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Surface ozone measurements and meteorological influences in the urban atmosphere of Campo Grande, Mato Grosso do Sul State

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ABSTRACT. The objective of this research was to develop a model to predict ozone concentrations on the meteorological variables. Concentration measurements of ozone were conducted at the Federal University of Mato Grosso do Sul, in the period 2007-2011. Predictor variables related to climate (relative humidity, wind speed, precipitation and temperature) have been provided by Embrapa-Gado de Corte, Campo Grande, Mato Grosso do Sul State. The model is able to explain over 70% of the variability concentrations of surface ozone.

Keywords: urban ozone, Campo Grande, health, modeling.

Medidas do ozônio de superficie e influências meteorológicas na atmosféra urbana de Campo Grande, Estado do Mato Grosso do Sul, Brasil

RESUMO. O objetivo desta pesquisa foi de desenvolver um modelo para prever as concentrações de ozônio em função das variáveis meteorológicas. As medidas de concentração do ozônio foram realizadas na Universidade Federal de Mato Grosso do Sul, no período de 2007 a 2011. As variáveis preditoras referentes ao clima (umidade relativa, velocidade do vento, precipitação e temperatura) foram cedidas pela Embrapa-Gado de Corte, Campo Grande, Estado do Mato Grosso do Sul. O modelo desenvolvido é capaz de explicar mais de 70% da variabilidade nas concentrações de ozônio de superfície.

Palavras-chave: ozônio urbano, Campo Grande, saúde, modelagem.

Introduction

Increased tropospheric ozone concentrations are currently a matter of great concern since background ozone concentrations have more than doubled during the last decades (STAEHELIN et al., 1994). The assessment of ozone levels is extremely important since ozone, as a greenhouse gas, is a key element for the control of the chemical composition of the troposphere and climate. Troposphere ozone rises from two basic processes: (i) tropospheric-stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere; and (ii) production of ozone from photochemical reactions occurring within the troposphere. The production of ozone in the troposphere is accomplished through a complex series of reactions referred to as the 'photochemical smog mechanism'. Air pollution in many cities is currently an issue of great concern to the population, with a high profile on the political agenda. Numerous situations in which the near-surface ozone concentration exceed the adopted threshold values have attracted considerable public attention due to the well-known harmful impact on biosphere, human health, animal populations, agriculture productivity and forestry (BRAUER; BROOK, 1997; LIPPMANN, 1993; SCHENONE; LORENZINI, 1992; ZIEROCK; BARTAIRE, 1988). Despite the above-mentioned concern, little is known about the mechanisms of chemical transformation and transportation of air pollutants within the complex geometry of an urban environment.

Although ozone chemistry has been extensively investigated in many chamber experiments and in photochemical modelling studies, there are still significant difficulties in accurately predicting environmental ozone levels and its spatial distribution, behavior and associated trends. It seems that there are more parameters than just precursor concentrations that lead to ozone formation and destruction processes in the air.

Knowledge of ozone and of the conditions that contribute towards its formation is required for ozone tracking and predicting. It is necessary to apply models that describe and understand the complex relationships between ozone concentrations and the many variables that cause or hinder ozone production. Other factors, such as the regional transport of ozone and its precursors, may affect ozone levels. Ozone concentrations are strongly linked to meteorological conditions. In addition, favourable meteorological conditions (clear skies, warm temperatures and soft winds) have great influence on ozone concentrations (VECCHI; VALLI, 1999). Land-sea breezes also influence ozone concentrations at coastal sites. In Europe, the highest ozone concentrations take place in summer under stable high-pressure systems with clear skies. During these episodes, ozone levels well above the international guidelines (UN-ECE, 1988; WHO, 1987) have been observed in large areas and ozone concentrations of 100-150 ppb may last for several days. The situation in the Mediterranean area is given below (MILLÁN et al., 1991, 1996). The ozone threshold by European Union guidelines for damages to human health (120 mg m^{-3}, 8h average) is exceeded systematically for at least 4 months of the year, or rather, for the population (180 mg m^{-3}, hourly average) it is exceeded frequently between April and August, and for vegetation (65 mg m^{-3} as a 24-h average) it is exceeded systematically during more than 6 months of the year.

