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Research Paper

Spatiotemporal assessment of particulate matter (PM_{10} and $PM_{2.5}$) and ozone in a Caribbean urban coastal city

Ana L. Duarte [a,*], Ismael L. Schneider [a], Paulo Artaxo [b], Marcos L.S. Oliveira [a,c]

[a] Department of Civil and Environmental, Universidad de la Costa, Calle 58#55-66, 080002 Barranquilla, Atlántico, Colombia
[b] Instituto de Física, Universidade de São Paulo, São Paulo, Brazil
[c] Universidad de Lima, Avenida Javier Prado Este 4600, Santiago de Surco 1503, Peru

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ABSTRACT

Air pollution has become a critical issue in urban areas, so a broad understanding of its spatiotemporal characteristics is important to develop public policies. This study analyzes the spatiotemporal variation of atmospheric particulate matter (PM_{10} and $PM_{2.5}$) and ozone (O_3) in Barranquilla, Colombia from March 2018 to June 2019 in three monitoring stations. The average concentrations observed for the Móvil, Policía, and Tres Avemarías stations, respectively, for PM_{10}: 46.4, 51.4, and 39.7 $\mu g/m^3$; for $PM_{2.5}$: 16.1, 18.1, and 15.1 $\mu g/m^3$ and for O_3: 35.0, 26.6, and 33.6 $\mu g/m^3$. The results indicated spatial and temporal variations between the stations and the pollutants evaluated. The highest PM concentrations were observed in the southern part of the city, while for ozone, higher concentrations were observed in the north. These variations are mainly associated with the influence of local sources in the environment of each site evaluated as well as the meteorological conditions and transport patterns of the study area. This study also verified the existence of differences in the concentrations of the studied pollutants between the dry and rainy seasons and the contribution of local sources as biomass burnings from the Isla Salamanca Natural Park and long-range transport of dust particles from the Sahara Desert. This study provides a scientific baseline for understanding air quality in the city, which enables policy makers to adopt efficient measures that jointly prevent and control pollution.

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1. Introduction

Air pollution is a major environmental problem in urban areas. It is estimated that more than 80% of people living in urban centers are exposed to levels of air pollution higher than the guidelines of the World Health Organization (WHO), constituting a threat to public health (Shaddick et al., 2020). Chronic exposure to polluted air increases the risk of mortality and morbidity, such as chronic obstructive pulmonary disease (COPD), bronchitis, emphysema, lung cancer, and decreased immune function (Li et al., 2013; Mi et al., 2019). The WHO reported that annually there are 4.2 million premature deaths throughout the world attributed to air pollution, both for cities and rural areas (WHO – World Health Organization, 2016a). In Colombia, it was determined that air contamination causes 13.9% of deaths from ischemic heart disease, and 17.6% of deaths from chronic obstructive pulmonary disease (ONS – Observatorio Nacional de Salud, 2018).

Although various pollutants are present in the urban atmosphere, the so-called criteria pollutants are: particulate matter (PM_{10} and $PM_{2.5}$), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), and ozone (O_3) (Xie et al., 2015; Agudelo-Castañeda et al., 2016; Thurston, 2017). Various sources, both natural and anthropogenic, can release these pollutants into the atmosphere. Anthropogenic sources include industrial activities (Clarke et al., 2014; Landim et al., 2018), construction and demolition activities (Paschalidou et al., 2016), transport (To, 2015; Kinnon et al., 2019), among others.

Urban air pollution has been studied in depth in the main urban areas worldwide (Amador-Muñoz et al., 2011; Zeri et al., 2011; Ma and Jia, 2016; Wagner and Schäfer, 2017; Rovira et al., 2020), focusing mainly on understanding the interactions between emissions, air quality, and regional and global climatology (Baklanov et al., 2016). However, the problem of air pollution became one of the most important aspects in developing countries, in particular in Latin American (Franceschi et al., 2018). In Colombia, urban air-quality studies have been carried out in cities such as Bogotá, Medellín, and Manizales (Zárate et al., 2007; Franco et al., 2015; Nedbor-Gross et al., 2017; Gómez et al., 2018; Rodríguez-Villamizar et al., 2019), but little information is available for urban areas in the Colombian Caribbean.

The recent air pollution episodes between March and June 2018 and between March and June 2019 in the Colombian Caribbean that exceeded the air pollution standards of the criteria atmospheric pollutants were due to the intense process of urbanization and industrialization, added to the significant contributions of biomass burning,

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[*] Corresponding author at: Department of Civil and Environmental, Universidad de la Costa, Calle 58#55-66, 080002 Barranquilla, Atlántico, Colombia.
E-mail address: aduarte2@cuc.edu.co (A.L. Duarte).

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motivating the monitoring and studies of air quality in this region (Barranquilla Verde, 2020a). Barranquilla is one of the main cities in Colombia and has been characterized in recent years by its economic, population, and industrial growth (Agudelo-Castañeda et al., 2020). However, little is known about the air-quality conditions in this region due to the lack of research on the subject. Therefore, the main objective of this study is to evaluate the spatiotemporal variation of particulate matter (PM_{10} and $PM_{2.5}$) and ozone during the monitoring period from March 2018 to June 2019. The relationship between pollutants, as well as the influence of meteorological parameters were also evaluated.

2. Methods

2.1. Study area

Barranquilla City (10° 59′ 16″ N, 74° 47′ 20″ W) is located in northern Colombia. Borders with the Magdalena River at the east side and with the Caribbean Sea by the north. The climate is dry tropical, which is divided in two periods: dry (from December to March) and wet (from April to November). Barranquilla's annual average temperature is 27.4 °C, with an average relative humidity of 80% and an average annual precipitation of 824.3 mm (CIOH – Centro de Investigaciones Oceanográficas e Hidrográficas, 2010). With approximately 1.2 million inhabitants and an automotive fleet distributed according to fuel type in Diesel and Biodiesel (18,705 cars), Natural Gas and Gasgasol (4171 cars), Gasoline (165,416 cars), and others (7342 cars) (Datos Abiertos, 2020).

