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Prediction of Tropospheric Ozone Levels from Temperature in the Urban Area of Durango, Dgo

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Prediction of Tropospheric Ozone Levels from Temperature in the Urban Area of Durango, Dgo., Mexico.

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Abstract: Air pollution in urban centers depends directly on anthropogenic activities. Tropospheric ozone depends on chemical precursors that promote an increase in its production, mainly in wind-dominated areas and large green areas. It is a gas produced by a series of complex chemical reactions catalyzed by sunlight in the atmosphere. It can be concentrated to a greater or lesser extent depending on factors such as the amount of volatile organic compounds, the amount of nitrogen dioxide (NO_2), the intensity of solar radiation or by climatic conditions such as temperature and other factors. The objective of the present study was to predict tropospheric ozone levels from temperature data in the city of Durango, Dgo. Temperature and tropospheric ozone values were obtained from 18 sampling points in the urban area of the city of Durango, of which 15 were obtained by collecting from the Ventusky service and the rest from three fixed monitoring stations established in the city, specifically located in (SRNyMA, ITD and CIIDIR). These values were interpolated in order to determine the spatial values for the entire city. A correlation analysis was performed for three different periods in the day established as follows (24:00-03:00-06:00, 09:00-12:00-15:00 and 15:00-18:00-21:00). Subsequently, a linear regression analysis was performed by time period. The results showed a higher positive correlation between ozone concentration and temperature from 15:00 hrs to 21:00 hrs; likewise, this period showed a higher goodness of fit in the ozone prediction (R^2=0.99; RMSE: 1.12 ppbv). Temperature allows spatial prediction of ozone concentrations in urban areas with acceptable accuracy.

Keywords: Air pollution; tropospheric ozone; linear regression; Kriging spatial interpolation; temperature; precursors; volatile organic compounds

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1. Introduction

Atmospheric pollution is considered a modification of the environment by any physical, chemical or biological agent that modifies the natural characteristics of the atmosphere. Among the causes that mostly provoke such modifications are anthropogenic activities and forest fires, which emit large concentrations of contaminants from the soil into the atmosphere. These atmospheric pollutants are mainly suspended particulate materials such as carbon monoxide, ozone, nitrogen dioxide and sulfur dioxide and are the main cause of respiratory diseases causing high morbidity and mortality rates in society [1]. According to Brunekreef and Holgate [2], exposure to high concentrations of ozone and particulate matter, considered as air pollution, has been associated with an increase in hospital admissions of urban dwellers for respiratory and cardiovascular diseases, which represents a problem of global importance in health issues.

On the other hand, there are anthropogenically generated chemicals including emissions of nitrogen oxides (in their forms (NO_x= NO + NO2), volatile organic compounds (VOC), reduced sulfur

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compounds that give a mostly complex series of chemical transformation by photolysis resulting in the formation of tropospheric ozone in urban areas, which are also risk factors for public health [3]. In ozone formation, the reaction of NO (nitric oxide) with oxygen in the oxidation process converts it to NO_2 (nitrogen dioxide) which can be easily broken down by the action of light or UV radiation to form ozone and recycle NO. This reaction can vary significantly as it depends on the area, the season of the year, as well as the magnitude of nitrogen oxide emissions, so it is necessary to know the ozone concentrations in urban areas for monitoring and action plans to avoid the health problems described above [4]. This monitoring includes the regulation of fossil fuel combustion, since it currently represents the largest contribution to the production of nitrogen oxides as ozone precursors in urban areas [5]. The level of atmospheric pollution from anthropogenic sources is present today in all urban centers, and these levels depend directly on these activities. One of the main atmospheric pollutants due to its harmful effects on the planet is tropospheric ozone, so called because it belongs to the layer of the atmosphere closest to the earth's surface, the troposphere. Because of its importance for air quality and climate change, ozone has received increased attention in the last three decades, both from the scientific and regulatory communities[6]. According to Di, et al. [7] the troposphere has an approximate thickness of 10 to 18 km, which causes tropospheric ozone to have a spatial and temporal variability in its concentration level, depending on the latitude, temperature, season of the year and its atmospheric pressure decreases as the altitude increases from 1013 millibar (mb) to 140 mb of pressure at an altitude of 14 km on average.