Nevertheless, the same authors agree that such measurements may only be proposed after improving the current state-of-the-art in the main parameters involved in the formation of photochemical oxidants. This is particularly important for Spain where the experimental evidence of oxidants and precursors is very limited (MILLÁN et al., 1991; SÁNCHEZ; SANZ, 1994; ZURITA; CASTRO, 1983).

In the case of Brazil, the primary and secondary standard is 160 ug m^{-3} or about 81.2 ppb, according to Resolution 3 of the 1990 National Council on the Environment-Conama (CONAMA, 1990).

Urban ozone formation is a complex phenomenon since the pollutant is not emitted into the atmosphere directly but it is produced through the interaction of meteorology, NOx and VOCs (FINLAYSON-PITTS; PITTS, 1986; SAUNDERS et al., 2002). Therefore, several surveys have tried to assess the impact of meteorological factors taking into consideration ozone levels in order to detect changes in ozone precursor emissions (BLOOMFIELD et al., 1996; COX; CHU, 1996; DAPENG et al., 1996; GARDNER; DORLING, 2000; KORSOG; WOLFF, 1991; PRYOR, 1998; SMITH; SHIVELY, 1995).

Current study comprises an investigation into the importance of meteorology in determining surface ozone concentrations and deals with the use of linear regression method for predicting ozone concentrations as a function of meteorological parameters. The study focuses on the impact of meteorological parameters on ozone variability in an urban environment in the city of Campo Grande, Mato Grosso do Sul State (population of approx. 724,000, spread over an area of 8,096 km^2) between January 2007 and December 2011. Analysis aimed at studying ozone concentrations and the influence of the most relevant meteorological variables on precursor emissions.

Material and methods

The city of Campo Grande (S 20º 26'16"; W 54º 32'16"; altitude 677 m) in the state of Mato Grosso do Sul is located in central-western Brazil. It lies approximately 1200 km south of the southern Amazon Basin and about 150 km east of the Pantanal, the world's largest floodplain. It is situated on the plateau of Marazion, the watershed between the basins of the Paraná and Paraguay rivers and about 100 km east of the Andes. According to Köppen-Geiger climate classification, the climate of Campo Grande is tropical, characterized by high temperatures, 18 to 28ºC, with a temperature range of 5 to 7°C and well-defined rainy and dry seasons. It displays high rainfall, around 1500 mm $year^{-1}$, with the rainy season starting in October and lasting until April, and the dry period during the remaining months of the year (SOUZA et al, 2009).

Information on daily levels of ozone (O_3) was obtained from the Department of Physics of UFMS. The Ozone Analyzer used for measurements adopts the working principle of ultraviolet radiation absorption by ozone molecule. The analyzer was installed near Campo Grande, away from local ozone sources. Measurements were performed continuously 24 hours a day and rates of ozone concentration were given every 15 minutes. The daily calculation of the arithmetic mean was presumed to be the estimate of air pollution in Campo Grande. Information on rainfall, average temperature and relative humidity was obtained from Embrapa, Gado de Corte, Campo Grande, Mato Grosso do Sul State.

Current study comprises a descriptive analysis of variables and the latter were subsequently associated with ozone concentration data and climatic variables such as rainfall, maximum temperature, relative humidity and wind speed for the period between 2007 and 2011.

