Analysis of dynamic of tropospheric ozone and nitrogen dioxide in the highest region of the Quito city

Cristian Salazar[1,*], *Freddy* Mullo[2]

[1]Peoples' Friendship University of Russia (RUDN University), Faculty of Ecology, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation
[2]Peoples' Friendship University of Russia (RUDN University), Agrarian and Technological Institute, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation

Abstract. A descriptive study of behavior of daily concentrations of ozone (O_3) and nitrogen dioxide (NO_2) in the period from January 2017 to December 2019 was conducted with the purpose to describe air pollution in the south of the city of Quito. The data collected was processed using the Excel and SPSS v25. The statistical analysis included central tendency values, percentages of violation of the threshold limit value (TLV), maximum values and 25th, 75th and 95th percentiles. The correlation between pollutants was evaluated using the Spearman's Rho coefficient. Multiple linear regression models were made for each pollutant and meteorological variables (wind speed and mean ambient temperature). Inverse moderate correlation was found between the contaminants analyzed. The daily and monthly concentrations of O_3 and NO_2 were lower than the TLV, therefore, the air quality in the period studied with respect to the analyzed pollutants is satisfactory.

1 Introduction

The development of human activities in recent times had caused an increase in emissions of toxic substances into the atmosphere, which led to an increase in the concentration of greenhouse gases and a gradual worsening of air quality.

Different environmental laws around the world regulate the abundance of various air pollutants, given that their presence in the ambient air above certain concentration levels implies an imminent threat to public health and the integrity of goods, materials and even forests and crops [1].

The studies on the concentration of primary pollutants (CO, SOx, NOx) and secondary pollutants (O_3) in the air of Quito in previous years reported low concentrations of carbon monoxide and sulfur dioxide, moderate to high tropospheric ozone concentrations and high concentrations of nitrogen dioxide, which exceeded the concentrations established by the national ambient air quality standards [2-3].

Monitoring of tropospheric ozone and nitrogen dioxide in ambient air is significant for two reasons: due to its impact on public health and direct effect of ozone on the oxidative capacity of the atmosphere.

[*] Corresponding author: cristian_salazarf@hotmail.com

As for the first reason, the presence of atmospheric pollutants such as nitrogen dioxide and ozone is directly related to a high risk of stroke, heart disease, asthma and lung cancer [4]. Therefore, it is necessary to monitor the levels of these pollutants in the air in order to warn the population if concentration values exceed the permitted values established by the standards of each country. In Ecuador the ambient air quality guideline [5] for ozone is set at the level of 100 $\mu g/m^3$ for daily maximum 8-hour mean and an annual mean concentration for nitrogen dioxide of 40 $\mu g/m^3$.

The second reason for the importance of environmental ozone monitoring is explained from the physical perspective of the mechanisms of secondary pollutants formation. That is, the presence to a greater or lesser degree of ozone in the ambient air directly influences on the formation of OH radicals and at the same time the combined action of these two oxidants impacts on the formation of the aerosol fraction of the fine particulate matter [6].

The mechanism of tropospheric ozone production has been extensively studied by several authors. Ozone is formed when the primary emissions of volatile organic compounds (VOCs) react with the hydroxyl radical (OH) to form hydroperoxyl radicals (HO_2) and other organic radicals, collectively called RO_2. Also, many of the organic compounds are photolysed in daylight and produce radicals. Once RO_2 species are formed, they react with primary NO emissions and form secondary NO_2. Now NO_2 has a photolysis peak of 400 nm, that is, at the beginning of the visible light spectrum. For this reason, daylight acts on primary and secondary NO_2 emissions, with the products of photolysis being atomic oxygen and NO. Finally, atomic oxygen combines with molecular oxygen and forms polluting ozone at the Earth's surface [7].

The distribution of ozone concentrations in mountainous areas can be very heterogeneous and is influenced by the meteorological processes associated with a complex relief, mainly by the regime of slope and valley winds. In these areas an increase in ozone levels is frequently related to altitude and a higher intensity of solar radiation respectively that favors photochemical reactions [8].

The present study focuses its interest specifically on two most problematic pollutants in recent years in the city of Quito: tropospheric ozone and nitrogen dioxide with the objective of describing the status of air pollution in the highest region of the city, in the period from January 2017 to December 2019.

2 Study area

Quito is located in the north of the Republic of Ecuador near the equator. It has a complex topography with heights between 1800 and 4000 meters above sea level. The air quality monitoring network of the city is equipped with eight automatic stations to measure concentrations of carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and particulate matter.

The Guamani automatic station is located in the south of the municipality (78°33'5" W, 0°19'51" S), in the highest part of the city at 3,600 masl (fig. 1).

All information on air quality is public and can be consulted and downloaded from the official website of the city municipality.