In accordance with the U.S. Environmental Protection Agency (EPA) emissions inventory for 2021, greenhouse gas emissions were as follows: fluorinated gases 3%, nitrogen oxides 6%, methane 11% and carbon dioxide 79%. Within the inventory of NOx emissions, it was reported that anthropogenic agricultural activities contributed 79% of the NOx contribution in China's agricultural soils. These concentrations of emissions are mainly due to the use of nitrogen fertilizers in an agricultural region of approximately 300,000 km2 considered biogenic sources and overlooked in the design of atmospheric emissions control in this country, electricity production accounts for 10%, followed by urban solid waste with 5.8% and industrial processes with 5%, and forest biomass and land use and land use change contribute 1% to the emission of this O_3 precursor [8,9]. It is a gas originated by a series of complex reactions in the atmosphere. It can be concentrated to a greater or lesser extent depending on factors such as the amount of volatile organic compounds, the amount of nitrogen dioxide (NO_2), the intensity of solar radiation or by climatic conditions such as temperature and other factors[10]. Depending on the place it occupies in the atmosphere, ozone can be classified as tropospheric or stratospheric ozone, specifically talking about tropospheric ozone (O_3), the concentrations of it depend on a photochemical process in reaction with some precursor pollutants, this process is necessary for the production of O_3, this is how indirectly the concentration of pollutants in the air is affected by meteorological variables such as temperature [10, 11]. The photochemical production of O_3 in the troposphere due to the interaction of VOCs and NOx leads to a complex process of chemical reactions involving the formation and destruction of this compound between its ascent to the layers from the troposphere to the stratosphere, additionally the highest increase of this pollutant was recorded in the spring and summer season as a consequence of the efficient photochemical conversion of O_3 precursors and the same O_3 formed in the troposphere [12].

Elevated concentrations of these precursors have been found under conditions of high concentration of UV radiation from the sun, so meteorological conditions as a primary variable should be considered as a key starting point that drives such ground-level ozone production [13]. The spatial distribution and global variation of O_3 is influenced by precursor emissions, which increases due to the increase of global methane emissions in large cities. through, industrial and transportation activities abound in urban areas, generating O_3 precursors such as nitrogen dioxides (NOx) and volatile organic compounds (VOC´s), sin embargo there is a decrease in the seasonal passage of spring [14].

Photochemical O_3 production in the Northern Hemisphere in summer is mostly due to the combination of local natural and anthropogenic NOx and VOC emissions, highlighting the strong dependence of biogenic emissions on temperature and solar radiation [10, 15]. The concentration of pollutants in

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the atmosphere is affected by meteorological variables such as temperature. Hot, dry and stagnant conditions are often associated with increased ozone levels, as these days tend to favor ozone formation and persistence[11, 16]. Some studies in different parts of the world have shown a dependence between temperature and ozone concentrations [17-19]. During the most critical period of the SARS COV-2 health emergency confinement (May 2020), in Mexico City, tropospheric ozone concentrations remained at their typical values when the other pollutants showed a decrease during that period of time; a spatial analysis showed a positive relationship in ozone formation with green areas and wind speed, This is attributed to the reaction of nitrogen oxides and biogenic volatile organic compounds that through photolysis promoted ozone production in these areas [20]. However, the lack of fixed monitoring stations has vean the main limitation for its monitoring. Geomatics, allows us to provide a solution to this limitation, within geostatistics we are able to predict a variable in space, i.e., using the methodology of spatial interpolation[21, 22]. The city of Durango has only three air quality monitoring stations and does not have a total coverage of the urban area due to its location, having a limited representativeness in air quality monitoring [23]. The objective of this study was to predict tropospheric ozone concentrations from temperature data in the urban area of the City of Durango.

2. Materials and Methods

The city of Durango is the capital of the State of Durango and is located between the coordinates 24° 4' 43.34'', -104° 34' 57.03'', 23° 58' 53.83'', -104° 36' 30.22'', with an altitude of 1,890 m. The Fig. 1 shows the study area, formed by the urban area of the city, and the 18 temperature and ozone sampling points, whose meteorological stations were extracted from the "Ventusky" service (https://www.ventusky.com/).

