Assessment of the NO2 distribution and relationship with traffic load in the Caribbean coastal city

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Abstract

NO_2 ambient concentrations were measured in a coastal Caribbean city. Barranquilla is a Caribbean city located in the North of Colombia that has approximately 1.200.000 inhabitants and possesses a warm, humid climate. In order to obtain the concentration of the contaminant in an adequate resolution, 137 passive diffusion tubes from Gradko© were installed. Diffusion passive tubes prepared with 20% TEA/water were located at the roadside between 1 and 5 m from the kerb edge. The sampling period was two weeks, from 3/16/2019 to 3/30/2019. Samples were analyzed on the UV CARY1 spectrophotometer by Gradko©. Results showed an average of 19.92 ±11.50 $\mu g/m^3$, with a maximum and minimum value of 70.27 and 0.57 $\mu g/m^3$, respectively. Spatial NO_2 correlation with low traffic load was higher than with maximum traffic. The expected results include analyzing the areas of the city with high concentrations of this pollutant that exceed the WHO guidelines in six (6) points. Overall, the multiregression analysis is a very effective method to enrich the understanding of NO_2 distributions. It can provide scientific evidence for the relationship between NO_2 and traffic, beneficial for developing the targeted policies and measures to reduce NO_2 pollution levels in hot spots. This research may subsidize knowledge to serve as a tool for environmental and health authorities.

Keywords: *NO_2, spatial variability, regression model*

Introduction

Urban air pollutant distribution is a concern in environmental and health studies. Nitrogen dioxide (NO_2), one of the primary air pollutants, may contribute to the formation of atmospheric particles through various photochemical reactions, including nitrate particles, which form an essential fraction of $PM_{2.5}$ and, in the presence of ultraviolet light, of ozone (O_3) that leads photochemical smog events (Felix et al., 2019). It is a severe problem in large cities because the primary sources of anthropogenic NO_2 emissions are combustion processes, vehicular traffic load, industrial boilers, and shipping. Under certain weather conditions, elevated NO_2 concentrations in urban areas with high population density can accumulate to dangerous levels and contribute to adverse health effects, such as inflammation of the airways and reduced lung function. Epidemiological studies have shown that bronchitis symptoms in asthmatic children increase in association with long-term exposure to NO_2 and reduced lung function growth (Achakulwisut et al., 2019). The increase of NO_2 concentrations not only severely affects human physical health due to reduced lung function but also to aquatic ecosystems due to acid deposition and eutrophication of soil and water (Coughlin et al., 2017). Understanding near-road NO_2 impacts are essential due to the number of people living close to primary transportation sources (Kimbrough et al., 2017).

Diffusion passive tubes are lightweight, economical, and need no maintenance, on-site energy, and pumping. There are various methods of measuring atmospheric pollutants, within which passive sampling offers many advantages depending on the objective of the investigation. The advantages of this method include its operational simplicity and its minimal need for labor, as well as the ease of its use due to the lack of maintenance and calibration of air pumps, the possibility of prolonged sampling times, minimum probability of committing personal errors, the general reliability of the acceptable method (NTP 151). In addition to the possibility of knowing the concentration of the pollutant at several points simultaneously in order to cover a considerable area when there is limited monitoring equipment cost-effectively. Although they do not use a vacuum pump, this passive method requires more extended sampling periods (24 hours or more). The passive sampling method has an extensive use with several applications on the occupational exposure monitoring and mapping of the spatial variation of pollutant concentrations over geographical areas in cities (Felix et al., 2019; Lanzafame et al., 2016).

Barranquilla, driven by unprecedented economic growth, the explosive increase in urbanization and population, can experience severe NO_2 air pollution problems. Recent studies indicate increasing concentrations of NO_2 in developing countries, despite declining trends in developed countries, probably as a result of environmental regulation policies in the latter(Geddes et al., 2016; Zhang et al., 2017). However, much of the research up to now has been focused on megacities with different climates and seasons, while few studies exist in Caribbean cities where local environmental conditions may be different. Moreover, the study area has a deficiency in the number of monitoring points for NO_2. Therefore, it is essential to perform a spatial assessment of the relationship between NO_2 pollution and traffic load in a Caribbean coastal city.

