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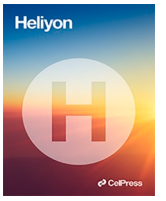

Research article

Spatio-temporal variability and trends of air pollutants in the Metropolitan Area of Curitiba

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ABSTRACT

Monitoring air pollutants over time is essential for identifying and addressing trends, which may help improve air quality management and safeguard public health. This study investigates the spatio-temporal variability of air quality in the Metropolitan Area of Curitiba (MAC), Brazil, focusing on six pollutants (SO_2, NO_2, NOx, O_3, CO, and PM_{10}) measured at eight monitoring stations from 2003 to 2017. We conducted statistical analyses, including diurnal cycles, seasonal variability, spatio-temporal correlations, conditional bivariate probability functions, Theil-Sen trend analysis, and comparison with national quality standards (NAQS) and World Health Organization (WHO) guidelines. The analyses revealed large variations in pollutant concentrations across the study area. For instance, stations strongly impacted by industrial emissions presented the highest mean annual SO_2 (20–28 μg/m^3) and PM_{10} (32–34 μg/m^3) concentrations, while those mostly impacted by traffic showed elevated NO_2 (31–39 μg/m^3), NOx (63–86 μg/m^3) and CO (0.6–0.8 mg/m^3) concentrations. The two residential stations recorded the highest O_3 concentrations (annual mean of 30–32 μg/m^3). Seasonal and diurnal patterns varied by pollutant, with winter experiencing higher concentrations and O_3 peaking in spring. SO_2 concentrations presented no clear seasonal or diurnal cycle patterns, and showed the highest spatial variability. Significant decreasing annual trends were observed for SO_2 (−5.9%), NO_2 (−2.6%), NOx (−2.6%), CO (−5.4%), and PM_{10} (−3.7%), which suggests the success of emission reduction programs implemented in the road transportation and industrial sectors. However, O_3 concentrations increased at most stations (+3.3%/yr), likely due to reduced NOx emissions, increased emissions of volatile organic compounds from on-road transport biofuels, and regional O_3 transport. Although exceedances of NAQS decreased over time, concentrations of most pollutants remained above WHO guidelines, except for CO. These results highlight the importance of targeted emission control strategies for both industrial and vehicular sources to improve local air quality and inform future policy decisions.

1. Introduction

Outdoor air pollution poses a significant global public health concern, resulting in 4.5 million premature deaths in 2019 [1]. Thus, the systematic monitoring of key air pollutants is an important tool for air quality management and for safeguarding human health. By

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providing real-time pollutant concentrations, monitoring systems enable cities and countries to identify and address areas of concern. Moreover, the analysis of long-term air quality data extends across various fields, from public health and environmental science to policy-making and urban planning, contributing to better air quality management and healthier communities.

For example, analyzing long-term datasets helps identify trends and determine whether air quality is improving or worsening in a specific location [2–4]. These data can also help quantify the relationship between air pollution exposure with health outcomes, such as respiratory diseases, cardiovascular issues, and even brain health [5–7]. They are also crucial for assessing the effectiveness of air quality control measures, such as emissions standards for on-road vehicles and industries [8,9].

Long-term datasets are also essential to validate air quality models that simulate future scenarios and forecast public health alerts [10]. Urban planners can use historical air quality data to inform decisions on land use, transportation infrastructure, and building design to minimize population exposure [11,12]. Additionally, measurements over extended periods allow the detection of changes in natural or anthropogenic emissions and sinks [13].

Despite these relevant applications, air pollution monitoring based on government-operated networks is uneven and incomplete in developing countries [14]. Latin America and the Caribbean —the most urbanized (81 %) developing region in the world [15]— face significant challenges in assessing and addressing air pollution due to scarce air pollution data and variable quality [2]. Considering the number of automatic stations per one million inhabitants, Brazil presents a lower metric (1.1) compared to USA (5.8) and several European countries (2.7–12.8) in the year 2023 [16]. Moreover, stations are installed in only 13 out of Brazil's 26 states, presenting an uneven spatial coverage. This inadequate coverage can be attributed to several factors, including political neglect of the issue, unclear objectives for data monitoring, shortages in human and technical resources within environmental agencies, and insufficient funding to establish and sustain effective air quality management [17].

