<td>8758</td>
<td>17.792</td>
<td>4.912</td>
<td>0</td>
<td>17.4</td>
<td>33.8</td>
</tr>
<tr>
<td>RH</td>
<td>8758</td>
<td>82.148</td>
<td>18.287</td>
<td>14.9</td>
<td>89.3</td>
<td>98.5</td>
</tr>
<tr>
<td>AP</td>
<td>8758</td>
<td>913.77</td>
<td>11.22</td>
<td>909.3</td>
<td>913.8</td>
<td>925.8</td>
</tr>
<tr>
<td>WS</td>
<td>8758</td>
<td>19.036</td>
<td>10.618</td>
<td>0.1</td>
<td>1.8</td>
<td>7.6</td>
</tr>
<tr>
<td>WD</td>
<td>8758</td>
<td>146.43</td>
<td>74.83</td>
<td>4.3</td>
<td>146.55</td>
<td>354</td>
</tr>
<tr>
<td>SR</td>
<td>8758</td>
<td>126.91</td>
<td>212.86</td>
<td>0</td>
<td>0</td>
<td>973.5</td>
</tr>
</tbody>
</table>

Mean concentrations ranging from 1.69 ppb with a minimum value of zero and a maximum of 46.6 ppb were recorded, with an average peak between January, November and December (2.99, 2.16 and 3.12) ppb. The median concentrations were 1.3 ppb. These concentrations of SO\(_2\) can be attributed to the fact that sulfur dioxide comes from non-point sources scattered throughout the city, such as aerosols, fertilizers and emissions, which degrade plants. The maximum SO\(_2\) emission in the city was founded during the summer (January-March), where the average temperature reached 17.8°C (Fig. 2). These values are generally below the air quality standards recommended by the environmental agency and WHO. This result indicates that the city does not suffer from SO\(_2\) pollution and therefore the health of the population is not under serious threat of SO\(_2\) (Table 2).

In developed countries, data for the last two decades have clearly shown a downward trend for some major primary pollutants, especially SO\(_2\) (e.g. Rome, Paris), for Campo Grande there is a growing trend of SO\(_2\) for the series of data. However, there is an exceptional case where SO\(_2\) data from China’s urban areas are oversized. SO\(_2\) values for the three urban sites in Southwest China (Chongqing, Guiyang and Chengdu) ranged from 32 to 159 ppb, with an average of 114 ppb (Lei et al., 1997). Measures conducted by Karam and Tabbara in northern Lebanon (2004), in an industrialized area with cement plants, showed concentrations that reached 10 times the maximum observed by Lei et al. in China, Buenos Aires, Argentina, the average concentration is 7.5 ppb, in Sao Paulo, 6.8 ppb (Gurjar et al. (2008) and Landin et al., 2018 measured for Porto Alegre high mean SO\(_2\) concentrations (~ 15 μg (6 μg m\(^{-3}\)), Canoas (3 μg m\(^{-3}\)), and Gravataí (2 μg m-3), and for the metropolitan regions of Porto Alegre: Triunfo (13 μg m\(^{-3}\)), Esteio (6 μg m\(^{-3}\)), Canoas (3 μg m\(^{-3}\)), and Gravataí (2 μg m\(^{-3}\)).

With the exception of such unusual data sets, the most studied results showed that SO\(_2\) concentration levels in urban areas do not exceed a range of 10 ppb. In fact, the lowest value of SO\(_2\) in urban areas was observed in Lompoc (USA) (1 ppb) (USEPA, 2008).

Overall results clearly show that occurrences of higher SO\(_2\) values tend to focus mainly on urbanized areas affected by industrial activities, while rural or suburban areas tend to register fairly low SO\(_2\) values. The background concentrations observed in Campo Grande are low and do not seriously affect human health. In addition, since no significant source of SO\(_2\) is present in the internal environment, the internal level of SO\(_2\) is generally much lower than the external level.