2. MATERIAL AND METHODS

2.1. Study area

Barranquilla, one of the principals and most important cities of Colombia, is located on the western edge of the Magdalena River, 7.5 km from its mouth in the Caribbean Sea. The study area is the main economic center of the Caribbean Region of Colombia, principally commerce and industry, with 154 km^2 of area and a population of about 1,193,952 inhabitants (Barranquilla, 2018; Morgado et al., 2018). Among the industries may be included vegetable fats and oils, pharmaceutics, chemicals, footwear, bus bodies, dairy products, sausages, beverages, soaps, building materials, furniture, plastics, cement, metalworking parts, clothing, and boats. Moreover, the maritime and fluvial terminals are engines of the industrial and commercial development of the Caribbean Region. Few industries use diesel as combustible, while mostly all use natural gas. The port of Barranquilla covers two main routes, the Magdalena River, which communicates with the interior of the country (advantage not possessed by other ports on the Caribbean coast) and the Caribbean Sea, which millions of tones traded with Europe and Asia. The study area has an extensive industrial area along the banks of the Magdalena River, along with several ports that store and export mineral coal and coke. In addition, it has several incinerators of hazardous waste and brickkilns.

The study area is characterized by few rainy days; annual totals do not exceed 1000 mm. The number of rainy days during the year ranges from 50 to 100 mm. The annual regime is bimodal type; the primary rain season extends from September to November, and in the first semester, there is a short rainy season in May. Dry seasons occur between December and April, the main one, and a second one, with lower intensity in the months of June, July, and August (IDEAM, 2019).

2.2. Selecting Diffusion Tube Sites and traffic data

The sampling period was two weeks from 3/16/2019 to 3/30/2019 in the areas called Riomar, and Norte Centro Historico in 114 points of Barranquilla. Figure 1 shows the diffusive passive NO_2 samplers' location. The passive diffusive samplers were positioned across different sites; on lampposts, street signs, a fence, or other appropriate sites according to Selecting Diffusion Tube Sites criteria established by the Gradko © Environmental. Some of these criteria include an immediate area opened, which had allowed the free air circulation and avoided locations where they were likely to be affected by turbulence. Diffusion tubes were located at the roadside between 1 and 5 m from the kerb edge and placed at a height between 2 and 3 meters to no under-estimate the concentrations to which pedestrians are exposed.

It was measured hourly traffic counts during peak hours (HP in veh/hr) and *average daily traffic* (ADT in veh/day). For each sampling site location, considering the road type, ADT was estimated using *peak hour volume* (HP) measured data in an entire day. Two thousand eighteen hourly mean data of the studying area was calculated from the local air quality station, in order to understand the atmospheric chemistry. Values were measured every 5-min, and 1h means were calculated after the validation methods were applied. Nitrogen oxides (NO, NO_2 and NO_X) and ozone (O_3) were measured by an automatic analyzer by the chemiluminescence, a UV method, respectively.