Barranquilla's economic activity is dynamic and focuses mainly on industry, commerce, finance, and services (Ramírez et al., 2020). The study area is also influenced by biomass burning episodes between March and June from the Isla Salamanca Natural Park (10° 56′ N and 74° 27′ W, Magdalena Department), located 10-min away across the Pumarejo bridge in Barranquilla (Fig. 1). The park is an important zone for fish reproduction and for the artisan fishing economy of villages (Rivillas-Ospina et al., 2020). The park preserves and protects ecosystems and species in danger of extinction. It also has a variety of vegetation (red mangrove, salty mangrove, yellow mangrove and Zaragoza mangrove) (Parques Nacionales Naturales de Colombia, 2009).

The main ecosystems of the protected area are mangrove forests, tropical dry forests, and riparian forests. In addition, the park has a great variety of landscapes, such as marine-coastal ecosystems, mangrove areas, and a marsh complex (Rivillas-Ospina et al., 2020). The main reasons for these forest fires are due to land preparation for agricultural use, animal hunting, and charcoal production for commercialization (Blanco-Donado, 2019). According to National Natural Parks of Colombia, in the last four years there have been 79 fires on Isla Salamanca, which have affected 17.4 ha of mangroves (4%); 160 ha of grasslands (74%); and 26 ha between roadside grass, thorny scrub, and stubble (22%) (El Heraldo, 2019).

2.2. Ambient air quality and meteorological data

Barranquilla's Environmental Protection Agency (EPA), Barranquilla Verde, provided hourly data of three criteria air pollutants (PM_{10}, $PM_{2.5}$ and O_3) for the three monitoring stations (Policía, Tres Avemarías, and Móvil) (Fig. 1) from March 1, 2018 to June 30, 2019. Policía station (10° 55′ 38.24″ N, 74° 47′ 29.50″ W) is near a main intermunicipal road, so traffic density is particularly high. The burden of industrial pollution near this sampling station is also heavy. Tres Avemarías station (11° 0′ 54.77″ N, 74° 48′ 27.60″ W) is in Tres Avemarías park, at the historical center-north, which is a residential area. Nonetheless, there are

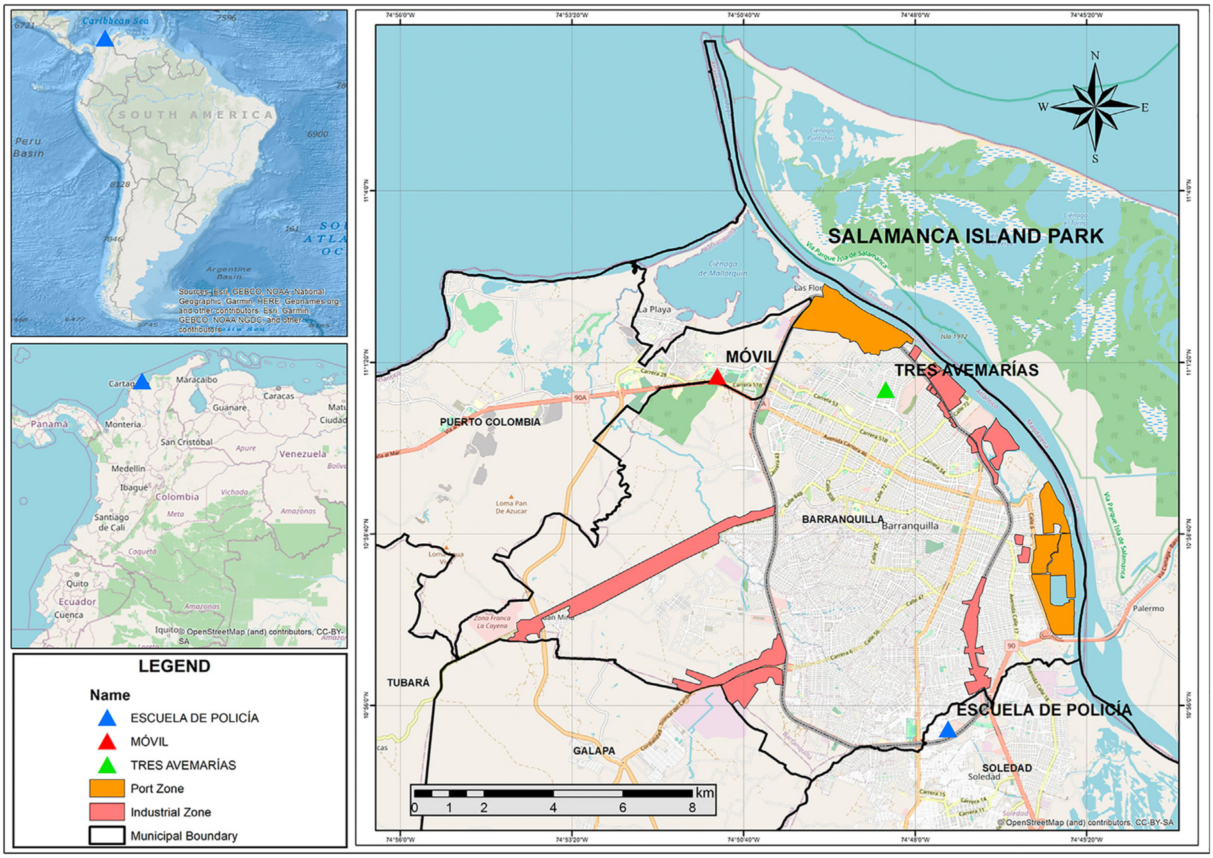

Fig. 1. Study area and location of the monitoring stations in the city of Barranquilla.

some main roads in the vicinity. Móvil station (11° 1′ 7.31″ N, 74° 51′ 4.66″ W) is situated at the north of the city, near to a university hall; this station is close to the Caribbean Sea.

The measurement of pollutants by the three air quality stations used Beta Gauge monitors (model MP101M from Environment S.A) for particulate matter and Photometric UV monitors (model O342M from Environment S.A) for ozone. Calibration and operational checking of the instruments followed protocols from EPA Barranquilla Verde. Calibration and verification routines are developed weekly, biweekly, and monthly depending on the parameter under study, following the EPA method (For PM EQPM-0202-142 and Ozone EQOA-0206-148) (USEPA – United States Environmental Protection Agency, 2017).