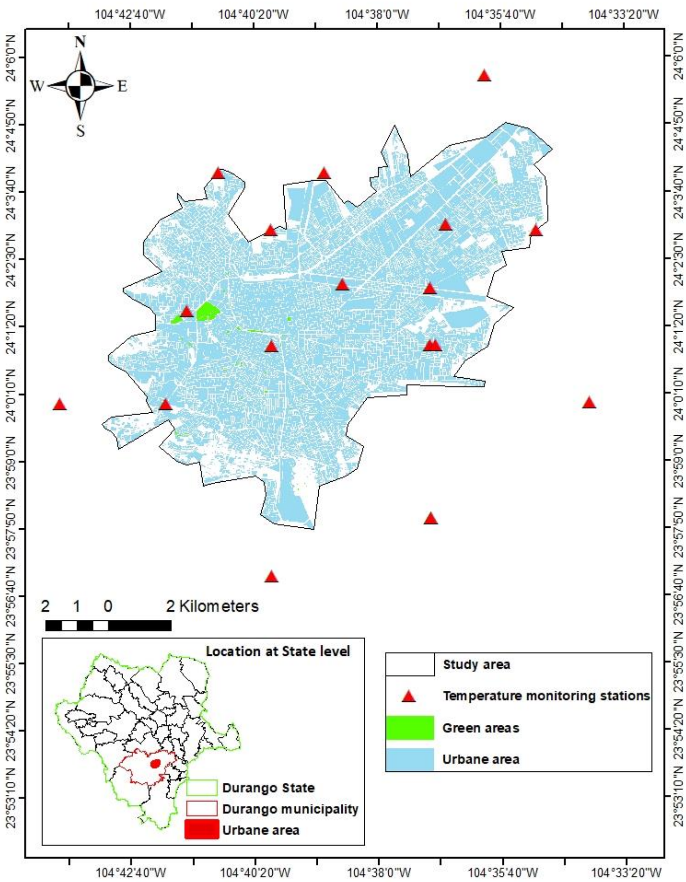

Figure 1. Study Area map.

Hourly ozone concentrations and data on atmospheric and meteorological variables were extracted from the database of the Secretariat of Natural Resources and Environment (SRNyMA) of the city of Durango, corresponding to data measured at the three monitoring stations available in the urban area, together 15 temperature sampling data were extracted from the Ventusky service (https://www.ventusky.com/). Which is a web application that allows the visualization of meteorological data from around the world and has a HRRR (High Resolution Rapid Refresh) model. This is a real-time model with a resolution of 3 kilometers (km), and is updated hourly, with atmospheric correction from NOAA (National Oceanic & Atmospheric Administration).

Data corresponding to the month of May 2021 were used, considering only the season with the highest ozone concentrations and highest temperatures during the year. The hourly averages of both variables were obtained (8 data corresponding to the 8 hours of the day). The eight hours selected were 24:00 hrs, 03:00 hrs, 06:00 hrs, 09:00 hrs, 12:00 hrs, 15:00 hrs, 18:00 hrs and 21:00 hrs. This time span was divided into three moments during the day: the first one considering the temperature and ozone from 24:00 to 06:00 hrs (T246; O246), the second one considering the period from 09:00 hrs to 15:00 hrs (T915; O915), and finally a third one from 15:00 hrs to 21:00 hrs (T1521; O1521).

Statistical analysis

In order to evaluate the linear association between ozone and temperature, a Pearson correlation analysis (r) was used for each time period and then a linear regression analysis was applied to predict ozone concentrations in the city, where the dependent variable corresponds to ozone concentrations and the independent variable is temperature. The simple linear regression model corresponds to the following equation

$$Y = \beta_0 + \beta_1 X + \varepsilon.$$

Where "Y" is the ozone concentration, "B_0" is the cut-off height of the Y-coordinate axis, "B_1" is the increment in Y according to X, "X" is the temperature and "ε " is the error.

Goodness-of-fit coefficients such as the Coefficient of Determination (R^2) and the Root Mean Square Error (RMSE) were calculated to evaluate the model's ability to fit. Once the model was evaluated, the spatial ozone concentration map was generated. These analyses were performed with Rstudio software [12].

$$R^2 = 1 - [\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y}_i)^2} \quad (1)$$

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-p}}$$

Where: y_i = Observed parameter, $\hat{y}_i$ = Estimated parameter, $\bar{y}_i$ = Mean of parameter, n = Number of total observations, p = Number of model parameters.