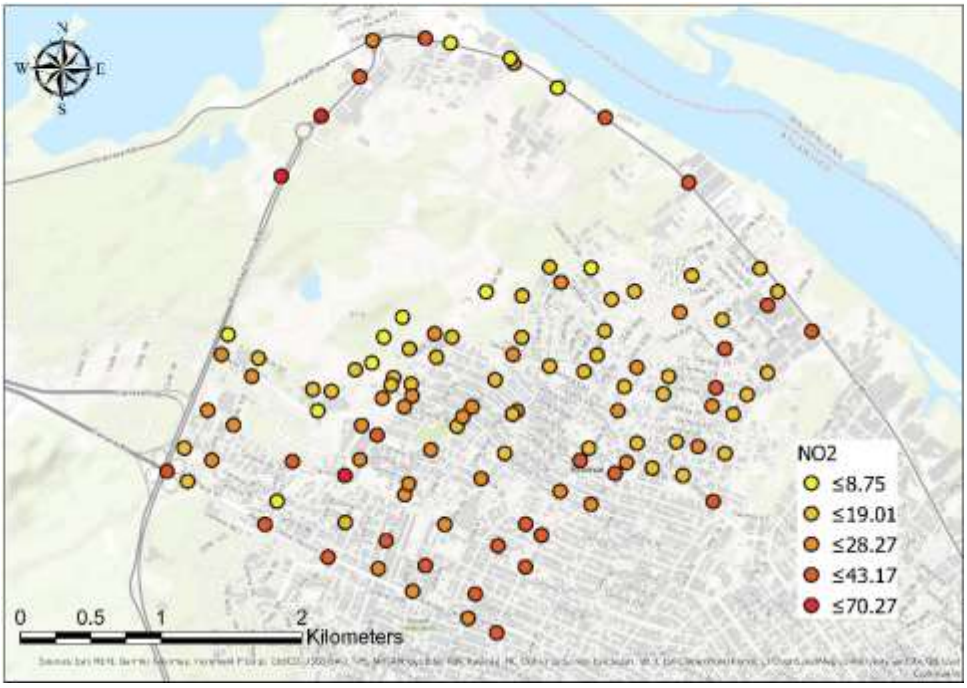


Figure 1. Location of diffusive passive NO_2 samplers and NO_2 concentration ranges

2.2. Overview of NO_2 concentration Measurement

In this research, the NO_2 concentration measurement was conducted in two steps: sample collection and laboratory analysis. Samples were collected for 337 hours average using passive diffusion tubes prepared with 20% TEA/water from Gradko © Environmental. Figure 2 shows the NO_2 sample collection tube passive mechanism.

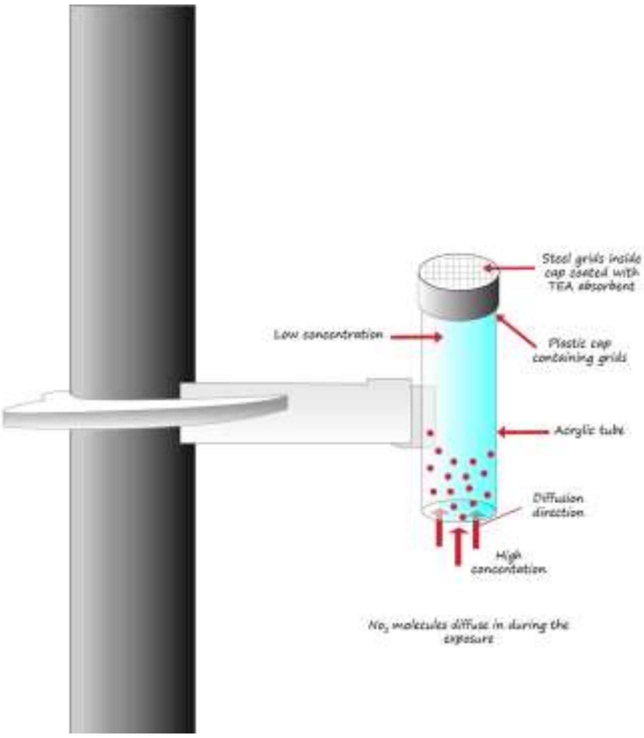


Figure 2. NO_2 sample collection tube passive mechanism

Tubes were stored plastic containers and sealable clean plastic bags in a refrigerator to avoid contamination during transportation, including blanks as control. All tubes were clearly labeled with a unique sample code. A survey sheet was filled with site details and timings for each sample and provided to the laboratory. Samples were analyzed on a UV CARY1 spectrophotometer by Gradko © Environmental. The detection limit was 1.11 $\mu g/m^3$. Figure 3 shows samples collecting and analyzing procedures.

Figure 3. Samples were collecting and analyzing procedures.