Each air quality station had a meteorological station from which the hourly data of the study were taken. Temperature (°C), relative humidity (%), wind direction (°), wind speed (m/s), atmospheric pressure (mm Hg), solar radiation (W/m^2), and precipitation (mm) were measured. The wind rose diagrams were constructed to study the influence of the wind direction and wind speed on the atmospheric pollutants' concentrations, using WRPLOT VIEW Version 8.0.2 software.

2.3. Data processing and statistical analysis

Daily and monthly average concentrations of air pollutants were calculated. The concentrations were considered valid just if the day had 80% of the concentrations of the pollutant evaluated, complying with the guidelines of the USEPA – United States Environmental Protection Agency (2008). A sensitivity analysis was performed where the missing data were attributed using the moving average imputation method (Rodríguez-Villamizar et al., 2019). Statistical analysis of the data was also carried out to determine if the database had the appropriate type, quality, and quantity to support the intended use in the study (USEPA – United States Environmental Protection Agency, 2006). For the data quality-assurance protocol of the database, the following steps were established: preliminary review of the data, determination of concentrations, review of data distribution for each variable, time series plots to identify outliers, and descriptive statistics.

2.4. Spatiotemporal variation

The database corresponds to a *k-sample*, with which several population means are compared simultaneously (USEPA – United States Environmental Protection Agency, 2006). Validated data from the period between March 2018 and June 2019 were used for three air quality monitoring stations in Barranquilla. The Kruskall-Wallis analysis was used to calculate if there were statistically significant differences in the concentrations of air pollutants between the monitoring sites.

To present the temporal characteristics, the daily and monthly average was determined for the entire validated data set of air pollutants (PM_{10}, $PM_{2.5}$ and O_3) for the three monitoring stations. The Kruskall-Wallis analysis was used to calculate whether there were statistical differences in the concentrations of atmospheric pollutants on dry and wet periods. Likewise, the hourly behavior profile was determined for each of the pollutants.

2.5. Correlation analysis

The relationship between the hourly concentrations of air pollutants between the three stations was evaluated. Also, the relationship between air pollutants and meteorological parameters was calculated. For the data analysis of this study, the Spearman correlation coefficient was used, since it is less sensitive to extreme values (USEPA – United States Environmental Protection Agency, 2006). All analyses were performed using the statistical software package IBM SPSS Statistics 25 and the established statistical significance for p value was <0.05.

3. Results

3.1. Spatial variation of pollutants

In Barranquilla, the wind direction and speed remained relatively constant in the three air quality stations, with prevailing winds coming from the Northeast (ocean and Isla Salamanca Park) during all evaluated period (Supplementary Fig. S1). Wind speed increased between December and March by about 4.3 m/s (Tables S1–S3), whereby the importance of wind intensity to the impact of emission sources and atmospheric pollutants transport is highlighted.

The hourly average concentrations of the atmospheric pollutants studied (PM_{10}, $PM_{2.5}$, and O_3) in the city of Barranquilla for the period from March 2018 to June 2019 are summarized in Table 1. For the case of PM_{10}, it was found that the Móvil, Policía, and Tres Avemarías sites had an average of (46.4 ± 28.3) $\mu g/m^3$, (51.4 ± 26.4) $\mu g/m^3$, and (39.7 ± 24.0) $\mu g/m^3$, respectively. Regarding $PM_{2.5}$, the average concentrations were (16.0 ± 11.0) $\mu g/m^3$, (18.1 ± 12.4) $\mu g/m^3$, and (15.1 ± 10.3) $\mu g/m^3$, respectively.

As presented in Table 1, the highest concentrations of particulate matter (PM_{10} and $PM_{2.5}$) were recorded at the Policía station, located in the southern sector of the city. This occurs mainly due to the transport of emissions from the different sources located in the urban area of Barranquilla (located upwind of the Policía station), as can be seen Supplementary Fig. S1. In this way, the action of the winds generates the transport of the emissions produced in the urban area (vehicular traffic, industries, resuspended soil, port) and the surroundings (marine aerosols, biomass burning, among others).

The average concentrations recorded for O_3 were (35.0 ± 14.8) $\mu g/m^3$ for the Móvil station, (26.6 ± 14.4) $\mu g/m^3$ for the Policía station, and (33.6 ± 12.1) $\mu g/m^3$ for Tres Avemarías station. The highest concentrations of ozone were observed in the northern zone (Móvil and Tres Avemarías station), while the lowest concentration was observed in the Policía station, in the south of the city. This is possibly associated with the consumption of this pollutant in the urban area of the city, since NO, emitted mainly by traffic mobile sources, reacts chemically with O_3 to form NO_2 (Domínguez-López et al., 2014; Agudelo-Castañeda et al., 2016). Barranquilla presents wind directions originating from the Northeast sector (Supplementary Fig. S1), so that no anthropogenic sources of precursors of O_3 are observed with wind direction above of the Móvil and Tres Avemarías monitoring stations. This may be an indication that the predominant source of O_3 can be long range transport, and the formation from the precursors emitted by the Isla Salamanca Park.

To verify the existence of statistically significant differences between the average concentrations of air pollutants between the monitoring stations, the Kruskal-Wallis analysis was used (Table 2).

The statistical test for air pollutants shows that all p-values were <0.05, which means that such differences between monitoring stations are statistically significant. These may be associated with the direct influence of various sources close to the air quality stations and that result

Table 1
Average concentrations of atmospheric pollutants in Barranquilla ($\mu g/m^3$).

Station	Pollutant	N	Minimum	Maximum	Mean	Standard deviation
Móvil	PM_{10}	9.980	0.50	253.2	46.4	28.3
	$PM_{2.5}$	9.567	0.50	112.0	16.0	11.0
	O_3	10.676	0.92	95.5	35.0	14.8
Policía	PM_{10}	10.139	0.50	263.5	51.4	26.4
	$PM_{2.5}$	8.546	0.50	102.8	18.1	12.4
	O_3	8.786	0.92	92.7	26.6	14.4
Tres Avemarías	PM_{10}	7.867	0.50	247.2	39.7	24.0
	$PM_{2.5}$	8.725	0.50	99.5	15.1	10.3
	O_3	9.122	0.92	91.4	33.6	12.1

Table 2
Kruskal Wallis test for spatial evaluation of PM_{10}, $PM_{2.5}$ and O_3 in Barranquilla.