Statistical evaluation and effect of meteorological factors on pollutant levels

As meteorological parameters play an important role in the dispersion of pollutants emitted into the atmosphere, the effects of temperature, humidity, air pressure, wind speed, wind direction and solar radiation on concentrations of the studied gases were evaluated using multiple regression analysis.

The mean correlation coefficients between the concentrations of the six variables presented positive values for temperature (r = 0.042, n = 8767); wind speed (r = 0.029, n = 8758); direction of the winds (r = 0.080, n = 8758) and solar radiation (r = 0.035, n = 8758) and negative for air humidity (r = 0.023, n = 8767). Means and a higher wind speed is required to transport the pollutants from the emission source to the sampling site.

The SO\(_2\) concentration shows a negative correlation, explaining the higher concentrations of SO\(_2\) obtained on colder days and its relation with the higher occurrence of winds during the cold days. Humidity can also act in the ambient SO\(_2\) and generate acid rain. These situations generally showed that SO\(_2\) concentrations increased due to high relative humidity (Luvsan et al., 2012). Akpin et al. (2008) reported an inverse relation of relative humidity and concentrations of pollutants, since SO\(_2\) controls its rate of absorption. Relative humidity can also act on air pollutants and form secondary pollutants such as acid rain. The variation of SO\(_2\) with relative air humidity shows that SO\(_2\) depending on the site, can increase or decrease with increasing humidity (Luvsan et al., 2012). In addition, lower temperature and height of the boundary layer and weaker winter winds may further exacerbate environmental pollution (Li et al., 2017).
In the present study, the relationship between the concentrations of the monitored air pollutant, SO$_2$ and meteorological factors such as wind speed, temperature, relative humidity, solar radiation and atmospheric pressure according to the results of linear regression analysis a moderate and weak level of relationship between atmospheric pollutant concentrations and factors.

**Principal Component Analysis (PCA)**
To identify the sources of pollutants, PCA was applied with Varimax rotation. All major components with eigenvalues $>1$ were retained as suggested by the Kaiser criterion. Table 4 shows that PCA produced two factors that explain about 53% of the total variation and the factor loads for these two components extracted after the rotation. The first factor was composed of SO$_2$, atmospheric temperature (T), solar radiation (SR) and wind speed (WS) and this explains 36.4% of the data variance. The second factor, formed by humidity, pressure and wind direction, explained 16.6% of the variance. Principal component analysis reveals that SO$_2$ formation is also governed by meteorological parameters (temperature, solar radiation, wind speed). In addition, a factorial load on the main components also confirms that the meteorological and SO$_2$ parameters follow an inverse relation with the humidity, pressure and direction of the winds.

Hierarchical analysis of clusters was used to identify groups of relatively homogeneous variables. Objects that belong to the same cluster are similar to the default selection criteria. The resulting clusters exhibit high internal homogeneity (within a cluster) and external homogeneity (between clusters). A cluster analysis was applied using the Ward method with Euclidean distances as a criterion for the formation of agglomerates. This form of cluster analysis is considered very ingenious, although it tends to create small clusters. Since the variables have a great number of differences in the sizing, the standardization was done before the computation. Figure 4 & 5 shows two clusters: (1) SO$_2$ - pressure, humidity and wind direction; (2) temperature, solar radiation and wind speed. It is observed, however, that clusters 1 and 2 group together implying, probably, their common source.

**Figure 4** Dendogram resulting from Ward’s method of hierarchical cluster analysis.

**Figure 5** Residual deviations and values observed as a function of the adjusted values, histogram of the response variable for the SO$_2$ adjustment model as a function of the studied year.