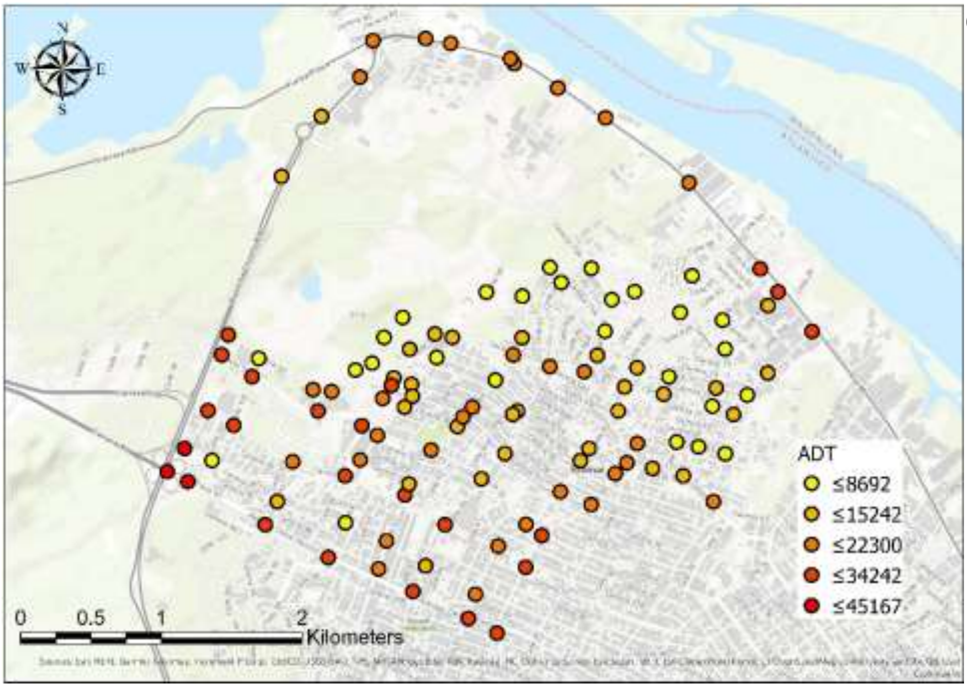
2.4 Data Analysis for NO_2 spatial variation and traffic load assessment

The data was systematized in a spreadsheet by location data, ID passive sampler, exposure data, NO_2 concentration in µg/m^3, and average daily traffic (Vehicles*day^{-1}·m) as independent variables. Data analysis was performed to determine the significant statistical relationship and degree of association between variables: NO_2 concentration µg/m^3, and ADT with 95% confidence ($p < 0.05$). In addition, a logistic regression model was performed to establish the variable's influence of non-compliance with the maximum concentration of NO_2. This influence was corroborated by a neural network that allows identifying the situations in which the NO_2 concentration WHO guidelines would be exceeded.

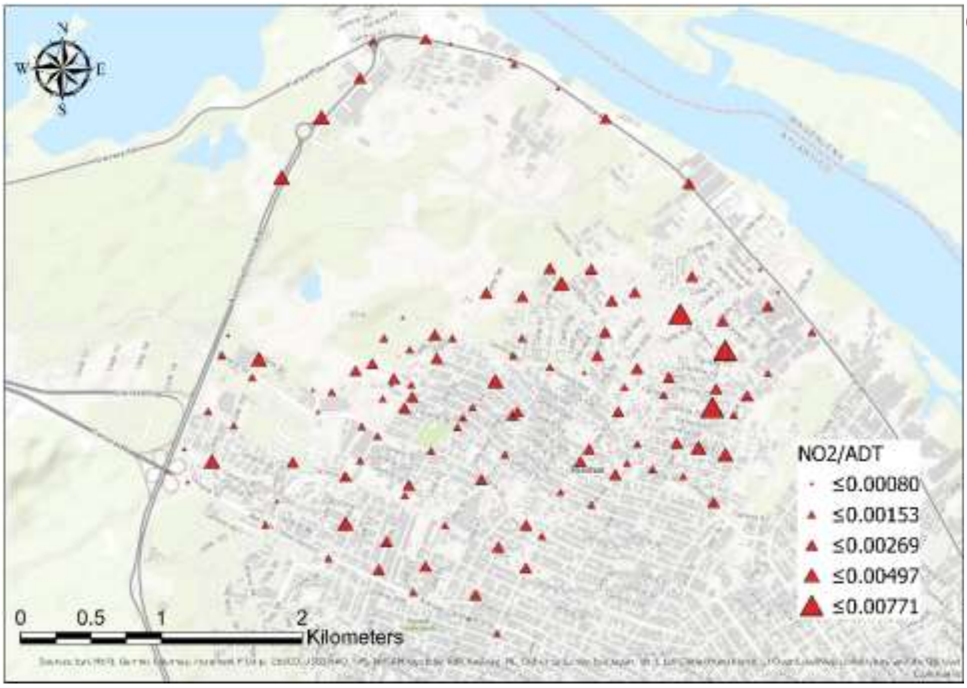
3. Results

Results showed an average of 19.92 ±11.50 µg/m^3, with a maximum and minimum value of 70.27 and 0.57 µg/m^3, respectively. 35%, 26% and 17% of the results were in these ranges 8.4-16.2 µg/m^3, 16.2-24.0 and 24.0-31.8 µg/m^{3,} respectively, summing 78% of data. Figure 1 shows the results of NO_2 concentration over the study area during the sampling period. It can be seen the relatively low level of NO_2 concentration, although the high traffic density, high temperatures, and ozone concentrations. In comparison with other studies made in Europe, results indicate an urban background environment and not near road street location values