Spatial interpolation with ordinary Kriging:

With the temperature data, a spatial interpolation was performed for each period of the day under the Ordinary Kriging method. The ordinary kriging model is Z(s)=μ+ε(s). It is based on a constant mean of the data (μ) having no trend and errors ε(s) with spatial dependence. The prediction of the value of a location is:

$$Z(s0) = \sum \frac{N}{i=1} \lambda_i z(s_i)$$

Where Z (s0) is the predicted value of a location, $\lambda_i$is an unknown weight that is calculated for each observed value and $z(s_i)$ is the observed value at a location. The estimated value will differ as little as possible from the observed value; this difference is called estimation error[13].

To predict ozone through the temperature maps obtained, the first raster was entered into Rstudio (corresponding to the 24:00, 03:00 and 06:00 hrs period), and then this raster was substituted into the equation obtained with the regression parameters of the same period, i.e., the temperature raster took the value of the "X" in the equation.

The same was done with the other periods of the day (09:00, 12:00, 15:00; 15:00, 18:00 and 21:00 hrs). In this way, three raster's were generated with the predicted ozone value in each of its pixels.

Subsequently, with the three linear regression equations obtained and knowing the parameters of the simple linear regression, they were substituted into the equation allowing to know the corresponding ozone concentration depending on the temperature value. This allowed generating a predicted ozone surface through the temperature surface obtained with the ordinary kriging method.

3. Results

3.1. Temperature interpolation model

The Figure 2 shows the result of the generation of the interpolation of the temperature variable in the City of Durango in the period from 24:00 to 6:00 hours, it can be seen that in this period higher temperatures (20.53°C) occur to the Northeast, while the lowest (15.47°C) to the Northwest of the City.

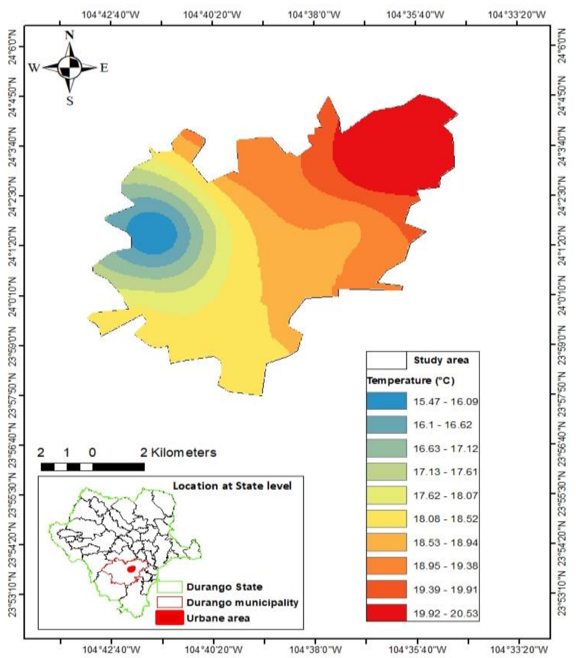

Figure 2. Interpolation with temperature levels in the period 24:00 to 06:00 hours, in the urban area of the city of Durango.

In the period from 9:00 to 15:00 hours (Figure 3), in the same way, the highest temperatures (20.28°C) occurred in the Northeast, while the lowest temperatures (19) occurred in the Southeast of the city. Finally, the results of the interpolation of the temperature for the period from 15:00 to 21:00 hours are shown in Figure 4, it can be observed that the temperature varies throughout the urban area. Towards the Northeast and Southwest there were points of low temperatures at this time (26.21°C), while the East part of the city presented the highest temperature of 30.13°C.