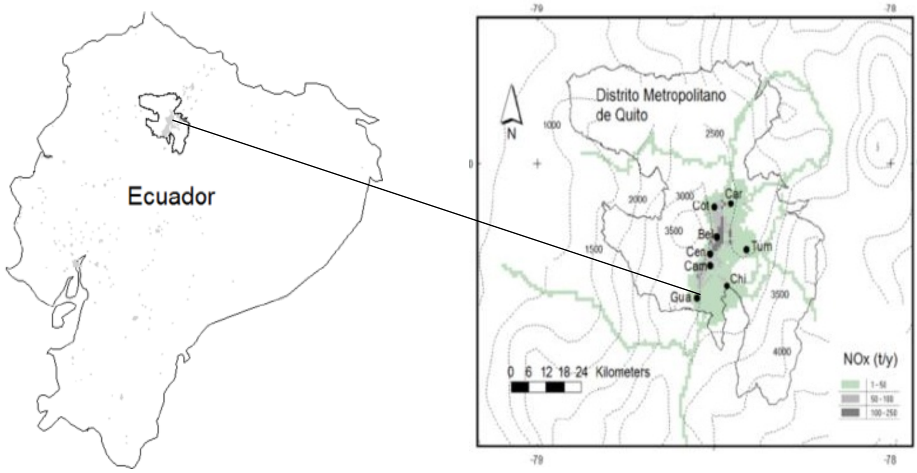


Fig. 1. Location of Guamani (Gua) automatic air quality monitoring station in Quito

3 Research method

The universe of the present study constitutes the daily concentrations of tropospheric ozone and nitrogen dioxide, obtained from Guamani monitoring station for the period between the years 2017-2019.

The Guamani monitoring station is equipped with Thermo Scientific ™ 49C / 49i ozone analyzer that utilizes UV Photometric technology to measure the amount of ozone (EPA equivalent method No. EQOA-0880-047) and a Thermo Scientific ™ 42C / 42i (NO-NO_2-NOx) analyzer that is based on chemiluminescence technology to measure the amount of nitrogen oxides in the air (EPA reference method No. RFNA-1289-074). The location and operation of the monitoring stations in Quito comply with the recommendations of the United States Environmental Protection Agency (US-EPA) (EPA. 40CFR58, Appendix E) and the World Meteorological Organization (WMO, No. 8) [9].

The Kolgomorov-Smirnov test was used to evaluate the goodness of fit of the studied pollutants concentrations distribution. In order to evaluate the relationships between the pollutants, Spearman's Rho coefficient was calculated, given the asymmetric distribution of the majority of data collected. Subsequently, multiple linear regression models were built between each pollutant and meteorological variables (average ambient temperature and wind speed).

4 Results and Discussion

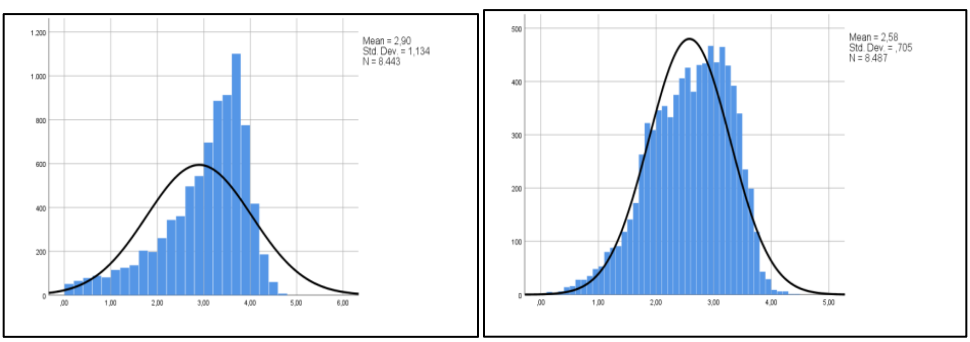
Table 1 shows that for both ozone and nitrogen dioxide, the arithmetic means do not transgress the allowed values, however, in the case of NO_2 at the 95^{th} percentile, the values are close to those established by the Ecuadorian standard. Maximum value of ozone is close to the reference value, and in the case of NO_2 it exceeded more than two times the permitted value, the latter pollutant showed the highest percentage in its frequency of violation of the norm.

