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 µg/m$^3$, with a maximum and minimum value of 70.27 and 0.57 µg/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 (NO₂), 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 PM₂.₅ and, in the presence of ultraviolet light, of ozone (O₃) that leads photochemical smog events (Felix et al., 2019). It is a severe problem in large cities because the primary sources of anthropogenic NO₂ emissions are combustion processes, vehicular traffic load, industrial boilers, and shipping. Under certain weather conditions, elevated NO₂ 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 NO₂ and reduced lung function growth (Achakulwisut et al., 2019). The increase of NO₂ 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 NO₂ 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 NO₂ air pollution problems. Recent studies indicate increasing concentrations of NO₂ 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](image)
2.2. Overview of NO₂ concentration Measurement

In this research, the NO₂ 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 NO₂ sample collection tube passive mechanism.

![Figure 2. NO₂ sample collection tube passive mechanism](image)

Tubes were stored in 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 μg/m³. Figure 3 shows samples collecting and analyzing procedures.
2.4 Data Analysis for NO₂ spatial variation and traffic load assessment

The data was systematized in a spreadsheet by location data, ID passive sampler, exposure data, NO₂ concentration in µg/m³, and average daily traffic (Vehicles*day⁻¹*km) as independent variables. Data analysis was performed to determine the significant statistical relationship and degree of association between variables: NO₂ concentration µg/m³, 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 NO₂. This influence was corroborated by a neural network that allows identifying the situations in which the NO₂ concentration WHO guidelines would be exceeded.

3. Results

Results showed an average of 19.92 ±11.50 µg/m³, with a maximum and minimum value of 70.27 and 0.57 µg/m³, respectively. 35%, 26% and 17% of the results were in these ranges 8.4-16.2 µg/m³, 16.2-24.0 and 24.0-31.8 µg/m³ respectively, summing 78% of data. Figure 1 shows the results of NO₂ concentration over the study area during the sampling period. It can be seen the relatively low level of NO₂ 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.
**Figure 4 a,b.** Average daily traffic - ADT (a) and relation between NO₂ concentration/ADT (b)

Multi-regression statistical analysis was performed for the NO₂ 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 R² of 78.44%. A logarithmic fitted model was obtained with intervals showed in Figure 5.

\[
\text{NO}_2 = -12,8936 + 4,59836 \times \ln(\text{HP})
\]

Eq. (1)

| 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|             |         |         |
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.

$$\text{NO}_2 = e^{(0.29953 \times \ln TPD)}$$

Eq. 2

| 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|             |         |         |

Table 2: Analysis of Variance
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       | 66.6667                     |
| Total  | 129     | 96.12403                    |

![Classification Plot](image)

(a) Input layer (2 variables)  
Pattern layer (129 cases)  
Summation layer (2 neurons)  
Output layer (2 groups)

(b) Classification Plot

Supero

0 1
**Figure 7.** Schematic representation of the multicap perceptron neural network used to classify NO\textsubscript{2} concentration by WHO standards (a) and estimated values for meeting standards (b).

In order to better understand the relationship between NO\textsubscript{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\textsubscript{2}]/[NOx] (a), [NO\textsubscript{2}]/[OX] (b), and O\textsubscript{3} as a function of NOx. In some studies, analysis of the [NO\textsubscript{2}]/[NOx], [NO\textsubscript{2}]/[OX] ratio values have been used to explore the ground–level O\textsubscript{3} concentration variations and the relationship between NO\textsubscript{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\textsubscript{2}]/[OX] ratio, there are low values of NOX, implying that in these instants, OX concentrations are predominantly marked by high O\textsubscript{3} concentrations. Moreover, for increasing the NOx concentrations, a significant part of OX is in the form of NO\textsubscript{2}. Mostly, all values of [NO\textsubscript{2}]/[NOx] were 1, explained by the oxidation process of NO to NO\textsubscript{2}, with concentrations of NOx being marked mainly by the concentration of NO\textsubscript{2}. Also, the relationship of NO\textsubscript{2} with O\textsubscript{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\textsubscript{2} and O\textsubscript{3} and obtain proper functions.
Figure 8. Variation of the daily mean \([\text{NO}_2]/[\text{NOx}]\) (a), \([\text{NO}_2]/[\text{OX}]\) (b) and \(\text{O}_3\) as a function of NOx
Conclusions

In this investigation, the aim was to do a spatial assessment of the NO\textsubscript{2} relationship with traffic load in a Caribbean coastal city. The findings of this research provide insights into the urban NO\textsubscript{2} distribution. This approach will prove useful in expanding our understanding of how the spatial variability of NO\textsubscript{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\textsubscript{2} distributions. It can provide scientific evidence for the relationship between NO\textsubscript{2} and traffic, beneficial for developing the targeted policies and measures to reduce NO\textsubscript{2} pollution levels in hot spots. This research may subsidize knowledge to serve as a tool for environmental and health authorities.