In the case of assessment of how meteorological conditions affect variations in ozone levels, the authors used multiple linear regression analysis for the period 2007 - 2011, including an analysis for the seasons of the year. This is one of the most widely used methods for predicting how ozone concentrations depend on meteorological factors. The general equation for the model is:

$$Y = a_0 + a_1X_1 + a_2X_2 ++ ... + a_mX_m + \varepsilon$$

where:

y is an objective variable (ozone concentrations); m is the number of independent variables (meteorological variables); X_j are independent variables; a_j are regression coefficients (estimated by the least squares procedure); ε is an error term associated with the regression analysis.

Results and discussion

Table 1 presents the descriptive statistics for daily levels of air pollutants (ozone), rainfall, maximum air temperature, relative humidity and air speed.

Table 1. Descriptive statistical analysis of daily weather variables.

Variables	Registry	Mean	standard	minimum	median	maximum	trend
Rainfall	1827	3,6	9,6	0,0	0,0	97,8	growing
Ozone	1827	17,8	8,7	0,7	16,2	52,8	growing
Temperature	1827	30,1	3,8	11,1	30,7	39,5	growing
Humidity	1827	65,7	16,4	19,1	67,0	98,0	stationary
Velocity	1827	3,7	1,7	0.0	3,4	11,1	growing

O_3 is formed more frequently in winter and spring, although it is also formed at other times of the year. The maximum and minimum rates of O_3 in this series were 52.8 and 0.7 ppb respectively. Mean and median values were respectively 17.8 ± 8.7 and 16.2 ppb. Further, 1,827 pollutant-charged days were recorded although during the study period the standard air quality (80 ppb) was not exceeded (Table 1).

As shown in Figure 1, ozone concentration has the following behavior: maximum levels during daytime, with highest rate between 11 and 15h, and minimum rates at night. The average ozone concentration is 17.38 ± 5.32 ppb, with a maximum rate of 49.00 ppb at 12:15h, and a minimum rate of 1.00 ppb in the early hours. The average concentration of ozone can vary greatly from one day to another since it depends on cloud cover and climatological factors which determine an increase or decrease in its concentration. This lack of constancy or linearity is related to climatic conditions of the day. The daily variations of ozone concentration depend solely on weather conditions, such as cloud cover, solar radiation, rain and wind.

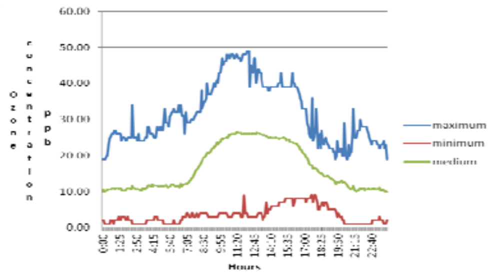

Figure 1. Average hourly concentration of ozone between 2007 and 2011. Ozone concentration ppb maximum minimum mean 60,00 = 60.00.

It is known that ozone concentration is higher on sunny days because the more radiation passes through the atmosphere, the greater the photochemical reactions that produce ozone. It has been noted that the days with minimum concentration rates coincided with the days with the highest rainfall rates for the respective month. Due to cloud cover during a rainy day, there is a decrease in ultraviolet radiation reaching the surface and therefore a decrease in the photochemical reactions for ozone production.

Wind is also a factor that influences ozone concentration since it transfers chemical pollutants from one region to another. Consequently non-polluting regions may also be affected by high ozone concentrations.

Meteorology plays an important role in ozone formation and transport. As a result, substantial variations in meteorological conditions (in all time scales) may have such a great impact on zone concentrations that they mask long-term trends in ozone that could reasonably be traced to changes in precursor emissions such as NOx. and VOCs. On the other hand, as several studies show, certain meteorological conditions are required for the formation and accumulation of high concentrations of O_3. These conditions often include a well-defined boundary layer, subsidence inversion, light winds, high temperatures and high solar radiation. Owing to the above, a survey to assess the behaviour of ozone concentration in surface air with several available meteorological variables was carried out. The analysis focused on the study of dependencies of ozone concentration levels and different meteorological parameters to identify the variables with the higher impact on ozone concentrations under weather conditions, with average hourly rates from the meteorological data. The selected variables were as follows: temperature (T in °C), relative humidity (H in %), wind speed (v in m s^{-1}) and rainfall (r in mm).