Trend studies in Brazil are based on data measured at official air-quality monitoring stations, and included some of the pollutants controlled by the national air quality standards: sulfur dioxide (SO_2), nitrogen dioxides (NO_2), ozone (O_3), carbon monoxide (CO), total suspended particles (TSP), particulate matter with aerodynamic diameters smaller than 10 μm (PM_{10}) and 2.5 μm ($PM_{2.5}$). These studies focused on few metropolitan areas with extended air pollution data available: São Paulo [18–21], Rio de Janeiro [2,22], Vitória [2], Belo Horizonte [2] and Curitiba [23,24].

Air quality studies in the Metropolitan Area of Curitiba (MAC) published in the literature are scarce, and analyzed few pollutants (NO_2, O_3 and SO_2) measured at three monitoring stations in the period 2005–2014. Despite a population of 3.7 million [25] and a strong manufacturing sector, MAC lacks thorough air quality research to assess the effectiveness of pollution mitigation policies aimed

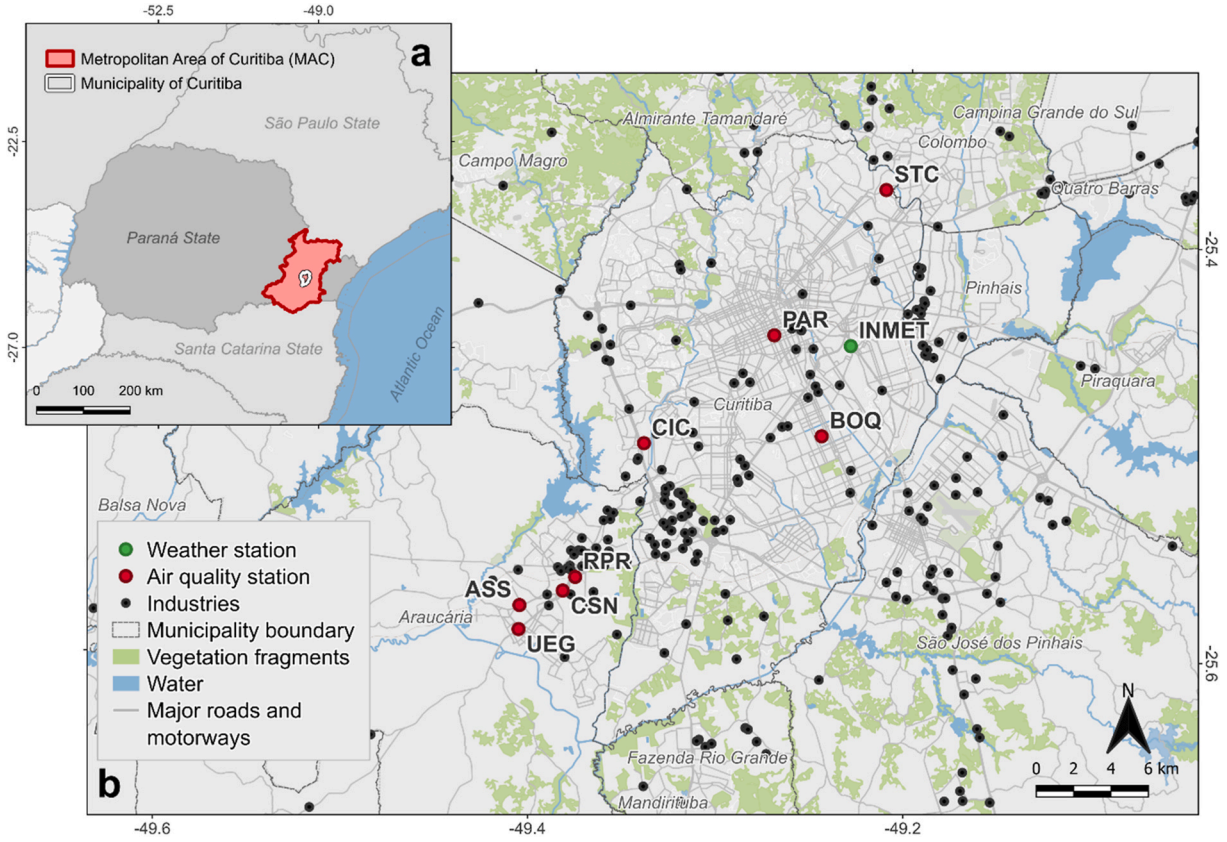

Fig. 1. Geographical location of MAC, weather station and air quality monitoring stations used in this study, along with the industries controlled by IAT in the year 2017.

at protecting the health of the local population.