Acknowledgments

Universidad del Norte supported this work. We acknowledge all grad students for their help during sampling. Also, the local environmental agency of the mayor’s office the Barranquilla Air Quality Monitoring Network. EPA – Barranquilla Verde, Barranquilla, Colombia

References

Achakulwisut, P., Brauer, M., Hystad, P., Anenberg, S.C., 2019. Global, national, and urban burdens of pediatric asthma incidence attributable to ambient NO\textsubscript{2} pollution: estimates from global datasets. Lancet Planet. Heal. 3, e166–e178. https://doi.org/10.1016/S2542-5196(19)30046-4

Adame, J.A., Serrano, E., Bolívar, J.P., de la Morena, B.A., 2010. On the tropospheric ozone variations in a coastal area of Southwestern Europe under a mesoscale circulation. J. Appl. Meteorol. Climatol. 49, 748–759. https://doi.org/10.1175/2009JAMC2097.1

Coughlin, J.G., Yu, Z., Elliott, E.M., 2017. Efficacy of passive sampler collection for atmospheric NO\textsubscript{2} isotopes under simulated environmental conditions. Rapid Commun. Mass Spectrom. 31, 1211–1220. https://doi.org/10.1002/rcm.7885

Cyrys, J., Eeftens, M., Heinrich, J., Ampe, C., Armengaud, A., Beelen, R., Bellander, T., Beregszaszi, T., Birk, M., Cesaroni, G., Cirach, M., de Hoogh, K., De Nazelle, A., de Vocht, F., Declercq, C., Dedele, A., Dimakopoulou, K., Eriksen, K., Galassi, C., Graulevičiene, R., Grivas, G., Gruzieva, O., Gustafsson, A.H., Hoffmann, B., Iakovides, M., Ineichen, A., Krämer, U., Lanti, T., Lozano, P., Madsen, C., Meliefste, K., Modig, L., Mölter, A., Mosler, G., Nieuwenhuijsen, M., Nonnemacher, M., Oldenwening, M., Peters, A., Pontet, S., Probst-Hensch, N., Quass, U., Raaschou-Nielsen, O., Ranzi, A., Sugiri, D., Stephanou, E.G., Taimisto, P., Tsai, M.Y., Vaskövi, É., Villani, S., Wang, M., Brunekreef, B., Hoek, G., 2012.
Variation of NO2 and NOx concentrations between and within 36 European study areas: Results from the ESCAPE study. Atmos. Environ. 62, 374–390. https://doi.org/10.1016/j.atmosenv.2012.07.080

Felix, E., Gidhagen, L., Alonso, M.F., Nahirny, E.P., Alves, B.L., Segersson, D., Amorim, J.H., 2019. Passive sampling as a feasible tool for mapping and model evaluation of the spatial distribution of nitrogen oxides in the city of Curitiba, Brazil. Air Qual. Atmos. Heal. 12, 837–846. https://doi.org/10.1007/s11869-019-00701-z

Geddes, J.A., Martin, R. V., Boys, B.L., van Donkelaar, A., 2016. Long-term trends worldwide in ambient NO2 concentrations inferred from satellite observations. Environ. Health Perspect. 124, 281–289. https://doi.org/10.1289/ehp.1409567

Kimbrough, S., Chris Owen, R., Snyder, M., Richmond-Bryant, J., 2017. NO to NO2 conversion rate analysis and implications for dispersion model chemistry methods using Las Vegas, Nevada near-road field measurements. Atmos. Environ. 165, 23–34. https://doi.org/10.1016/j.atmosenv.2017.06.027

Lanzafame, R., Monforte, P., Scandura Pier, F., 2016. Comparative Analyses of Urban Air Quality Monitoring Systems: Passive Sampling and Continuous Monitoring Stations. Energy Procedia 101, 321–328. https://doi.org/10.1016/j.egypro.2016.11.041

ul-Haq, Z., Tariq, S., Ali, M., Mahmood, K., Batool, S.A., Rana, A.D., 2014. A study of tropospheric NO2 variability over Pakistan using OMI data. Atmos. Pollut. Res. 5, 709–720. https://doi.org/10.5094/APR.2014.080

Zhang, L., Lee, C.S., Zhang, R., Chen, L., 2017. Spatial and temporal evaluation of long term trend (2005–2014) of OMI retrieved NO2 and SO2 concentrations in Henan Province, China. Atmos. Environ. 154, 151–166. https://doi.org/10.1016/j.atmosenv.2016.11.067

IDEAM. Atlas climatológico de Colombia. http://atlas.ideam.gov.co/visorAtlasClimatologico.html

Barranquilla, 2018. Alcaldía de Barranquilla. [WWW Document]. URL http://www.barranquilla.gov.co/index.php?option=com_content&view=article&id=27&Itemid=118. (accessed 7.31.18).

Morgado Gamero W.B., Ramírez M.C., Parody A., Viloria A., López M.H.A., Kamatkar S.J. (2018) Concentrations and Size Distributions of Fungal Bioaerosols in a Municipal Landfill. In: Tan Y., Shi Y., Tang Q. (eds) Data Mining and Big Data. DMBD 2018. Lecture Notes in Computer Science, vol 10943. Springer, Cham