Pollutant	Sample 1-Sample 2	Test statistic	Error dev.	Dev. test statistic	Sig.
PM_{10}	Tres Avemarías-Móvil	2194.703	121.807	18.018	0.000
	Tres Avemarías-Policía	4253.535	121.385	35.042	0.000
	Móvil-Policía	−2058.832	113.920	−18.073	0.000
$PM_{2.5}$	Tres Avemaría-Móvil	555.090	114.691	4.840	0.000
	Tres Avemaría-Policía	1928.948	117.913	16.359	0.000
	Móvil-Policía	−1373.858	115.317	−11.914	0.000
O_3	Policía-Tres Avemaría	−4086.241	123.345	−33.128	0.000
	Policía-Móvil	4839.702	118.859	40.718	0.000
	Tres Avemaría-Móvil	753.461	117.653	6.404	0.000

Asymptotic significances are displayed (two-tailed tests). The level of significance is $\rho < 0.05$.

in spatial variation when compared with each other. In the case of PM_{10}, can be highlighted specially the influence of construction activities and resuspended soil. For $PM_{2.5,}$ another important source to be considered is the formation of secondary aerosols from the precursor gases (SO_2, NO_x, and organic compounds), that can be emitted by the industrial park and by natural sources (decomposition of organic matter, mangroves, among others) located close to the sampling sites. The production of O_3 is more complex because it depends on the dynamics of the precursors and the speed of the photochemical reaction (Blanchard and Tanenbaum, 2003; Motallebi et al., 2003). There is a lack of information about this topic for Barranquilla city, but it is known that the region has a high solar radiation intensity (Supplementary Fig. S6), which will lead to fast reactions, since these are favored by the increase in temperature/radiation (Agudelo-Castañeda et al., 2020).

3.2. Time series of atmospheric pollutants

The time series graphs in Figs. 2–4 for the studied air pollutants (PM_{10}, $PM_{2.5}$, and O_3) present the hourly concentrations of the data between March 2018 and June 2019.

In the PM_{10} time series (Fig. 2), it is clear that the seasonality is not very strong, with the highest concentrations corresponding to the months of June and July 2018, with monthly averages of PM_{10} between 58.6 and 84.0 μg/m^3 (Supplementary Tables S1–S3). The lowest concentrations were found between September 2018 and January 2019 for the Móvil and Policía stations, with monthly average concentrations for PM_{10} between 22.1 and 54.6 μg/m^3 (Supplementary Tables S1–S3). Likewise, for $PM_{2.5}$ (Fig. 3) the Policía station does not show a monthly seasonal variation, while the Móvil and Tres Avemarías stations followed the behavior of PM_{10} with higher concentrations between May and June 2018 (Tables S1–S3). This last two stations are in the northern sector of Barranquilla, so similar activities and processes may be affecting both PM fractions. This can be verified by comparing the existing relationships between atmospheric pollutants in these two sampling sites: for $PM_{10}/PM_{2.5}$ a relationship of 2.90 is observed for Móvil station and 2.63 for Tres Avemarías station. While $PM_{2.5}/O_3$ is observed as 0.46 and 0.45, respectively.

Although the highest concentrations are recorded in months categorized as a wet period according to the historical series of precipitation records, the rainfall measured during the present study was practically null (3.6 mm for the Tres Avemarías station, and for the other two stations was 0 mm). Also, in June 2018, civil works were intensified throughout the city, such as canalization works and adaptation of sports scenarios on the occasion of the Central American and Caribbean games held in Barranquilla in 2018. Núñez-Blanco (2019) indicates that the influence of construction activities corresponds to 34% of PM_{10} concentrations and 12% for $PM_{2.5}$. For $PM_{2.5}$, although May typically corresponds to one of the months with the highest rainfall (111.3 mm and 75 mm, for the Policía and Tres Avemarías stations, respectively), the rains can also influence on a contrary effect to the removal of atmospheric pollutants. This occurs because traffic stops and vehicles slowdown, which consequently contributes to a higher emission of pollutants (Schneider et al., 2015; Kwak et al., 2017; Rojas et al., 2019).

The biomass burning that occurs in the park via Isla Salamanca can also be another source that influences the concentrations of particulate matter (PM_{10} and $PM_{2.5}$). Supplementary Fig. S2 shows the number of alerts identified by the Global Forest Watch system for the study period of this research. The highest number of alerts were registered between March and April 2019, with a total of 48 and 50 alerts, respectively. High number of alerts were also reported in the period from December 2018 to February 2019 (Table S4). These data coincide with the dry season of the study area, which is characterized by the absence of rain and a high wind speed regime. Therefore, a higher impact of biomass burning events occurs due to preparation of land for agricultural use, hunting of animals, and production of charcoal for commercialization (Blanco-Donado, 2019).