Hence, this study provides a comprehensive analysis of air quality data measured at eight automatic stations in the MAC and includes: i) spatial variations of SO_2, NO_2, NOx, O_3, CO and PM_{10}, ii) seasonal variability and daily cycles for weekdays, Saturdays and Sundays, iii) spatio-temporal correlation of air pollutant concentrations, iv) identification of air pollution sources, v) long-term trends in air pollutant concentrations and their relationships with atmospheric emission reduction programs, and vi) comparison of pollutant concentrations with national air quality standards (NAQS) and World Health Organization (WHO) guidelines.

2. Methodology

2.1. Study area

The MAC is located in the eastern part of Paraná state in southern Brazil (Fig. 1a), covering a total area of 22,824 km^2 at a mean altitude of 934 m. It encompasses the city of Curitiba (the state capital) and 28 other municipalities. As of 2023, half of its population resided in the capital [25]. The climate of the region is humid subtropical with cool summers (Cfb in the Köppen-Geiger classification), featuring an annual mean temperature of 17.4 °C, annual mean precipitation of 1576 mm, and abundant rainfall during summer (December to February). MAC contributes 2.1% of the national gross domestic product, making it the seventh-largest economy in Brazil [26].

2.2. Local emission sources and regulations

Industrial emission licenses are issued in Paraná state by either state (Environmental Institute of Paraná State, IAT) or municipal institutions, depending on the size of the industrial establishment. Large industries are controlled by IAT, and according to their database, there were 386 industries with atmospheric emissions in the MAC in the year 2017 (Fig. 2). The industrial activity in the MAC is relatively concentrated in the capital (24% of the industries), followed by São José dos Pinhais, Colombo and Araucária municipalities. Lime production is concentrated in the three municipalities of Colombo, Almirante Tamandaré and Rio Branco do Sul, located north of the capital. Metal production stands out in São José dos Pinhais and Araucária, while chemical industries and oil refineries are prominent in Araucária (Fig. 2).

The on-road vehicle fleet in the MAC increased by 110% between 2003 and 2017, with motorcycles (MC) seeing the largest increase at 198%, followed by light-commercial vehicles (LCV) at 184%, passenger cars (PC) at 93%, trucks (TRK) at 71%, and buses (BUS) at 67% (Fig. 3).

In the year 2017, there were 2.2 million vehicles, corresponding to a density of 625 vehicles per 1000 inhabitants. Of these, 95% were light-duty vehicles (68% PC, 14% MC and 13% LCV) and 5% heavy-duty vehicles (4% TRK and 1% BUS). Regarding fuel consumption, 80% of the vehicles operated on gasohol, a gasoline blend containing 27% (v/v) anhydrous ethanol. An additional 11% run on pure ethanol, while 9% used diesel (blended with 7% biodiesel). For diesel engines, two sulfur content options were available: low