Table 1. Summary values and percentages of violation of the threshold limit values (TLV) of the daily means of O_3 and NO_2

Pollutant	Mean ($\mu g/m^3$)	Percentiles				Maximum concentration ($\mu g/m^3$)	Percentage that exceeds the TLV (%)
		25	50	75	95		
O_3	27.09	11.78	25.35	39.42	60.43	120.44	0.08
NO_2	16.45	8.04	14.05	22.90	36.40	89.33	2.68

In a study conducted in the period 2005-2012 [10], the arithmetic mean of ozone was higher than that obtained in the present work (33.43 $\mu g/m^3$) and for nitrogen dioxide it was lower (15.57 $\mu g/m^3$). The low concentration of nitrogen dioxide in the previously conducted study is explained by the fact that in this period the vehicle technical inspection by the city municipality began, so that the atmospheric pollution by the automotive fleet decreased, moreover, the strongest solar radiation was recorded compared to the other periods [9], as large quantity of nitrogen dioxide reacted to form ozone.

In another study carried out within the period 2013-2016 [11] mean concentrations of ozone 30.31 $\mu g/m^3$ and nitrogen dioxide 20.35 $\mu g/m^3$ were obtained, but in comparison with data obtained in the current study these concentrations are higher. This increase in the concentration of nitrogen dioxide is largely due to the fact that in this period a large number of forest fires were recorded compared to other periods [12].



a) b)

Fig. 2. Histogram of the distribution of concentration data a) O_3, b) NO_2

When applying the Kolmogorov-Smirnov test, the napierian logarithm of the variables was determined, and it was found that the studied pollutants do not follow a normal distribution (NO_2: 0.05, $p < 0.05$; O_3: 0.13, $p < 0.05$) (Fig. 2a and 2b).

Although the studied pollutants did not show a normal distribution, multiple linear regression models between their concentrations and the previously described meteorological variables were constructed in order to have an approximation of their interaction.

Regarding NO_2 mean temperature (beta = -0.092, $p < 0.01$) and daily wind speed (beta = -0.542, $p < 0.01$), the highest concentrations were associated with low temperatures and light wind speed. This behavior according to PAHO [13] is due to the fact that low temperatures together with weak winds in a city with a stable climate, such as Quito, cause a thermal inversion, which leads to an accumulation of pollutants.

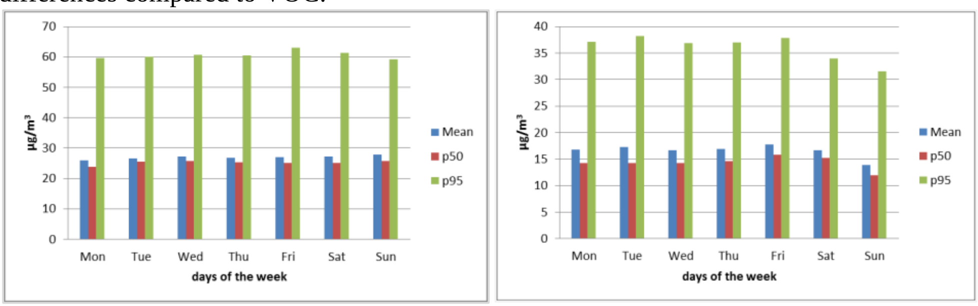
Tropospheric ozone has a direct and significant relationship with temperature (beta = 0.524, $p < 0.05$) and with wind speed (beta = 0.290, $p < 0.05$). The highest concentrations of ozone were recorded with increasing temperature and increasing wind speeds. This behavior of ozone is due to the fact that the increase in atmospheric temperature associated with the heating of the day, favorably affects the kinetics of the ozone formation reactions [2].

 https://doi.org/10.1051/e3sconf/202016901017

Table 2. Spearman's correlation coefficient between contaminants

Pollutant	NO_2	O_3
NO_2	1.00	-0.58, p<0.05
O_3	-0.58, p<0.05	1.00

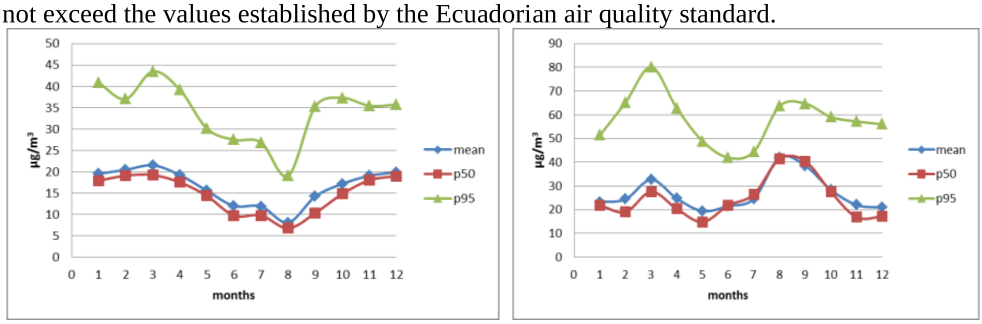
As the pollutants do not follow a normal distribution, the Spearman correlation was used to establish the correlation between them, where nitrogen dioxide and ozone have a moderate negative correlation (see table 2), this is due to the fact that in a city with low traffic flow, for example, the city of Quito, out of two most important ozone precursors (NO_2 and VOC), nitrogen dioxide limits the formation of ozone [14], but in this case without significant differences compared to VOC.