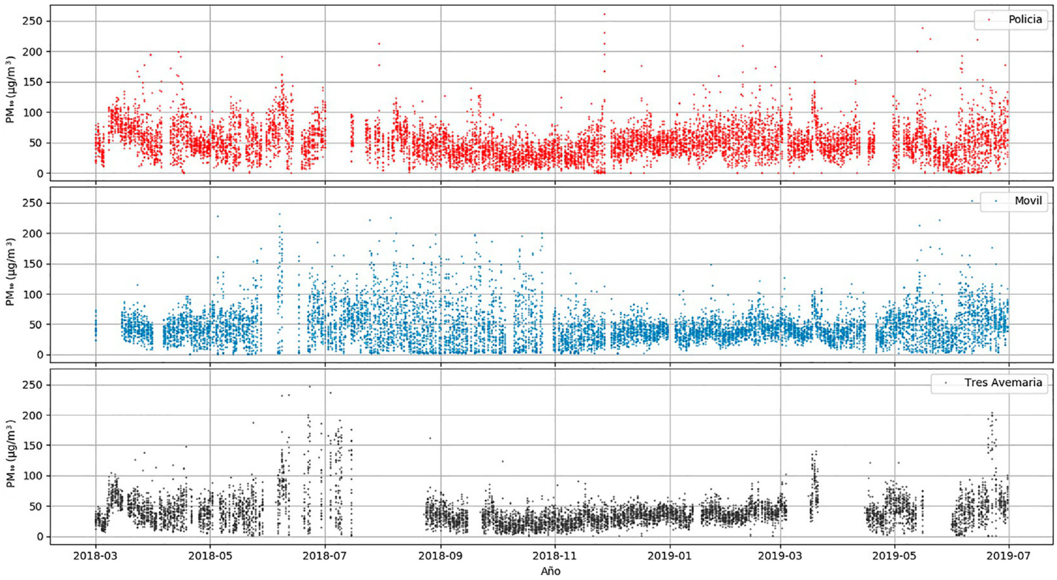

Fig. 2. Time series of PM_{10} concentrations.

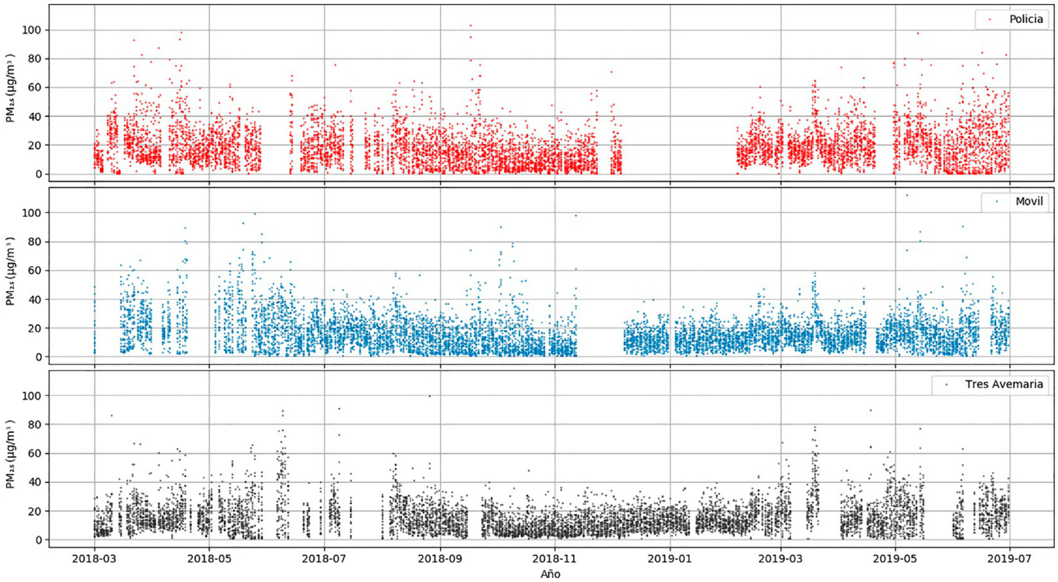

Fig. 3. Time series of $PM_{2.5}$ concentrations.

Another source that contributes to particulate matter concentrations in Barranquilla is the long-distance transport of dust particles from the Sahara Desert. On June 25, 2018, dust storms were recorded, so a possible influence of intercontinental transport of particulate matter can be assumed (Supplementary Fig. S3). This phenomenon occurs annually, but the activity of the Sahara Desert usually increases in mid-June, reaching its peaks at the end of this month until mid-August, when it begins to decline rapidly. Colombia is in the equatorial zone of the planet, and because of this the intertropical convergence zone (ITCZ) generally passes through Colombian territory twice a year. In Barranquilla, the ITCZ affects mainly the wind speed, being more intense in the season where it is further south (November–April) and less intense when it is further north (May–October) (Barranquilla Verde, 2020b). Due to this, the influence of particulate matter from the Sahara Desert during May–October impacts the northern part of the country (Caribbean Region) (Petit et al., 2005), while from November to April the influence reaches up to the Amazon region (Koren et al., 2006).

The lowest PM_{10} concentrations were observed between September and December 2018 and January 2019. For $PM_{2.5}$, lower concentrations ($<12.8\ \mu g/m^3$) were observed between October and December 2018 for the Móvil, Policía, and Tres Ave Maria stations (Tables S1–S3); this is a function of rains from September to November that influence atmospheric washing, and consequently to the reduction of the ambient concentration of atmospheric pollutants. The rainfall recorded for the Tres Avemarías station in September was 58.6 mm, in October was 125 mm, followed by November with a value of 7.6 mm (Table S3). For December and January, considered to be within the dry period, there is typically a higher wind-speed regime compared to the rest of the year (average wind speed between December and February of 4.2 m/s and NE wind direction and average speed from April to November 2.75 m/s and ENE wind direction) (Supplementary Fig. S1 and Supplementary Tables S1–S3), which contributes to the dispersion and transport of particulate matter and its consequent decrease in the city (Grundström et al., 2015; Fu et al., 2018).

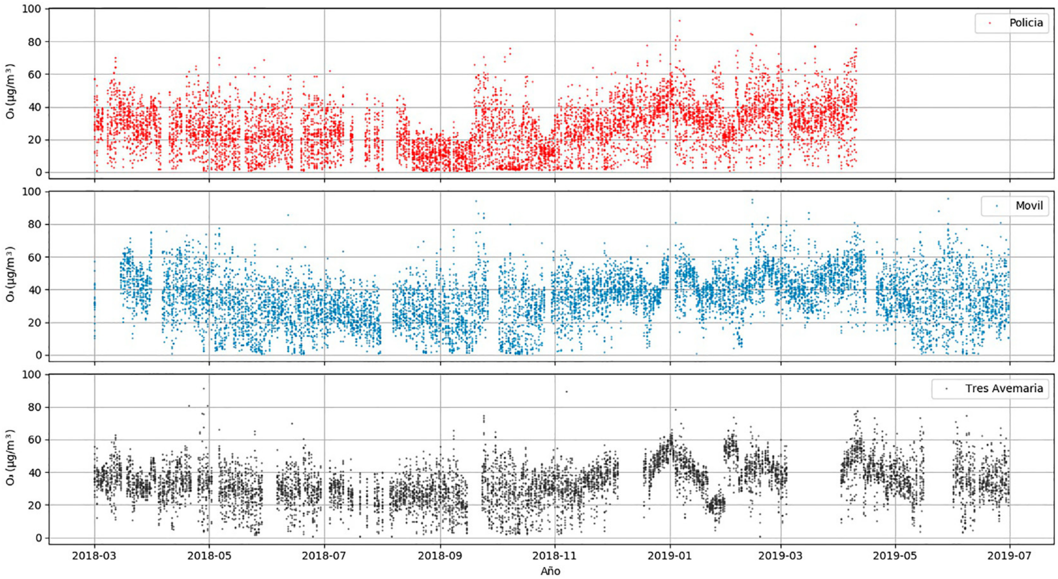

Fig. 4. Time series of O_3 concentrations.