(Cyrys et al., 2012). In order to better understand the results, ADT was analyzed (Figure 4), too, and compared with NO_2. Some hot spots clearly show a relation with high traffic areas, although someones with industrial areas. One major source of high values of NO_2 is the usage of diesel and petrol generators for electricity during the electric power outage in industries or local commerce (ul-Haq et al., 2014). Thus, the highest values corresponded to industries because of the significant electrical blackouts in the study area. Figure 1 shows, too, high NO_2 values near the river caused by some local harbors. Some points presented high values in 4-lines vehicular intersections downwind locations after the roadways, too. NO_2 concentration/TPD results show 0.0008 up to 0.00771, thus confirming what we stated above.



(a)



(b)

Figure 4 a,b. Average daily traffic - ADT (a) and relation between NO_2 concentration/ADT (b)

Multi-regression statistical analysis was performed for the NO_2 concentration and peak hour volume (HP). ANOVA results may be observed in Table 1, were p-value < 0.05 for equation 1 with an adjusted R^2 of 78.44%. A logarithmic fitted model was obtained with intervals showed in Figure 5.

$$NO_2 = -12{,}8936 + 4{,}59836 * \ln(HP) \qquad \text{Eq. (1)}$$

Table 1. Analysis of Variance

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Model	55855,67	1	55855,67	465,80	0,0000
Residual	15349,05	128	119,9145		
Total	71204,72	129			

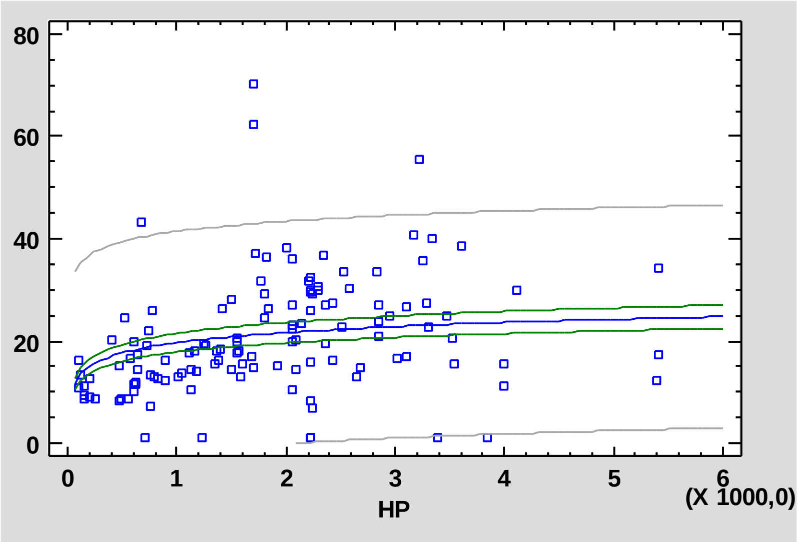


Figure 5. The plot of the fitted model between NO_2 and HP.

For further analysis, a multi-regression statistical analysis was performed for the NO_2 concentration and ADT. ANOVA results showed significance (Table 2), were p-value was < 0.05 for equation 2 with an adjusted R^2 of 92.86%. An exponential fitted model was obtained with intervals showed in Figure 6.

$$NO_2 = e^{(0.29953*\ln TPD))} \qquad \text{Eq. 2}$$

Table 2. Analysis of Variance

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Model	1018,759	1	1018,759	1664,15	0,0000
Residual	78,3589	128	0,6121789		
Total	1097,118	129			