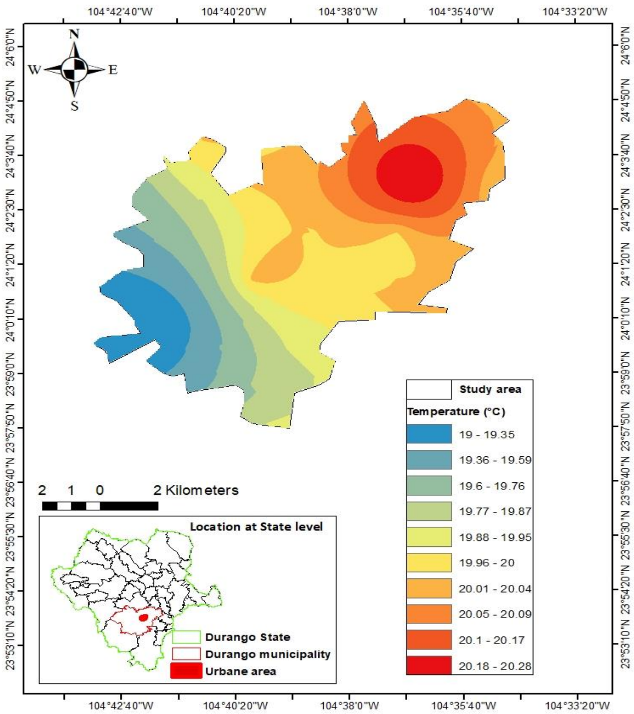

Figure 3. Interpolation with temperature levels in the period of 09:00 to 15:00 hours, in the urban area of the city of Durango.

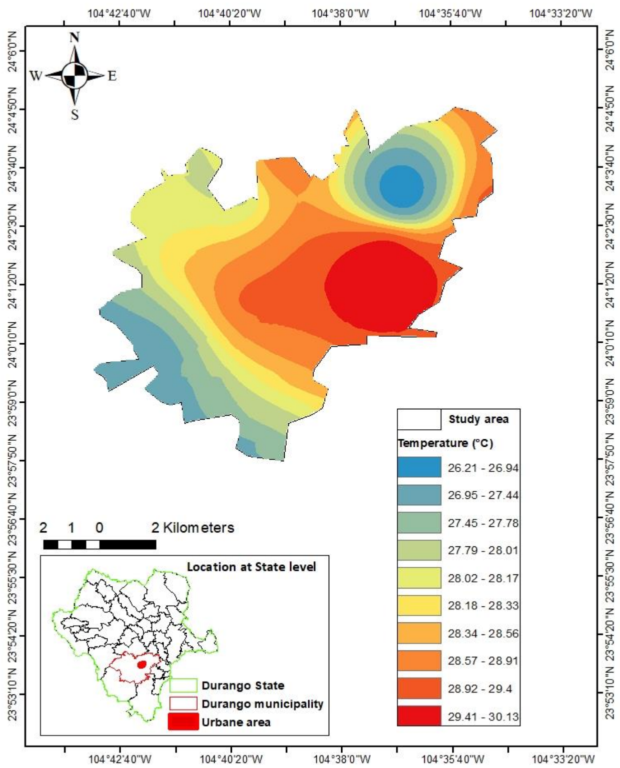

Figure 4. Interpolation with temperature levels in the period of 15:00 to 21:00 hours, in the urban area of the city of Durango.

3.2. Prediction of ozone concentrations

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The results of the correlation analysis between the O_3 concentration with the temperature recorded in the three periods of time are shown in Figure 5. It can be observed that the temperature presented a significant correlation in the three periods of the day analyzed. The highest correlation (r=0.99) occurred between 15:00 and 21:00 hours (O1521; T1521) in the seasons with a positive linear association between the two variables.