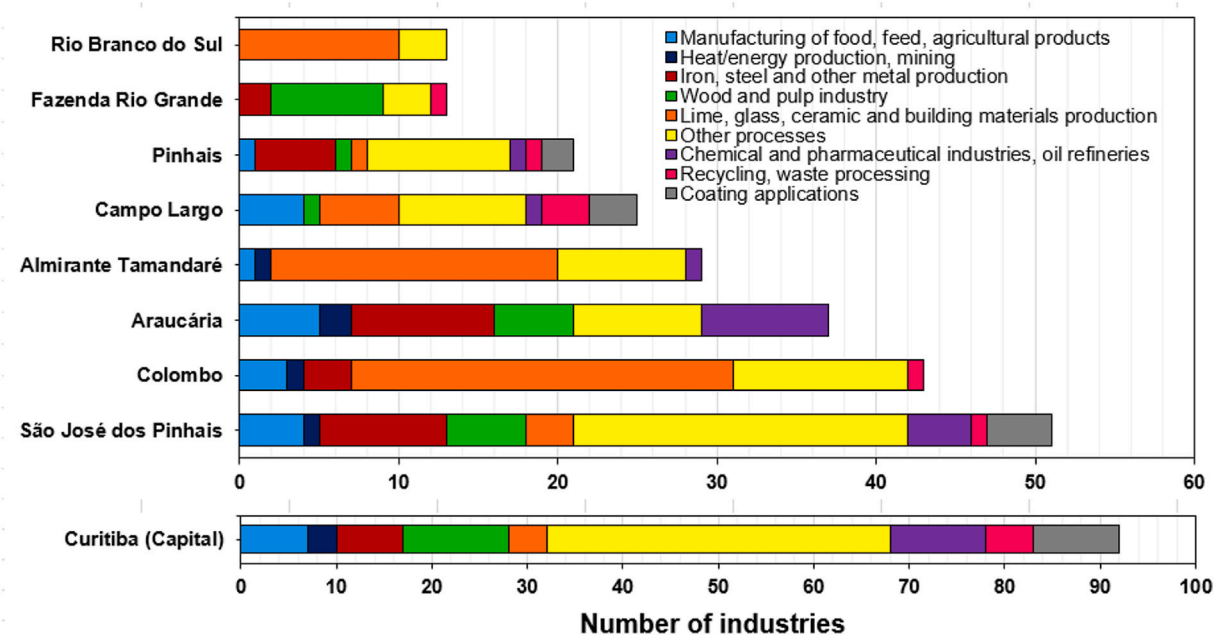

Fig. 2. Distribution of industries with atmospheric emissions across selected municipalities in the MAC (at least 10 industries per municipality). All industries are controlled by IAT and classified by sector. Data source: IAT.

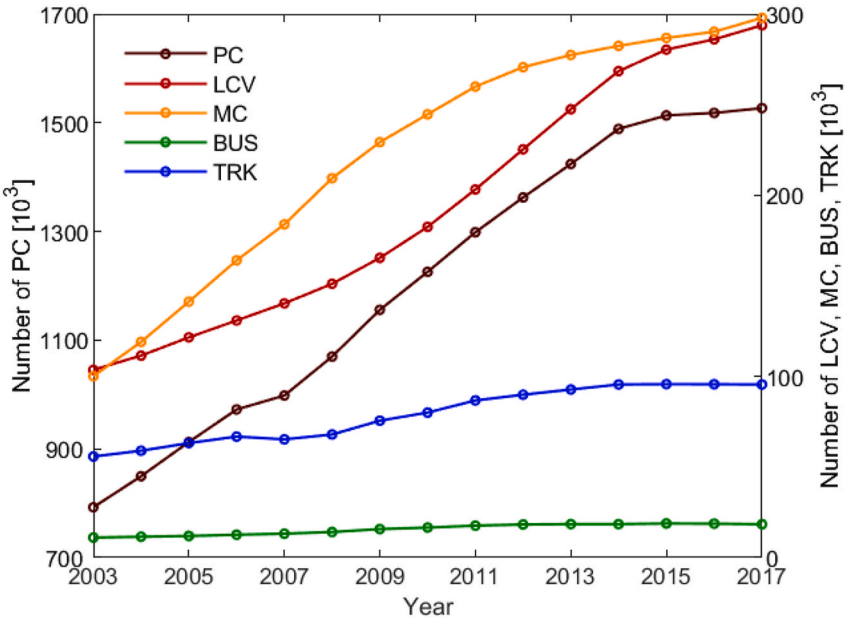

Fig. 3. Evolution of the on-road vehicle fleet in the MAC in the period 2003–2017. Data source: Paraná State Department of Traffic (DETRAN-PR).

sulfur (10 ppm) and high sulfur (500 ppm). The low sulfur diesel is only suitable for vehicles manufactured after 2012.

The sole official emission inventory for Paraná state was compiled for the base year 2011, including industrial activities and on-road transportation for several criteria air pollutants [27]. The MAC presented the highest emissions of SOx, NOx, and CO in the state, totaling 24.8, 35.5, and 167.1 kt/yr, respectively. On-road sources predominantly contributed to SOx, NOx and CO emissions (76–86%) in the city of Curitiba, whereas this dominance is observed only for CO (80%) in the MAC. Industrial emissions of particulate matter (PM) were relevant both for the capital and MAC, accounting for 72% and 87%, respectively.

In Brazil, the Motor Vehicle Air Pollution Control Program (PROCONVE) was established in 1986 to reduce CO, hydrocarbons, NOx, and PM from on-road vehicles by setting emission standards, improving fuel quality, promoting technological advances, and monitoring compliance through testing and certification [28]. In turn, the regulation of industrial emissions involves a combination of federal resolutions [29,30], state regulations, and licensing processes. Specifically, Resolution SEMA 016/2014 in Paraná state [31] sets more restrictive limits for air pollutant emissions (PM, SO_2, NOx, CO, and volatile organic compounds (VOC) than the federal legislation.