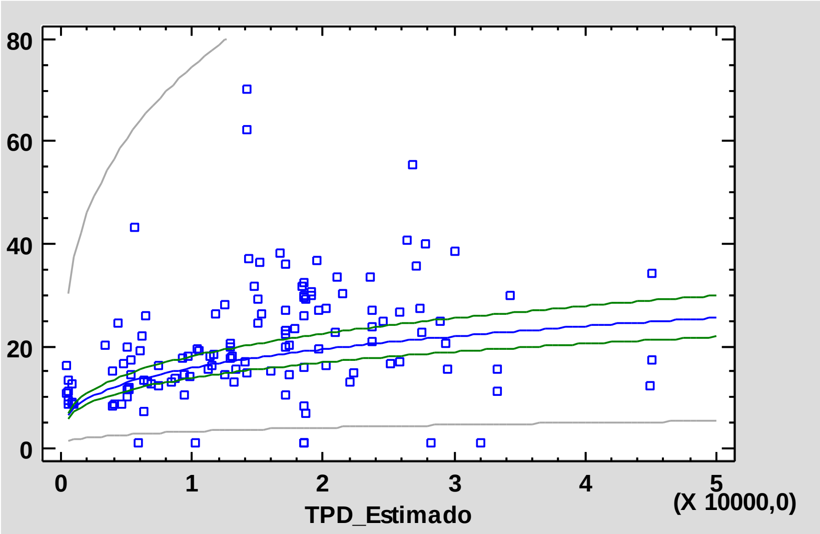


Figure 6. The plot of the fitted model between NO_2 and TPD.

Moreover, a Goodness-of-Fit Tests for Residuals using Kolmogorov-Smirnov normality test was done, were p-value was higher than 0.05, showing normality in the results (Table 3). Residuals from models demonstrated significant spatial autocorrelation, as evidenced by a significant correlation of the residuals. These results indicate that for more traffic load, higher NO_2 values may be obtained.