a) b)

Fig. 3. Daily behavior of a) O_3, b) NO_2

Figures 3a, and 3b describe the behavior of the studied pollutants according to the days of the week. According to the mean and the 50th percentile, the weekend effect is evident in the south of the city of Quito, especially on Sundays, where the level of ozone concentration is lower than on the other days of the week, while the concentration of nitrogen dioxide is the highest. On Saturdays there is no aforementioned behavior, since in the south of the city, on this day, commercial activities with the large influx of people are organized that causes greater vehicular flow. The concentrations of the pollutants did not show noticeable differences during the rest days of the week, where the 95th percentile in both pollutants did not exceed the values established by the Ecuadorian air quality standard.



a) b)

Fig. 4. Monthly behavior of a) O_3, b) NO_2

Figure 4a shows maximum values of the mean, median and 95th percentile of ozone concentrations in the following months: March, August and September. The high values in March and September are largely due to the arrival of the equinox, a phenomenon in which the sun rays fall perpendicularly in the equator, as Quito is located in a mountainous area, the city is more prone to the influence of solar radiation favoring the formation of ozone.

When analyzing figure 4b, the monthly behavior of nitrogen dioxide denotes that between February and April the highest concentrations were recorded. These months coincide with the winter season, which is prone to thermal inversions by radiation, making the dispersion of pollutants in the air closer to the Earth's surface less favorable during the night and early morning hours [13]. The lowest concentrations for the mean, median and 95th percentile were recorded from June to August, which corresponds to the period of student vacations, when vehicle flow drastically reduces.

In the city of Quito, the transport sector is one of the most important sources of tropospheric ozone precursors (nitrogen oxides and volatile organic compounds). With the start of metro operation in 2020, it is expected that the concentrations of the pollutants under study will decrease, as it emits far less pollution compared to other types of transport, moreover, the traffic congestion will be reduced.

5. Conclusions

According to the results obtained, it is determined that the air quality in the south of Quito in the period between the years 2017 to 2019 with respect to the analyzed pollutants is satisfactory, this is due to the fact that the arithmetic means of the daily concentrations of ozone and nitrogen dioxide were lower than the maximum permissible concentrations by 72% and 58%, respectively. Moreover, as per the monthly analysis of the pollutants the maximum value of the 95th percentile of the monthly ozone concentration was 20% lower than that established by the Ecuadorian air quality standard, as for the 95th percentile of nitrogen dioxide, it exceeded the allowed value in March by 8%, however, in the rest months it remained below the standard.

The weekend effect is mainly evident on Sundays, where the arithmetic mean of ozone compared to the day with the greatest contamination was 2% higher, and in the case of nitrogen dioxide 19% lower.

The publication has been prepared with the support of the "RUDN University" Program 5-100.

References

1. A. Kurbatova, Y. Mikhaylichenko, A. Dorontsova, *IOP Conference Series: Earth and Environmental Science*, **272(2)**, 022107 (2019)
2. M. Cazorla. ACI, J. **5**, 67-78 (2013)
3. R. Parra, E. Franco, AIR 2016, **207**, 169–180 (2016)
4. O. Roman, M. Prieto, P. Mancilla, REV MED CHILE, **132**, 761-767 (2004)
5. Ministerio del Ambiente de Ecuador, *Norma Ecuatoriana de la calidad del aire* (MAE, Quito, 2011) (in Spanish).
6. J. Seinfeld, P. Spyros, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley&Sons, 2016).
7. M. Jacobson, *Atmospheric Pollution: History, science and regulation* (Cambridge University Press, 2002).
8. E. Gégo, P. Porter, A. Gilliland, S. Rao. J APPL METEOROL CLIM, **46**, 994 – 1008 (2007).
9. Secretaría del Ambiente. *Informe de la calidad del aire de Quito 2016*. (MDMQ, Quito, 2016) (in Spanish).
10. P. Bazante, *Análisis de la concentración de contaminantes atmosféricos en el DMQ* (USQF, Quito, 2015) (in Spanish).

11. J. Manosalvas, *Análisis temporal multivariante de la contaminación atmosférica dentro del DMQ* (UPM, Madrid, 2017) (in Spanish).
12. K. Ochoa. *Emergencia en Quito: El número de incendios forestales se quintuplicó* (Metro, Quito, 2014) (in Spanish).
13. Organización panamericana de la salud. *Curso básico sobre contaminación del aire y riesgos para la salud* (OPS, México, 1991) (in Spanish).
14. R. Parra, ACI, J. **9**, 104-111 (2017).