A regression analysis was carried out with SPSS 10.0 software to find the meteorological factors influencing ozone concentration and to assess them in order of importance.

A correlation on ozone concentrations and other meteorological factors available was carried out. The study was performed taking into consideration: (1) all data.

The relationship between ozone concentration and temperature may be explained on theoretical grounds. Temperature plays an enhancing role in the propagation rate of the radical chain and has an opposite effect on the chains´ termination rate. The evolution of ozone concentration with temperature may be observed in Figure 2 which shows that the evolution of both variables is similar. This behaviour remains unaltered until June and an increase in the temperature may be observed in July, August and September, coupled to an increase in ozone concentration through crop residue burning during this period for the preparation of the soil for planting.

Table 1 shows the meteorological variables, rainfall (mm), maximum temperature (°C), relative humidity (%) and wind speed (m s^{-1}). The lowest rate recorded in the data series for temperature was 11.1°C for maximum temperature. In the series of maximum temperatures the highest rate recorded was 39.5. These are the extremes of temperature found in the series. For the variable relative humidity minimum and maximum values were 19.2 and 98%. Rainfall in this data series, rates ranged between 0.0 and 97.8 mm and wind speed had a minimum rate between 0 and 11.1 m s^{-1}.

High relative humidity and wet and rainy weather are usually associated with low ozone concentrations due to a reduction of photochemical efficiency and an increase of ozone deposition on water droplets (DI CARLO et al., 2009; LELIEVELD; CRUTZEN, 1990). It is well known that relative humidity is negatively correlated with temperature, which may be considered one of the primary ozone predictors. Environment humidity affects the minimum temperature via two mechanisms (HUBBARD; COBOURN, 1998): (1) through the absorption of long-wave radiation emitted by the earth that would otherwise, under dry and cloudless conditions, be lost into space; (2) through the release of condensation latent heat as temperature falls to dew point. High rates of ozone concentrations are associated with low relative humidity rates (R = –0.47).

Regarding the percentages of occurrence of daily doldrums and the intensity of the winds at the surface, it appears that, between May and September, the lowest and highest rates occur, respectively. This is justified by the higher frequency of the entrance of polar air masses by promoting a greater variation in pressure gradients. This fact reduces the residence time of particles in the atmosphere, but increases the chance of fires by increasing the oxygen flow. The distribution of wind directions at 10 meters in height and intensity has predominant north and northeast directions, with an intensity of 2.06 m s^{-1}.

Table 2 shows the highest rates of the regression analyses for the seasons of the years under investigation in which the coefficients β assuming negative and positive values depending on the variable, confirm that the concentration of ozone may increase or decrease as these values are positive or negative, for a confidence interval of 95% involving temperatures, relative humidity, rainfall and wind speed.

In the final model of multiple linear regression, the linear function, selected for the regression model, showed random distribution around the zero line and no outliers in its residual distribution. This factor featured a homogeneity of variance which validated the final analysis.

Table 2. Regression coefficients, error, correlation coefficient for the confidence intervals of 95% for the seasons of the years under analysis.

Seasons	I	β 1	β 2	β3	β 4	R	β	p
Summer	3.9	0.173	0.017	2.65	-0.029	0.74	4.07	0.028
Autumn	42.5	0.038	-0.406	-0.84	0.0119	0.75	1.93	0.058
Winter	-103,	2.52	0.079	12	0.052	0.81	4.8	0.011
Spring	-24.5	0.972	-0.167	9.09	-0.011	0.73	4.18	0.017

I-intercept; temperature-β1, β2, relative humidity, wind speed-β3, β4-precipitation; Є – error; R = correlation coefficient; p value.