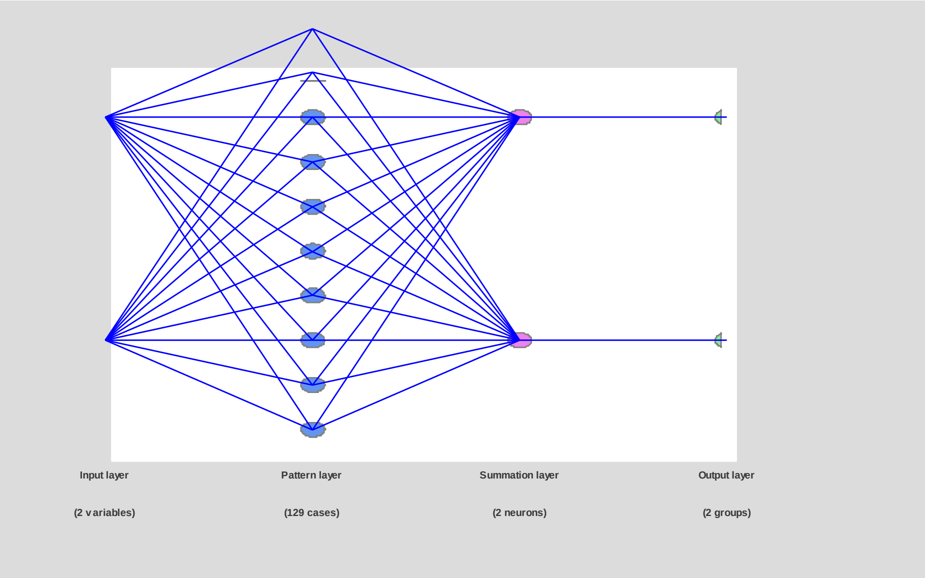
Table 3. Kolmogorov-Smirnov Test

	Normal
DPLUS	0,08856723
DMINUS	0,09492463
DN	0,09492463
P-Value	0,1957059

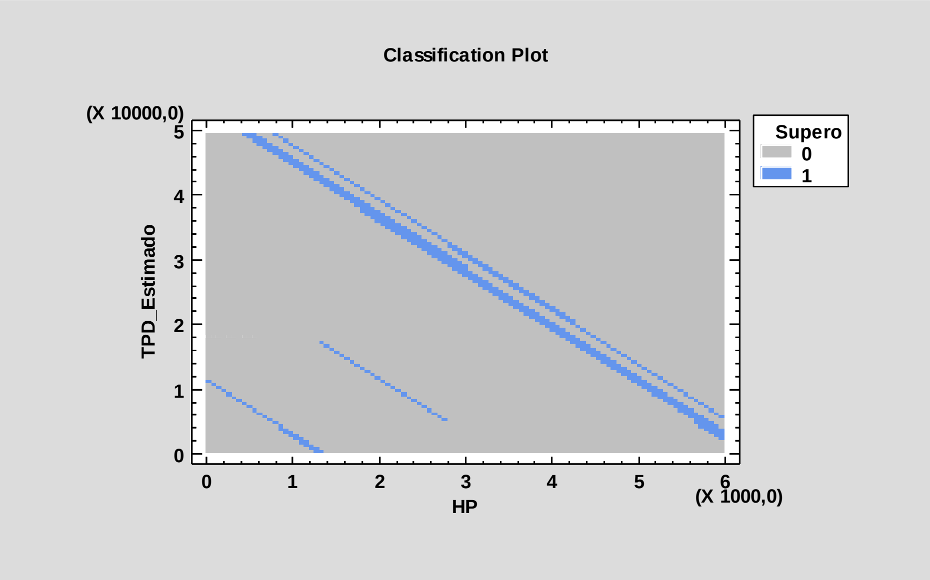
Applied artificial neural networks classified by WHO guideline value of 40 µg/m^3 may be observed in Figure 7 and Table 4, were six (6) samples surpassed this standard. High ozone levels are typical in the coastal cities, including the study area. Moreover, Figure 7 shows for certain values of traffic load and peak traffic per hour, NO_2 concentrations may be higher than WHO guidelines. For example, for 4816 peak hour volume of vehicles (HP) and 12984 ADT, high NO_2 concentrations are present (> 40 µg/m^3). However, the comparison with the air quality standard for the annual average is limited because we sampled only one 2-week period. However, these are outstanding results because values were lower than WHO standards for almost all points, even though the study area has several stationary sources, harbors, and high traffic. Probably, emitted NO and transformed to NO_2, reacts rapidly with other air pollutants such as organic compounds or ozone, although the correlation of NO_2 with other air pollutants is low (Figure 8).

Table 4. Training Set

Exceed	*Members*	*Percent Correctly Classified*
0	123	97,56098
1	6	66,66667
Total	129	96,12403



(a)



(b)

Figure 7. Schematic representation of the multicap perceptron neural network used to classify NO_2 concentration by WHO standards (a) and estimated values for meeting standards (b).

In order to better understand the relationship between NO_2 and local sources, ratio values with 2018 hourly mean data of the studying area was calculated. Figure 8 shows the variation of the daily mean $[NO_2]/[NOx]$ (a), $[NO_2]/[OX]$ (b), and O_3 as a function of NOx. In some studies, analysis of the $[NO_2]/[NOx]$, $[NO_2]/[OX]$ ratio values have been used to explore the ground–level O_3 concentration variations and the relationship between NO_2 data (Clapp and Jenkin, 2001), because a photostationary state relationship exists between these pollutants. The exponential relationship observed in Figure 8 reveals that for lower values of the $[NO_2]/[OX]$ ratio, there are low values of NOX, implying that in these instants, OX concentrations are predominantly marked by high O_3 concentrations. Moreover, for increasing the NOx concentrations, a significant part of OX is in the form of NO_2. Mostly, all values of $[NO_2]/[NOx]$ were 1, explained by the oxidation process of NO to NO_2, with concentrations of NOx being marked mainly by the concentration of NO_2. Also, the relationship of NO_2 with O_3 is low, thus implying that the latter is influenced by the atmospheric boundary layer, typical of coastal areas. Probably, formation and accumulation of ozone are favoured by the conditions under a pure sea-land breeze: that is, perpendicular wind directions toward the coastline, active recirculation of air masses, and formation of residual ozone layers above the sea (Adame et al., 2010). However, further studies should be conducted to understand the precise relationship between NO_2 and O_3 and obtain proper functions.