For ozone, the highest concentrations were recorded in March and December 2018 and January–April 2019 for all stations (Fig. 4), at an approximate average of 43.2 μg/m^3 for Móvil station, 34.5 μg/m^3 Policía station, and 40.0 μg/m^3 Tres Avemarías station (Supplementary Tables S1–S3). These months coincide with the dry season of the study area, so the absence of rain, higher intensity of solar radiation, and strong winds directly favor the formation of ozone (Elminir, 2005; Wang et al., 2017; Zhan et al., 2018). In addition, in this period of the year there are also burning processes that give rise to higher levels of ozone precursors (NO_x and VOCs) (Koppmann et al., 2005; Karl et al., 2007; Andreae, 2019), as can be seen in Supplementary Fig. S2 and Supplementary Table S4. The lowest concentrations of ozone were observed in July and August 2018 for the Móvil stations and Tres Avemarías, ~26 μg/m^3. For the Policía station the lowest values were identified in August and October (15.1 and 16.7 μg/m^3) (Supplementary Tables S1–S3). Although the average intensity of solar radiation for this time (July and August) was 219.6 W/m^2, it must be taken into account that in August there were rains of approximately 50.8 mm (Tres Avemarías station) (Supplementary Table S3) and 33.4 mm (Policía station) (Supplementary Table S2), which is related to cloud cover and is one of the meteorological factors that affects the low production of ozone (Austin et al., 2015; Wang et al., 2017). In addition, ozone precursors, such as NO_x, are highly soluble in precipitation, therefore, it affects its removal and consequently affects O_3 production (USEPA –United States Environmental Protection Agency, 1999; Vallero, 2014).

To verify if the differences between the dry and rainy season on the concentrations of atmospheric pollutants were statistically significant, the Kruskal-Wallis test was carried out (Supplementary Table S5). The results showed that there is a difference between both seasons for particulate matter and ozone in all monitoring stations. However, in the Móvil station, $PM_{2.5}$ seems to be unaffected by this condition. This may occur due to the influence of vehicular traffic, which, as mentioned above, even in the rainy season, vehicular stagnation favors the accumulation of this pollutant.

The analysis could also identify the diurnal profiles of the pollutants, represented in Supplementary Fig. S4. PM_{10} and $PM_{2.5}$ follow a uniform bimodal pattern with fluctuations in concentrations throughout the day. For PM_{10}, the morning peak is recorded at 7 AM at all stations. Concentrations of PM_{10} starts to increase around 4 a.m., for the Policía and Móvil stations, which indicates that the values follow the increase in the vehicle fleet that begins to transit through the roads near the monitoring stations. Regarding the Tres Avemarías station, located in a residential area, it shows the lowest concentrations in the analysis and the increase of PM_{10} concentrations occurs at 5 AM, when many people go to work. While the evening peak is between 7 and 9 PM for the Móvil and Tres Avemarías stations, at the Policía station it begins at 5 PM and lasts until 9 PM. The reason why there are higher concentrations in this last station is because it is surrounded by the main roads of the city. In these roads there is a high mobilization of light and heavy vehicles and of urban and inter-municipal buses, which transport people who work in Barranquilla and return to their surrounding municipalities.

The concentrations of $PM_{2.5}$ follow the behavior of PM_{10}, with the Policía station having the highest concentrations in the morning peak, but in the evening peak the three stations follow a similar pattern in the increase and decrease of $PM_{2.5}$. It is found that the Policía station has the one with the highest concentrations of PM, which is associated with the location of the monitoring station. In general, it is an area that presents vehicular stagnation of light and heavy fleets, especially at peak traffic hours.

For Móvil station, which is the second with the highest concentration, high PM_{10} values are observed in the early morning, this may be associated with marine aerosol. The wind direction predominates from the East, where the main source of contribution would probably be from the ocean. Núñez-Blanco (2019) found that marine aerosols present a contribution corresponding to 30% and 17% of the concentrations of PM_{10} and $PM_{2.5}$, respectively. In addition, the Móvil station is in an area where there are also vehicle stagnations in the university citadel and the Barranquilla-Cartagena highway.

Finally, for ozone, the diagrams in general show that concentrations begin to increase gradually from 6 AM, reaching their maximum near noon and beginning to decrease in the late afternoon (Supplementary Fig. S4c). The peak ozone concentration is recorded at 11 AM for the three monitoring stations, with a concentration of approximately 50 μg/m^3 for the Móvil station and 42 μg/m^3 for the Policía and Tres Ave Marías stations. The ozone profile was presented in accordance with the photochemical effects where it reaches its maximum point at noon for the high intensity of UV sunlight. Supplementary Fig. S4c clearly exemplifies this pattern in its unimodal distribution that has bell-shaped peaks at 11 AM. The decrease in ozone levels was followed by a reduction in solar radiation arriving in the evening hours at 5 PM.

The higher concentration of ozone observed for the Móvil station may be influenced by the meteorological conditions that are generally associated with the formation of sea breeze circulations and that favor the improved production of O_3 (Agudelo-Castañeda et al., 2020). In addition, warm temperatures and strong sunlight accelerate the reactions that produce O_3 and the continuous renewal of the city's air that comes from the ocean (Supplementary Fig. S1). Further, the vehicular traffic in the university area is quite dense and presents frequent stagnations at night and this process can also contribute to the formation of ozone. This occur because traffic congestion results in lower driving speeds, lower traffic volumes and higher emissions of pollutants related to the vehicle emissions (Zhang and Batterman, 2013; Liu et al., 2015; Schneider et al., 2015).