2.3. Air quality monitoring and meteorology data

Brazilian regulations do not provide specific guidelines for the minimum number of air quality monitoring stations necessary to collect adequate data for protecting human health. However, based on simplified assumptions related to population size, Ferreira et al. [16] suggested that the MAC would need at least four stations.

Automatic air quality monitoring in the MAC started in Curitiba (stations CIC ad STC) in 1998, while Araucária's first station (ASS) was established in 2000. Additional automatic stations analyzed in this study (Fig. 1b) were deployed between 2001 and 2003. From 1998 to 2017, IAT outsourced the operation and maintenance of the monitoring network, with most stations being managed by the Institute of Technology for Development (LACTEC).

We focused our analysis on the period 2003–2017 because a significant number of air quality analyzers became inoperative after

Table 1
Details of the monitoring stations and air pollutants in the period 2003–2017.

Station	Abbreviation	Municipality	[a]Type	Pollutants
Assis	ASS	Araucária	Industrial	SO_2, O_3, NOx, NO_2
Boqueirão	BOQ	Curitiba	Residential	SO_2, O_3, NOx, NO_2, CO, PM_{10}
Cidade Industrial	CIC	Curitiba	Industrial	SO_2, O_3, NOx, NO_2, CO, PM_{10}
Companhia Siderúrgica Nacional	CSN	Araucária	Industrial	SO_2, O_3, NOx, NO_2, CO, PM_{10}
Ouvidor Pardinho	PAR	Curitiba	Traffic	SO_2, O_3, NOx, NO_2, CO, PM_{10}
Repar	RPR	Araucária	Industrial	SO_2, O_3, NOx, NO_2, CO, PM_{10}
Santa Cândida	STC	Curitiba	Residential	SO_2, O_3, NOx, NO_2
Usina Elétrica a Gás	UEG	Araucária	Industrial-traffic	SO_2, O_3, NOx, NO_2, CO, PM_{10}

[a] Classified by IAT (industrial, traffic, or residential).

2017, due to lack of maintenance, vandalism or even deactivation of certain monitoring stations. This time frame represents a period with consistent data availability. Table 1 displays the main characteristics of the eight automatic stations included in this study and further information is presented in the Supplementary Material (Section A).

Air pollutant concentrations were measured using established online methods: ultraviolet fluorescence for SO_2, chemiluminescence for NO_2 and NOx, non-dispersive infrared absorption for CO, beta attenuation for PM_{10}, and ultraviolet absorption for O_3 [32]. A brief description of these methods is available in the Supplementary Material (Table S1). Routine calibration checks (zero and span) and maintenance were performed by LACTEC, adhering to the manufacturers' protocols.

Hourly weather data (air temperature, relative humidity, atmospheric pressure, precipitation, incoming solar radiation, wind speed and direction) were taken from an official meteorological station (station code: A807, Fig. 1b) managed by the Brazilian National Weather Service (INMET).

2.4. Data processing and analysis

All data were checked for consistency in units and formatting, and obvious outliers (negative concentrations) or spurious values were removed. All time references are in local time (UTC-3), with timestamps of hourly measurements reported at the end of each averaging period. Pollutant concentrations were reported in mass concentration units at standard atmospheric conditions (1 atm, 25 °C), and expressed as NO_2 equivalent for NOx.

Data collection failures often occur in air quality monitoring networks due to equipment calibration, maintenance, power outages and even vandalism. We adopted the following criteria to ensure data representativeness: at least 75 % valid hourly and daily data for calculating daily and monthly averages, and at least 50 % of valid monthly averages for annual calculations [33].

We analyzed monthly mean concentrations to address the variability in emissions and weather conditions along the year, and discussed these influences related to summer (December–February), autumn (March–May), winter (June–August) and spring (September–November). Additionally, we calculated mean daily cycles of pollutant concentrations separately for weekdays, Saturdays and Sundays, to account for variations in traffic patterns throughout the week.

Temporal correlations between paired pollutants were calculated using the Pearson correlation coefficient (R) for both intersite (different stations) and intrasite (same station) measurements. Spatial variability per pollutant was assessed using the coefficient of divergence (COD), with values close to zero indicating poor spatial variability and values closer to one indicating high spatial variability [34].