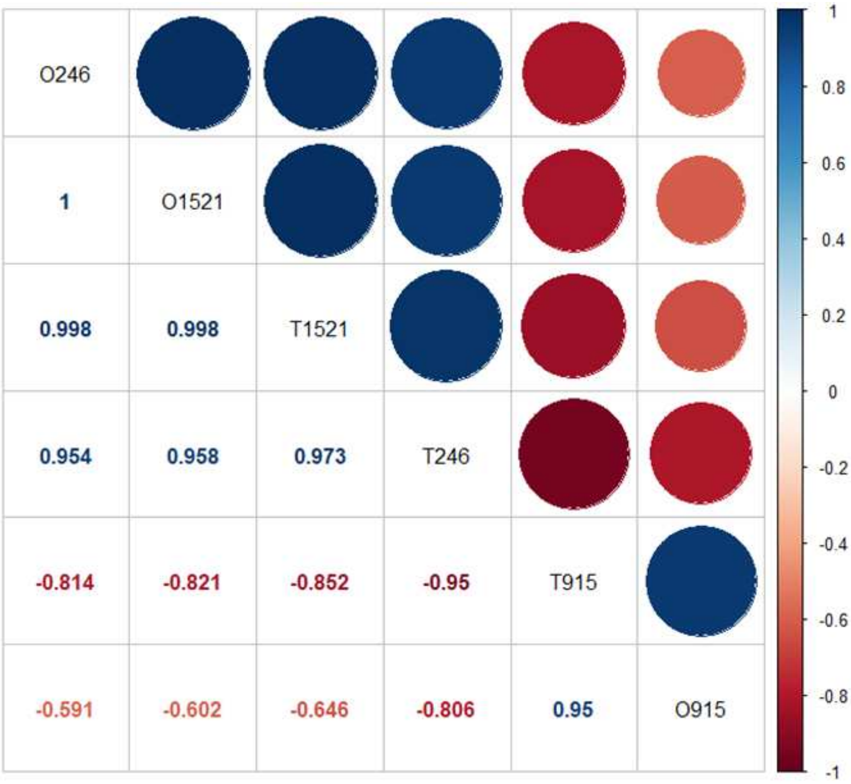

Figure 5. Analysis of correlation.

Once the linear association of O_3 with temperature was determined, the predictive models for each period were generated. The regression analysis showed a range of R^2 from 0.91 to 0.99 for the different hours of the day. The model that best predicted O_3 through the independent variable temperature was R^2=0.99 (RMSE=0.56 ppbv), which indicates that the regression model explained 99% of the total variance (Table 1).

Table 1. Simple linear regression parameteres.

Hours (hrs)	Model	r	Standard residual error	P-Value	R^2	RMSE
24:00 a 06:00 (O246; T246)	y = -83.658 + 6.787x	0.95	4.83	0.001	0.91	2.78
09:00 a 15:00(O915; T915)	y = -69.223 + 5.043x	0.95	10.60	0.202	0.90	6.11
15:00 a 21:00(O1521; T1521)	y = -19.329 + 3.066x	0.99	0.08	0.001	0.99	0.56

Where: y=dependent variable (ozone concentration=O); x=independent variable (Temperature=T).

Once the model was determined, the raster calculator was applied to generate the spatial distribution of O_3 concentrations in concentrations of particulate matter per billion in the city. In Figure 6, the highest concentrations of O_3 are found in the Northeast of the City between 24:00 to 6:00 hours and the lowest concentrations in the Northwest. Similarly, from 9:00 to 15:00 hours (Figure 7).

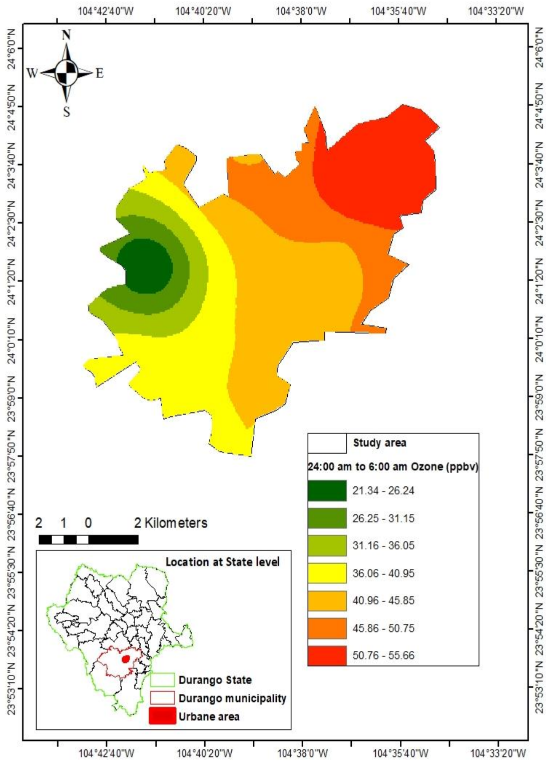

Figure 6. Spatial prediction of ozone at ppbv from predicted temperature values in the period 24:00 to 06:00 hrs, in the urban area of the city of Durango.