The proximity of the city to the sea should also be highlighted, so there may be a significant contribution of VOCs from the marine biota and mangroves. Also, because nearby there is a natural reserve of mangroves, which can generate significant amounts of VOCs (Rinnan et al., 2014). In this order of ideas, the station that would receive the greatest contribution from this source would be the Móvil station, due to its greater proximity to the sea, and it could be assumed that the higher concentrations of ozone in this area are due to the reaction of VOCs from the ocean and NO_x emitted by vehicular traffic from the northern part (university citadel). VOCs are probably carried by the wind to the urban area because the wind comes from the direction of the ocean, and that is where the formation of O_3 occurs. In Supplementary Fig. S1, it is evidenced that the wind direction is very constant, therefore, the contribution of this source (ocean) is significant throughout the day and year.

Still, to better understand all these processes, monitoring of VOCs and NO_x concentrations and emissions in this area (inventory of emissions from mobile and stationary sources) is required to check reaction the rates for ozone formation. Although the weekly behavior pattern of primary pollutants clearly reflects daily variations in local emissions and meteorological conditions, the patterns are less predictable for secondary pollutants since factors such as chemical reactions that take place in the atmosphere environment must be considered (Reche et al., 2018).

3.3. Correlations of air pollutants with meteorological variables

The Spearman correlation coefficient was calculated to evaluate the relationship between atmospheric pollutants (PM_{10}, $PM_{2.5}$ and O_3) and meteorological variables for the entire study period in each monitoring station in the city of Barranquilla (Table 3).

PM_{10} showed a positive correlation with $PM_{2.5}$ ($\rho = 0.64$ for the Móvil station, $\rho = 0.66$ for the Policía station, and $\rho = 0.66$ for the Tres Avemarías station; $p < 0.01$). This significant correlation is an indication that these two pollutants originate from similar sources, such as biomass burning, industrial sources, automotive fleet, loading, unloading and port activities, among others. In the case of meteorological parameters, it was found that relative humidity correlates positively for both PM_{10} and $PM_{2.5}$ for all stations (Table 3). Humid atmospheric conditions are often accompanied by low boundary layer heights,

Table 3
Spearman correlations between pollutants and meteorological variables for all monitoring stations.

Station		PM_{10} (μg/m^3)	$PM_{2.5}$ (μg/m^3)	O_3 (μg/m^3)	Wind Dir. (°)	Wind Speed (m/s)	Temp. (°C)	Rel. Hum. (%)	Pressure (mm Hg)	Precip. (mm)	Solar Rad. (W/m^2)
Móvil	PM_{10}	1.000	0.647[a]	−0.372[a]	0.039[a]	−0.131[a]	−0.210[a]	0.412[a]	0.004	−0.016	−0.355[a]
	$PM_{2.5}$		1.000	−0.295[a]	−0.039[a]	−0.121[a]	−0.324[a]	0.311[a]	−0.045[a]	0.003	−0.376[a]
	O_3			1.000	−0.328[a]	0.472[a]	0.210[a]	−0.644[a]	−0.077[a]	−0.018	0.391[a]
Policía	PM_{10}	1.000	0.660[a]	0.038[a]	−0.201[a]	0.169[a]	−0.055[a]	0.080[a]	−0.043[a]	−0.098[a]	−0.099[a]
	$PM_{2.}$		1.000	−0.198[a]	−0.025[b]	−0.103[a]	−0.237[a]	0.317[a]	0.133[a]	−0.068[a]	−0.244[a]
	O_3			1.000	−0.324[a]	0.555[a]	0.356[a]	−0.690[a]	−0.075[a]	−0.044[a]	0.396[a]
Tres Avemarías	PM_{10}	1.000	0.663[a]	−0.117[a]	−0.061[a]	0.037[a]	−0.204[a]	0.280[a]	−0.120[a]	−0.092[a]	−0.183[a]
	$PM_{2.5}$		1.000	−0.207[a]	0.015	−0.058[a]	−0.217[a]	0.338[a]	0.059[a]	−0.067[a]	−0.192[a]
	O_3			1.000	−0.301[a]	0.415[a]	0.203[a]	−0.503[a]	−0.059[a]	−0.059[a]	0.192[a]

[a] The correlation is significant at the 0.01 level (bilateral).
[b] The correlation is significant at the 0.05 level (bilateral).

increasing concentrations of near-surface PM (Sandeep et al., 2014). PM concentrations were negatively correlated with wind speed (Table 3), indicating that horizontal dispersion played an important role in reducing PM concentrations (Hahn et al., 2009; Galindo et al., 2011).

The relationship between particulate matter (PM_{10} and $PM_{2.5}$) and temperature and solar radiation was negative, indicating that high temperatures can lead to an efficient vertical dispersion of pollutants, resulting in an inverse relationship between this meteorological parameter and PM concentrations (Li et al., 2017). In addition, it should be noted that at higher temperatures an expansion process of the mixing height occurs, resulting in a dilution process in the concentrations of particulate matter (Hu, 2015).

The correlation between O_3 and particulate matter (PM_{10} and $PM_{2.5}$) was negative (Table 3). In the case of Barranquilla, the absence of episodes with high ozone concentrations may be mainly associated with the low presence of precursors, especially NO_x, which presented low concentrations (Agudelo-Castañeda et al., 2020; Barranquilla Verde, 2020b). O_3 is mainly associated with the high temperature observed in the study area, which could be evidenced for each of the monitoring stations analyzed. As a measure of incident solar radiation, temperature directly affects O_3 production by accelerating the rates of photochemical reactions that generate it (Peshin et al., 2017).