To determine the relationship between pollutant concentrations and wind direction and speed, we employed the conditional bivariate probability function (CBPF). This method provides directional information on pollution sources and the wind speed dependence of concentrations [35]. By analyzing the CBPF in a relatively flat terrain, we were able to identify pollution sources and their impact on specific receptor locations based on prevailing meteorological conditions. As recommended by Uria-Tellaetxe and Carslaw [35], we produced a large series of CBPF plots across a range of percentile intervals to determine where particular sources impact most the pollutant concentrations at the receptor sites.

Long-term trends of pollutant concentrations were calculated using the Theil-Sen method implemented in the *Openair* R package [36]. This non-parametric method estimates linear trends while accounting for outliers. To remove seasonal variations, the deseasonalized option was employed using the LOESS smoothing technique. Trends were assessed by year, day of the week, hour of the day, and wind direction sector. Only stations with at least 80 % data coverage during the period 2003–2017 were reported.

Finally, Brazilian NAQS [37] and WHO air quality guidelines [38] (see Table S2) were applied to pollution data to calculate hourly/daily exceedances associated with acute health risks, and annual exceedances related to long-term health risks.

3. Results

3.1. Mean air pollutant concentrations

The mean pollutant concentrations per station in the period 2003–2017 are displayed in Table 2. Across the study area, O_3 and PM_{10} presented the smallest inter-site variations (1.6–1.7 times between the lowest and highest mean concentrations), while CO, NO_2 and NOx, presented moderate variations (2.0–3.2 times) and SO_2 the highest variation (9.5 times).

High mean SO_2 concentrations (28.3 and 13.4 $\mu g/m^3$) were observed at two stations in Araucária (CSN and RPR), likely due to nearby industrial facilities. This observation aligns with the state's 2011 emission inventory, which identified industries as the primary

Table 2
Mean air pollutant concentrations at the stations in the period 2003–2017.

Pollutant	Units	ASS	BOQ	CIC	CSN	PAR	RPR	STC	UEG
SO_2	$\mu g/m^3$	6.8	3.0	5.1	28.3	3.3	13.4	3.5	3.0
NO_2	$\mu g/m^3$	20.2	19.5	25.6	35.2	31.4	25.9	15.8	38.8
NOx	$\mu g/m^3$	37.1	39.0	59.3	69.3	63.0	49.9	26.6	86.2
CO	mg/m^3	–	0.56	0.52	0.41	0.83	0.66	–	0.57
PM_{10}	$\mu g/m^3$	–	19.1	30.0	32.0	18.5	30.3	–	29.4
O_3	$\mu g/m^3$	26.4	29.8	29.3	20.7	26.1	25.4	32.2	23.3

source of SO_2 in the region. Notably, both stations are close to the Presidente Getúlio Vargas oil refinery (Repar), the fifth largest in Brazil, with a processing capacity of 207,660 bbl/d [39]. Similarly, high SO_2 concentrations were reported in Cubatão (an industrial hub in São Paulo state, Brazil) in the period 1996–2011, compared to other stations in the Metropolitan Area of São Paulo (MASP), attributed to extensive chemical and petrochemical industries operating in the area [40].

The highest NOx concentrations were observed at two stations in Araucária (UEG and CNS), influenced by both industrial and vehicle emissions. In contrast, the largest concentration in Curitiba was recorded at the PAR traffic station, consistent with the study by Grauer et al. [27] who found that traffic emissions are the main contributor to NOx pollution in the city. Moreover, this station displayed the highest mean CO concentration (0.83 mg/m^3), which reinforces that NOx and CO concentrations are usually found near busy roads and highways [8,41].

NO_2 concentrations were largest at UEG station (38.8 μg/m^3), followed by CSN (35.2 μg/m^3) and PAR (31.4 μg/m^3). These stations are all located near highways with heavy traffic, such as the BR-476, a major highway connecting Curitiba to southern Brazil. The mean NO_2/NOx ratios across stations varied between 0.43 (CIC) and 0.59 (STC), reflecting the interplay between emission source strength and oxidation processes. During the combustion of fossil fuels (both industrial and vehicular), high temperatures primarily produce NO, which can later be oxidized into NO_2 in the atmosphere. Ambient NO_2/NOx ratios typically range from 0.2 to 0.9, increasing rapidly away from the emission source [42].