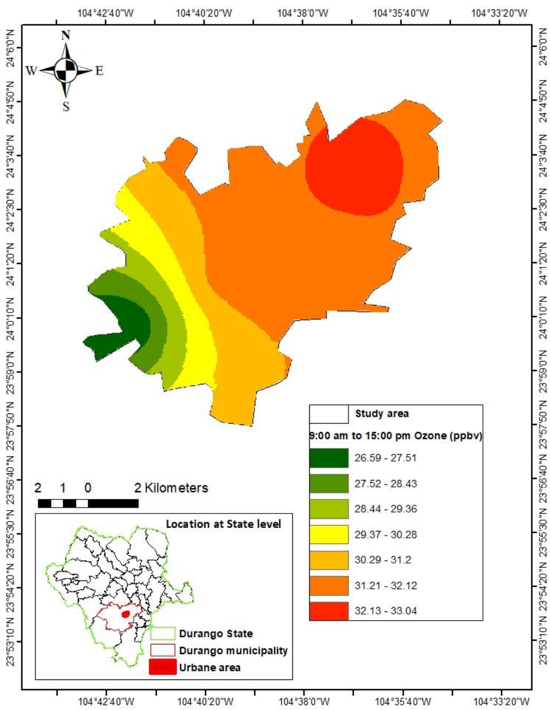

Figure 7. Spatial prediction of ozone at ppbv from predicted temperature values in the period 9:00 a 15:00 hrs, in the urban area of the city of Durango.

In the case of O_3 concentrations between 15:00 to 21:00 hours, there is a variation between the East and the Northeast of the city. In the three generated maps, the predicted O_3 surface is similar to the temperature map, due to the high correlation found between these two variables. When the temperature is at its lowest average level, ozone will tend to have lower average levels.

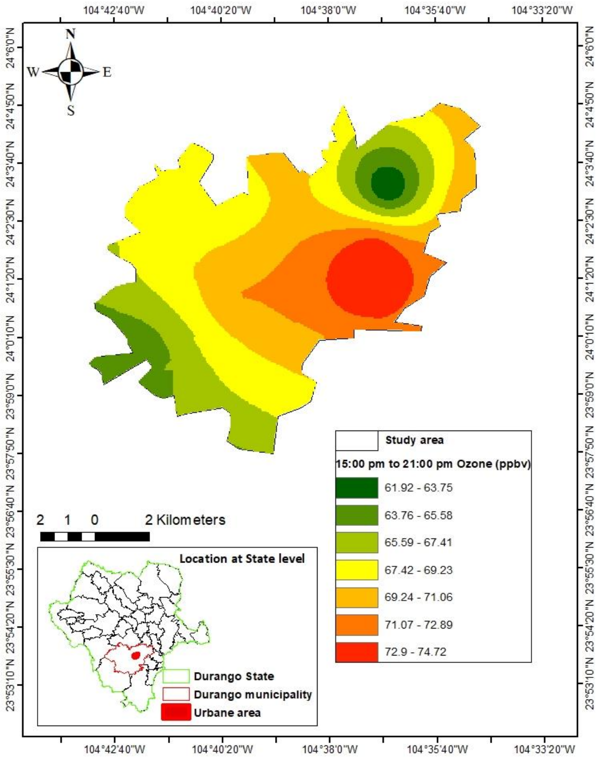

Figure 8. Spatial prediction of ozone at ppbv from predicted temperature values in the period 15:00 to 21:00 hrs. in the urban area of the city of Durango.

4. Discussion

The correlation analysis showed a high linear correlation between O_3 concentrations and temperature (r=0.99). This linear association is normal, since O_3 is a secondary pollutant of photochemical origin and therefore solar radiation favors its higher concentration [17, 26, and 27]. In this study, the correlation coefficients increased between 10:00 and 18:00. This result was similar to the study carried out in the metropolitan area of the City of Mexico by [28], where the behavior of the correlation between O_3 and temperature gradually decreases in the morning and at night and the maximum values were presented between the hours of 15:00 and 17:00 hours. In another study, Gunte [29] reported an r of 0.57 in India, in the season from June to September, highlighting the month of May with the most significant relationship, since in this month, the time of the year with more heat. On the other hand, [30] reported an r of 0.89 for these variables in the north and east of China, this study was conducted in the month of May, which represents the hottest month in the country [11, 16]. The variation in the concentration of O_3 varies with the presence of vegetation, in the present study, there is a public park, and there are less concentrations of O_3, in the same hot season, this is because the vegetation contributes to the photochemical generation of O_3 that is induced by the natural emissions of volatile organic compounds (VOC's) coming from the oxidation of nitrogen in the existing vegetation, which is why they become areas of influence of O_3 concentration [31]. Given the similarity of the results, the O_3 concentration depends directly on the temperature at the time and time of the year in each zone [14].