Positive correlation was found between ozone and wind speed, which indicates that ozone was probably transferred from other areas, indicating the regional formation of this pollutant. The NE direction is predominant in this period (Supplementary Fig. S1), so the increase in wind speed can transport a greater amount of precursors (VOCs of biogenic origin) from the ocean, thus affecting the relationship between the two variables. In this regard, it should be mentioned that the wind direction is also an important parameter because it affects the transport of pollution, giving rise to a high level of ozone in places downwind (Wang et al., 2017). The correlation between wind direction and ozone indicate the influence of the ocean in the formation of O_3 since the prevailing winds from lower directions between North and East correspond precisely to the direction of the Caribbean Sea. In coastal cities like Barranquilla, the ozone concentrations studied are associated with strong winds from the northeast, especially between December and April, which carry air masses from the ocean to urban areas.

Finally, a negative correlation was found between O_3 concentrations and relative humidity (Table 3). Elminir (2005) indicated that low ozone concentrations occur when high humidity levels are observed, because it can indicate precipitation events accompanied by cloud sweep. While Kavassalis and Murphy (2017) pointed out that the following factors can explain the strong negative correlation between O_3 and relative humidity: (1) The photolysis of ozone and the loss of O (1D) to H_2O, (2) The association of humid days with an improved cloud cover and, therefore, a reduced photochemistry, and (3) The association of wet days with rain and the reduction of precursor emissions.

3.4. Comparison with other studies

The comparison of the concentrations of PM_{10}, $PM_{2.5}$ and O_3 obtained in this study and other investigations carried out in urban and coastal areas (Supplementary Table S6) showed a similar pattern in terms of concentration ranges.

Cities such as Rio de Janeiro and Panama City showed values of PM_{10} (42 and 31 μg/m^3, respectively) and $PM_{2.5}$ (11 and 14 μg/m^3, respectively) (WHO – World Health Organization, 2018), similar to those were found for Barranquilla city (average of 45.8 μg/m^3 for PM_{10} and 16.4 μg/m^3 for $PM_{2.5}$). Likewise, studies of industrial and coastal cities such as Busan (South Korea) considered high traffic conditions, urban, commercial, industrial, and rural areas (Jang et al., 2017). These scenarios could give a detailed perspective of the behavior at a sectorized level in Barranquilla. However, locations of air monitoring stations were identified as a limitation, so it is necessary to examine if the spatial coverage is representative for each of the sectors mentioned above.

It is important to note that most of the research presented in Supplementary Table S6 highlights the role played by coastal dynamics on the influence of atmospheric pollutant concentrations, giving special attention to the sea breeze considering that in some cases, depending on of the topography of the site, can influence the dispersion of pollutants (Viana et al., 2005). In other cases, it leads to an increase in the water vapor content and, in turn, to a change in the size distribution from aerosols to larger aerosols (Li et al., 2019).

Worldwide, it is estimated that annual levels of PM increased by 8%, where the trend for PM_{10} and $PM_{2.5,}$ for the period 2008–2013, for regions of low- and middle-income countries showed an increase of more of 5% during the five-year period (West Pacific and Eastern Mediterranean), while for Latin America a uniform trend was observed in the study period (WHO – World Health Organization, 2016b).

The investigation carried out by Gómez-Peláez et al. (2020), provided information on the air-quality status in South America, where no integrated plan for urban air quality management is available. Despite the efforts to monitor air pollutants criteria concentrations in some cities, there is a lack of information because the status of this is very poor in dissemination, consistency, and presentation. Also, among these same improvement opportunities in emission inventories, most of them did not meet the principles of quality, transparency, and precision. The authors additionally identified that the main phenomenon that influence the behavior of air pollutants levels in South America is El Niño - Southern Oscillation (ENSO).

Moreover, it is evident that most air-quality management strategies focus on urban and capital regions, while smaller cities, rural areas, natural emissions, and other economic sectors are being left out. However, it is very important to highlight that the characterization of the multiple sources of air pollutants, responsible for both local and regional contributions, represent essential information to design an effective emission-control policy (Kawashima et al., 2020).

4. Conclusions

This study evaluated the spatiotemporal variation of atmospheric pollutants (PM_{10}, $PM_{2.5}$ and O_3) in the coastal city of Barranquilla. As well as the relationship between atmospheric pollutants and the influence of meteorological parameters on their concentrations. This research constitutes the baseline of spatiotemporal atmospheric studies in this urban coastal city because there are no precedents related to the subject. The monitoring sites were distributed in the south, north, and historic center-north of the city, representing the main activities areas of Barranquilla for a period between March 2018 and June 2019.

(1) The main results for spatial variation showed that: The highest concentrations of particulate matter were observed in the south of the city, due to the higher influence of traffic roads. Ozone higher concentrations were verified in the north of the city, probably influenced by biogenic emissions from the ocean and the reserve of mangroves located at the Isla Salamanca Park. The statistical analysis indicated the existence of differences in the concentrations of the pollutants studied between the monitoring stations.

(2) Regarding temporal variation it was observed that: The months with the highest concentrations for PM_{10} and $PM_{2.5}$ were June–July 2018, which may be associated with construction activities that took place in that period and the influence of dust from the Sahara Desert. The lowest concentrations for PM_{10} and $PM_{2.5}$ were found between October and December 2018, being October associated with the washing effect of the atmosphere due to rainfall and November–December with the increase in wind speed that favors to PM dispersion. For O_3, higher concentrations were observed between January and April 2019, coinciding with the season of strong winds and absence of rain. In addition, in this period, burning processes were recorded around the study area that give rise to precursors associated with the O_3 formation process. Kruskal-Wallis statistical test verified the difference between the dry and rainy seasons, which confirms the differences between the concentrations mentioned above. Diurnal profiles observed in the pollutants correspond to the behavior of urban areas. For particulate matter, a bimodal pattern is shown, with morning and evening peaks. While for ozone, a unimodal pattern, with a peak at noon causing the bell effect, which is associated with photochemical formation processes.

(3) According to the relationship between atmospheric pollutants it was found that: There is a positive and significant correlation between PM_{10} and $PM_{2.5}$ for each of the stations, which indicates that possibly the source and processes of both PM fractions is similar. The meteorological variables that had the greatest influence on pollutant concentrations were relative humidity, wind speed, temperature, and solar radiation.

The results of this study may be useful to governments for anticipating and taking measures to control air pollution episodes and to development of more effective Environmental Management plans.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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