The highest mean PM_{10} concentrations were recorded at industrial stations (RPR, CSN, CIC) and at the industrial-urban station UEG (29.4–33.5 μg/m^3). In contrast, the residential station BOQ and the traffic station PAR recorded lower values (19.1 μg/m^3 and 18.5 μg/

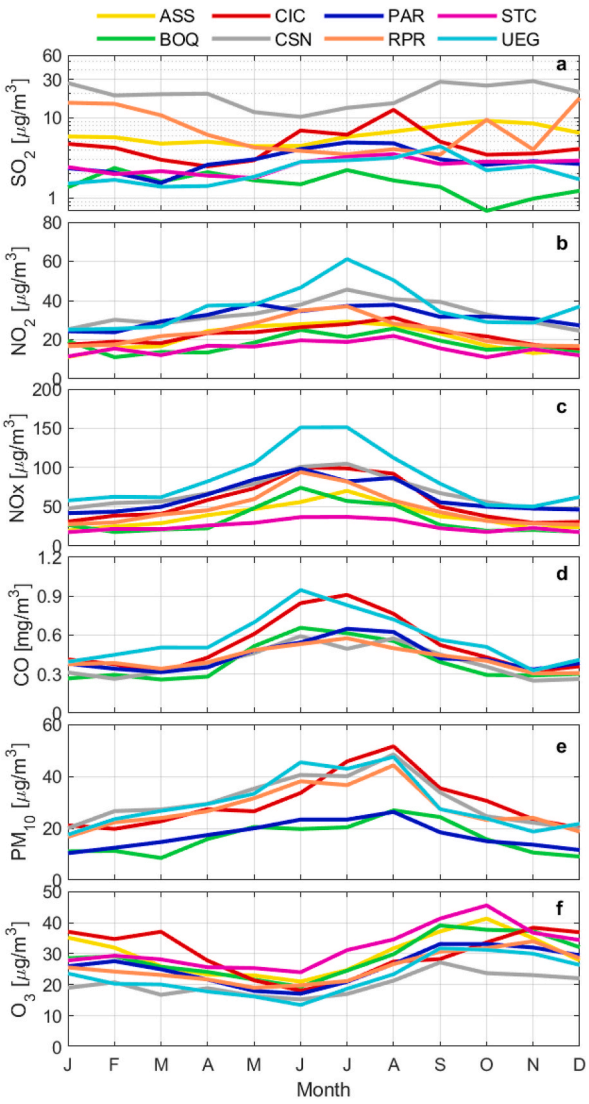

Fig. 4. Monthly mean concentrations per pollutant in the period 2003–2017. Note that SO_2 concentrations are plotted on a logarithmic scale for better visualization.