However, [32] found variations of O_3 depending on the different seasons of the year and demonstrated that atmospheric conditions favor the accumulation of this pollutant at ground level, increasing the concentration due to the absence of wind and rain. These are typical conditions in the city of Durango for this season, which is historically part of the hottest and driest season in the state. Other factors such as increased air turbulence, photochemical activity, increased concentration of particles like NOx, SOx need to be analyzed with respect to photochemical smog formation, which needs to be further elaborated in future work [33]. This is because the O_3 photochemical cycle exhibited a characteristic behavior of urban areas, with minimum values in the early hours of the morning and

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an increase after 8:00 am, with maximum values at noon. It must also be considered that the photochemical activity is higher in the summer period [34], so this study is limited to one month of this period; This study was started by calculating the ozone and temperature trend. Due to the random nature of the atmospheric levels of pollutants, an attempt was made to explain their behavior using regression models to find out the possible correlation between temperature and ozone. From a statistical analysis it was observed that the maximum hourly ozone concentrations did not exceed the national air quality standard on the days evaluated as in the case of other studies [23, 26].

In this context, the regression analysis presented in this study showed that the best O_3 prediction model was from 15:00 to 21:00 hours (R^2=0.99; RMSE=0.56). This result was higher than that found by [35], in his study carried out in Córdoba, Spain from 2006 to 2010 as R^2 from 0.49 to 0.47. On the other hand, in the study carried out by Navarro [36] in Biella, Italy, lower values of R^2 determination of 0.4 were observed in linear mode, and experimenting with the square of the temperature, a value of 0.4025 was obtained, assuming you have a better prediction of the temperature in quadratic form. On the other hand, Otero [18] in a study carried out in Germany, using generalized additive models in two periods of 10 years (from 1999 to 2008 and from 2009 to 2018) in Germany, obtained minimum values of 0.10 and maximum values of 0.46 in the first period and values between 0.07 and 0.43 in the second period, indicating that the lowest values correspond to those registered in the rural area and the high values to the urban area. The high values found in this study compared to the low values found in other studies can be attributed to higher concentrations of pollutant precursors present in the study area, as well as other factors such as humidity or wind speed. On the West side of the city a wave of low O_3 concentrations is perceived, according to previous research [23], the wind in May is usually in a Southwest direction, which contributes to this case that ozone concentrations travel in this direction. The O_3 relationship with temperature is linear, in studies of analysis of several years, to mention [37], studied a range of 21 years, the relationship was always linear, corresponding to what we observed in this study. They also highlight the need to control emissions in countries that are more vulnerable to the effects of climate change. Other authors exhibit the possibility of increasing tropospheric ozone concentrations in urban areas due to the gradual increase in temperature due to climate change [38]. For example, [39] analyzed the correlation of tropospheric ozone with temperature, finding that not only this meteorological variable, but others together manage to explain 40% in America and 60% in Europe the change in the ozone variable.

5. Conclusions

The present study demonstrated the application of interpolation techniques for the prediction of temperature and ozone concentrations in urban areas. The combination of climate data provided in the database of the Secretaría de Recursos Na-tural y Ambiente (SRNyMA) of the city of Durango, as well as data from the Ven-tusky service based on a High-Resolution Rapid Refresh (HHRR) model allowed the extension of a local database to enlarge the sample. Data from the month of May 2021, where the highest ozone concentrations and temperatures were present, were used.

The application of spatial interpolation using the Ordinary Kriging method made it possible to generate spatial temperature information for different times of the day throughout the urban area. The highest correlation between ozone concentrations and temperature in the city of Durango is found in the hours from 15:00 to 21:00 hrs. The prediction of ozone concentrations based on temperatures at different times of the day was determined with the best calculated model, which explained 99% of the total variance of ozone. In the present study, the main limitation is the number of climatological and pollutant monitoring stations in the urban area, so an increase in the number of stations should be prioritized in the areas with the highest incidence of temperature in the city, as shown in the present study, in order to establish mobile monitoring stations to improve the suitability of the model to predict the spatial distribution of ozone, even considering other variables such as wind speed, solar radiation, UV rays and biogenic organic compounds that may be derived from existing vegetation. Future work should further investigate the chemical composition of ozone precursors.

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Conflicts of Interest: The authors declare that there is no conflict of interest.

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