**Correlation matrix**
Pearson’s bivariate correlation coefficients within the measured and air pollutant parameters present results indicating that SO$_2$ has a positive correlation with solar radiation, atmospheric temperature, wind speed and negative correlation with relative humidity, pressure and wind direction. It is evident that the variation of the SO$_2$ in the surface is directly correlated to the atmospheric temperature and is inversely related to the humidity. The positive correlation between SO$_2$ and atmospheric temperature is due to
the fact that the radiation controls the temperature and, therefore, the efficiency of the photolysis will be greater. The negative correlation between surface SO$_2$ and moisture resides in the fact that when the humidity increases, the main photochemical pathways for SO$_2$ removal. Second, higher levels of moisture retard the photochemical process due to its association with higher cloud abundance, atmospheric instability and low solar radiation. In addition, surface SO$_2$ is depleted by the deposition of its molecules into water droplets (Londhe et al., 2008). The positive correlation between SO$_2$ and wind speed indicates SO$_2$ transport. Increasing wind speed implies increased air transport, so the influence of wind speed on primary pollutants may be different. In the case of primary pollutant, it acts as a diluting agent (Dragan, 2008).

Table 3 Rotated component matrix of SO$_2$ concentration in Campo Grande, ACP extraction, and varimax rotation, with Kaiser normalization.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2</td>
<td>0.073</td>
<td>0.644</td>
<td>0.42</td>
</tr>
<tr>
<td>T</td>
<td>0.874</td>
<td>0.004</td>
<td>0.764</td>
</tr>
<tr>
<td>RH</td>
<td>-0.908</td>
<td>-0.007</td>
<td>0.825</td>
</tr>
<tr>
<td>AP</td>
<td>-0.068</td>
<td>0.468</td>
<td>0.224</td>
</tr>
<tr>
<td>WV</td>
<td>0.434</td>
<td>-0.101</td>
<td>0.199</td>
</tr>
<tr>
<td>WD</td>
<td>0.054</td>
<td>-0.65</td>
<td>0.426</td>
</tr>
<tr>
<td>SR</td>
<td>0.865</td>
<td>0.032</td>
<td>0.75</td>
</tr>
<tr>
<td>Variance</td>
<td>2.5391</td>
<td>1.0681</td>
<td>3.6073</td>
</tr>
<tr>
<td>%</td>
<td>0.363</td>
<td>0.153</td>
<td>0.515</td>
</tr>
</tbody>
</table>

The regression equation is

SO$_2$ = 1.26 + 0.0172 T + 0.00308 RH - 0.00111 WD + 0.000258 SR

with error=1.02; 8758 cases used, 1 cases contain missing values

Table 4 Results of the regression analysis for the model with the values of intercept (constant), temperature, air humidity, pressure, wind velocity, wind direction and solar radiation.

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coef</th>
<th>SE Cef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1.2592</td>
<td>0.2416</td>
<td>5.21</td>
<td>0</td>
</tr>
<tr>
<td>T</td>
<td>0.017163</td>
<td>0.006153</td>
<td>2.79</td>
<td>0.005</td>
</tr>
<tr>
<td>RH</td>
<td>0.003084</td>
<td>0.001862</td>
<td>1.66</td>
<td>0.098</td>
</tr>
<tr>
<td>WD</td>
<td>-0.00111</td>
<td>0.000265</td>
<td>-4.19</td>
<td>0</td>
</tr>
<tr>
<td>SR</td>
<td>0.000258</td>
<td>0.000139</td>
<td>1.86</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Table 5 Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>4</td>
<td>128.506</td>
<td>32.127</td>
<td>9.42</td>
<td>0</td>
</tr>
<tr>
<td>Residual</td>
<td>8753</td>
<td>29860.75</td>
<td>3.411</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8757</td>
<td>29989.26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

When carrying out the multivariate regression, a coefficient of determination (R = 0.40) was produced, through the analysis of the trend line, with a percentage error of 1.03%. According to the results of the statistical indices, it was observed that the estimated values of the SO$_2$ concentration, using the model, are in agreement with the values observed (Table 3, 4 & 5).