Figure 2a, b, c and d show the temporal variation of the observed and predicted rates for the seasons of the year (Summer, Autumn, Winter and Spring) of ozone concentration, with a correlation coefficient ranging from R = 0.74, R = 0.75, R = 0.81 and R = 0.73 and mean square root error of 4.07, 1.93, 4.8, 4.18.

Figure 2 a, b, c and d - ozone concentration observed and estimated for the seasons of the year in Campo Grande for 2007-2011.

According to the multivariate linear regression, the model of ozone concentration remained stable throughout the analysis.

T tests (based on Student's *t* distribution) were performed to test the significance of the coefficients in the equations. Results show that regression coefficients for temperature, humidity, rainfall and wind speed are statistically significant. The t-values for both coefficients are less than 0.05 (p value < 0.05). The results of the high correlation from this analysis indicate that ozone concentrations are strongly affected by meteorological conditions during the Summer, with approximately (Ryy) = 74%, Autumn (Ryy) = 75%, Winter (Ryy) = 81% and Spring (Ryy) = 73%.

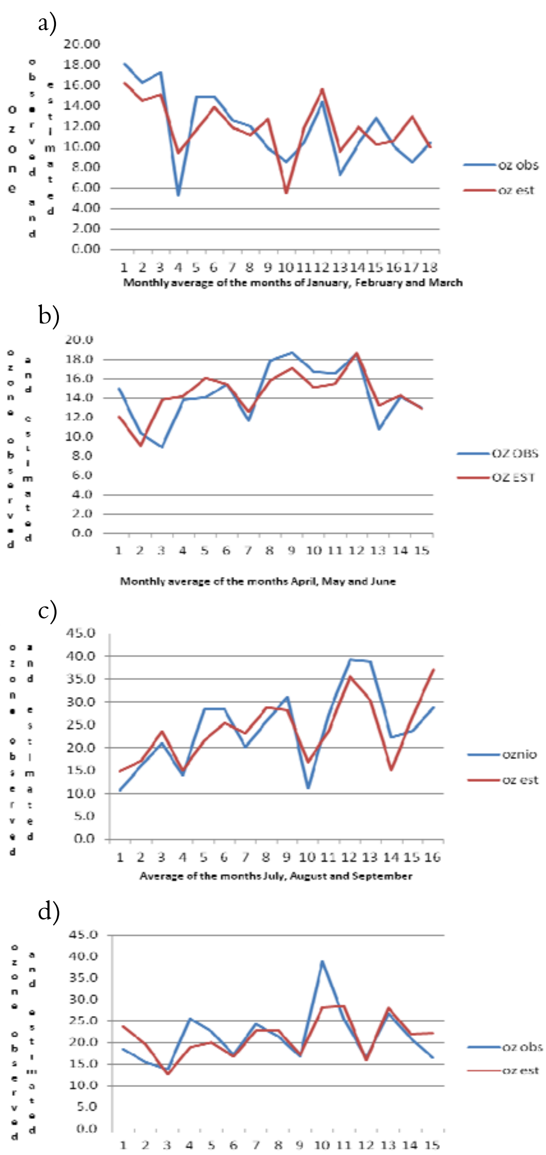

Figure 2. [Estimated and observed ozone. Mean for January, February, March, April, May, June, July, August, September, October, November, December].

Conclusion

Statistical regression analyses of the numerical model investigated the contribution of meteorological conditions for ozone concentrations around the year, during summer, autumn, winter and spring. Results show that there is a close relationship between changes in meteorological conditions and variations in ozone concentrations over the Campo Grande area. Throughout the year, during summer, autumn, winter and spring, up to 78, 73, 75 and 81% of long-term variations in peak ozone concentrations may be accounted for by changes in the seasonally average daily maximum temperatures and seasonally average wind speeds, humidity and rainfall. Results suggest that changes in meteorological conditions have significant impacts upon rising ozone concentrations in this area.

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