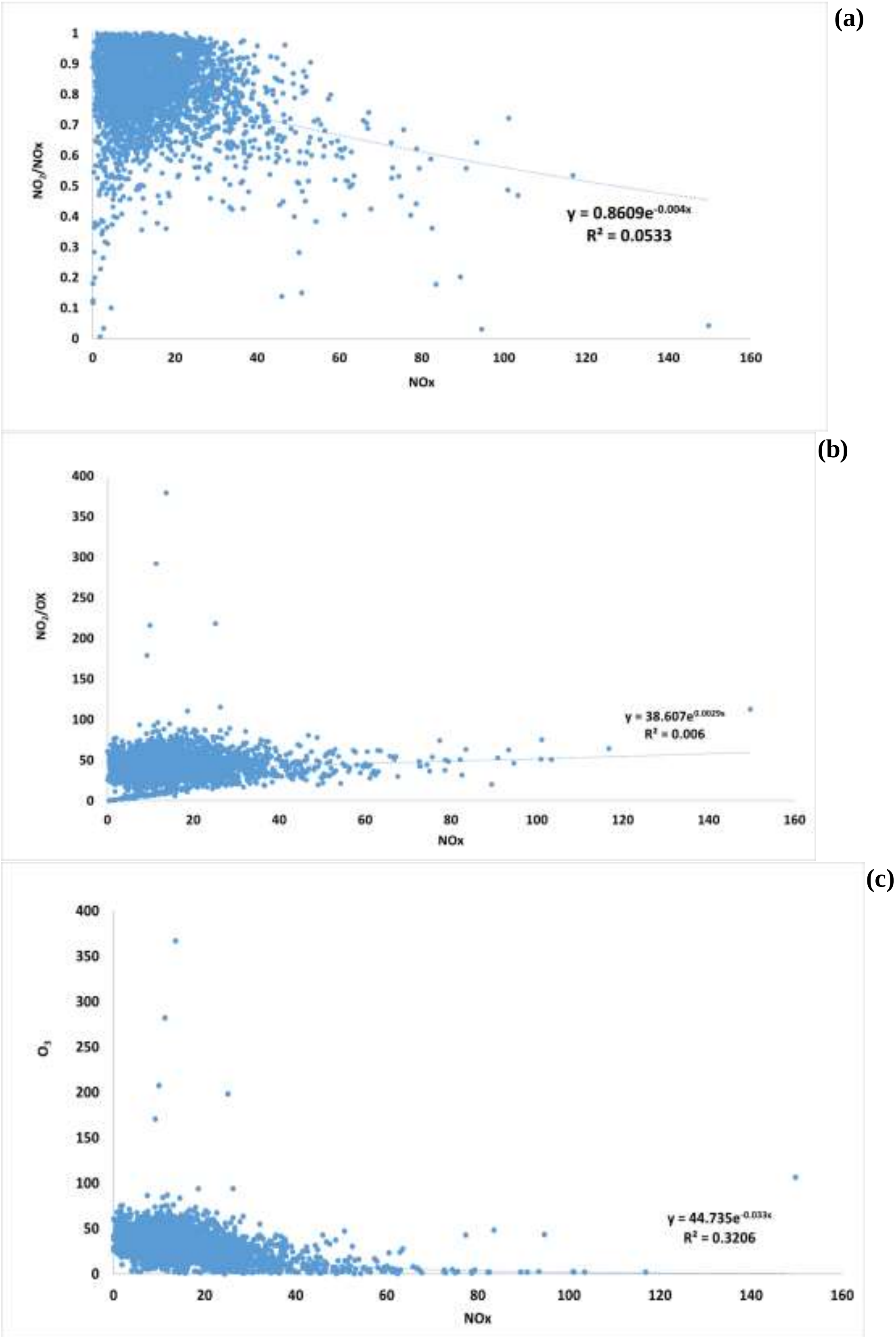


Figure 8. Variation of the daily mean $[NO_2]/[NOx]$ (a), $[NO_2]/[OX]$ (b) and O_3 as a function of NOx

Conclusions

In this investigation, the aim was to do a spatial assessment of the NO_2 relationship with traffic load in a Caribbean coastal city. The findings of this research provide insights into the urban NO_2 distribution. This approach will prove useful in expanding our understanding of how the spatial variability of NO_2 in Caribbean cities. Hot spots of the study area included stationary sources, harbors, and a high traffic load impacted intersection.

Overall, the multiregression analysis is a very effective method to enrich the understanding of NO_2 distributions. It can provide scientific evidence for the relationship between NO_2 and traffic, beneficial for developing the targeted policies and measures to reduce NO_2 pollution levels in hot spots. This research may subsidize knowledge to serve as a tool for environmental and health authorities.

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