Plume signature: RSN=SO$_2$/NOx. Sulfur dioxide in the gas phase (SO$_2$) is emitted during the combustion of all sulfur-containing fuels (petroleum, coal and diesel), while traffic is an important source of nitrogen oxides (NOx). The relationship between the two can be useful in identifying sources of pollution because the fuels used, say, for electricity generation and for transportation differ in their sulfur content and because the ratio is related to the combustion conditions. Generally, electricity production is expected to
result in a lower SO$_2$/NOx ratio than emissions from low temperature boilers burning high sulfur fuel oil. Benkovitz et al. (1996) mapped the nitrogen-sulfur ratios to reflect the general character of the sources of pollution. A study of the inverse S/N ratio indicates that in many European countries the ratio is close to 1. It is higher than 3 in some Central and Eastern European countries, most likely reflecting the presence of heavy industry. In industrialized and densely populated areas of North America, the proportion is greater than 1, while in areas located away from large stationary sources, it is about 0.1. In Campo Grande the mean SO$_2$ / NOx ratio of 0.13 for sources indicating that the source for Campo Grande is fixed (De Souza et al, 2017). These findings indicate that mobile and point sources can be identified by their characteristic RSN.

4. CONCLUSION

The research showed the influence of different local emission sources in the region and the meteorological conditions, including the increasing tendency of local emissions (refinery, thermo-electric plants, combustion of coal and fuel oil and traffic). There was a higher SO$_2$ concentration attributed to the traffic emissions that usually occur on rush hours in morning and at night. This level of variability of SO$_2$ during hot / cold periods.

The results indicated a growing trend, revealing that the strategies of emission control and technological improvements in the Campo Grande region did not cause enough impact to control SO$_2$ emissions. Local emission sources have grown, while industrial production a number of vehicles have increased in recent years. However, controlling SO$_2$ emissions remains a major challenge in improving air quality, especially in urban areas influenced by various local sources (fixed and mobile).

Positive autocorrelation was observed between SO$_2$ with temperature, wind speed and solar radiation indicating that seasonality and climatic conditions significantly affect ambient air quality. The trend of space-time variation of air pollutants, provides a solid scientific basis for its management and control, and information on air pollution concentration would be useful for urban planners and decision makers to effectively manage air quality for health and environmental issues.

These observations are useful for understanding the ambient air quality of a densely populated area and the anthropic activities that lead to worsening air quality. The results indicate that the maximum concentration of SO$_2$ was observed during the day due to photo-oxidation of the precursor gases originating from anthropogenic sources. The mean daytime maximum of SO$_2$ ranged from 11:00 p.m. to 10:00 p.m., and the average daytime low from 5:00 p.m. to 6:00 p.m. The statistical analyses showed that SO$_2$ formation is also dependent on SO$_2$ precursors and meteorological parameters, which was also indicated by PCA and cluster analysis and also shows that the variation of pollutants in the site was strongly influenced by the regional emission and chemicals. Finally, the tropospheric study of SO$_2$ and related trace gases as well as aerosols is becoming increasingly important because deteriorating air quality can have negative impacts on human health and vegetation. Therefore, control measures should be taken to avoid further exacerbation of air pollution.

Authors’ contributions

All authors performed the data analysis, applied the model, created the figures and prepared the original draft, analyzed the raw data and revised the original draft, helped to collect the raw data from the monitoring station.

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Conflicts of Interest

The authors declare no conflict of interest.

Database statement/Availability of data

The meteorological database is public domain and is available at: Center for Monitoring Weather, Climate and Water Resources of Mato Grosso do Sul (Cemtec / MS), an agency linked to the State Secretariat of Environment, Economic Development, Production and Family Agriculture (Semagro), http://www.cemtec.ms.gov.br/laudos-meteorologicos/.

The ozone pollutant database belongs to the physics institute of the federal university of mato grosso do sul and may be requested from Prof Dr Amaury de Souza, email: amaury.souza@ufms.br
Nomenclature
AP atmospheric pressure (mbar)
RH relative humidity (%)
SR solar radiation (cal/cm²)
T temperature (°C)
WS wind speed (m/s)
WD direction of the winds
PCA Principal Component Analysis
Plume signature: RSN

Highlights
SO₂ pollution was exacerbated by rapid urbanization.
SO₂ pollution was more severe in winter due to basic heating needs.
SO₂ concentrations increased with decreasing wind speed and temperature.
The concentrations of SO₂ increased with increasing relative humidity.

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