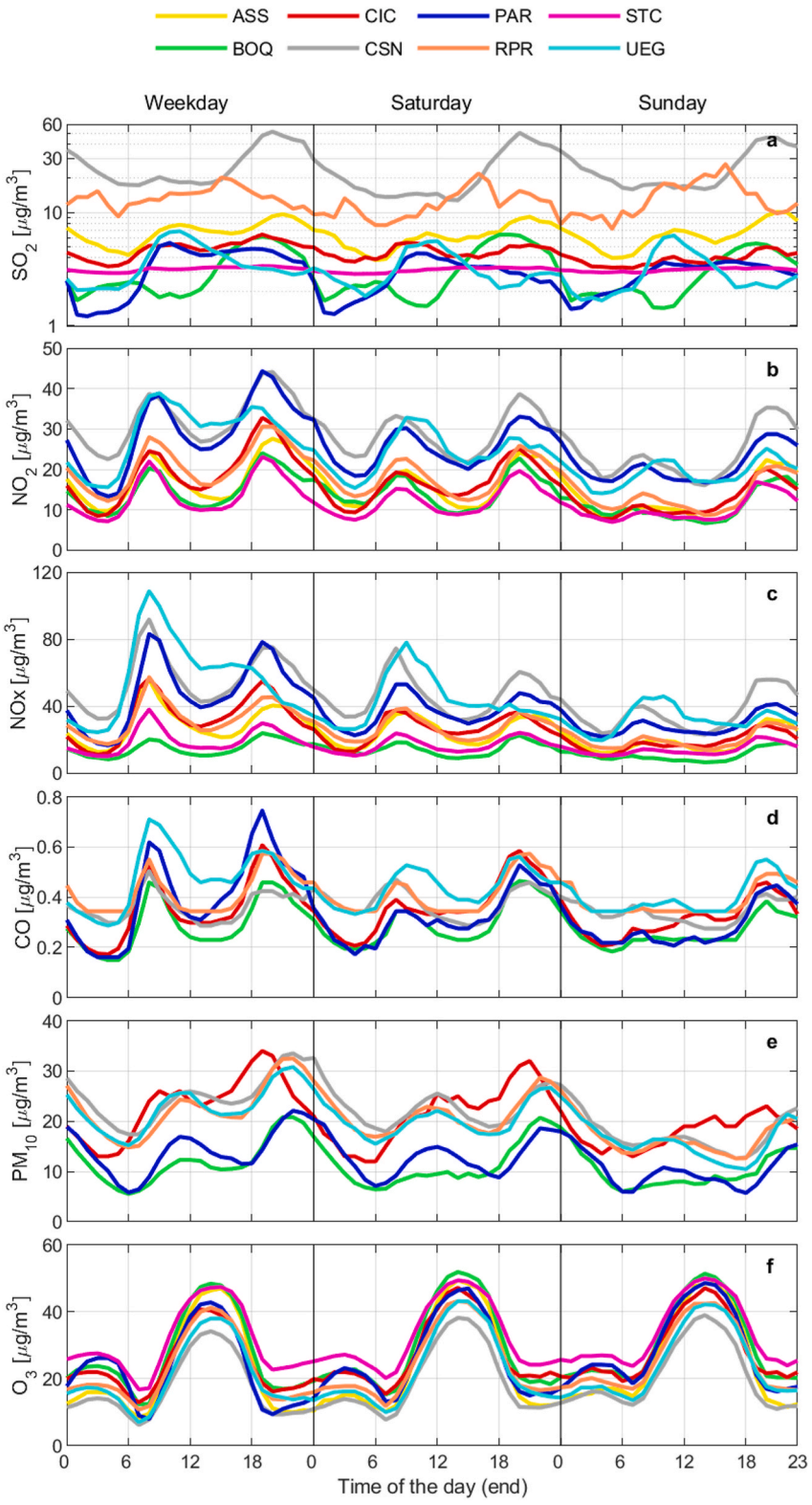

Fig. 5. Mean diurnal cycle per pollutant in the period 2003–2017, categorized by weekday, Saturday and Sunday. Note that SO_2 concentrations are plotted on a logarithmic scale for better visualization.

m^3, respectively). This pattern is expected, as industries are the largest source of PM_{10} emissions in both Curitiba and the MAC (Section 2.2). A study in the Metropolitan Area of Rio de Janeiro yielded similar patterns, with the annual mean PM_{10} concentration higher at an industrial-urban station (91–99 μg/m^3) than at urban stations (45–46 μg/m^3) in the period 1998–2013 [22].

Finally, the two residential stations (STC and BOQ) showed the highest mean O_3 concentrations (32.2 and 29.8 μg/m^3, respectively), while NOx concentrations were low. Conversely, the industrial CSN station displayed the lowest mean O_3 concentration (20.7 μg/m^3). Relatively high O_3 concentrations are common in residential or rural areas due to a higher NO_2/NOx ratio compared to urban areas, where primary pollutants inhibit O_3 accumulation [43].

3.2. Meteorological influence on seasonal air pollutant variability

Fig. 4 displays the monthly mean concentrations for each station grouped per pollutant in the period 2003–2017. Overall, NO_2, NOx, CO and PM_{10} concentrations peaked in winter and were lowest in summer. O_3 reached its highest level in spring and dipped lowest in autumn.

SO_2 did not show a clear seasonal pattern across the MAC, with mean concentrations differing among the monitoring stations (Fig. 4a). The stations with the highest annual mean SO_2 concentrations (CSN and RPR, Section 3.1) peaked in summer (34.0 and 21.3 μg/m^3, respectively), with the lowest values in winter (15.2 and 5.2 μg/m^3). In contrast, the stations less impacted by industrial emissions (BOQ, PAR and STC) showed maxima in winter (3.6, 4.7 and 3.9 μg/m^3, respectively). At ASS and UEG, the highest seasonal mean SO_2 concentrations were observed in spring (9.1 and 4.0 μg/m^3). Similarly, seasonal variations in SO_2 concentrations were absent in the Veneto Region (Italy) in the period 2008–2014, despite the surge in power plant and vessel activity in the summer to meet the air conditioning demand and the influx of tourists [44]. Conversely, high SO_2 concentrations in winter were related to coal consumption for space heating in Dücze (Turkey) combined with reduced mixing layer heights [45].

Across all stations, the highest mean NO_2, NOx, CO and PM_{10} concentrations were observed in winter, reaching 35.9 μg/m^3, 85.7 μg/m^3, 0.85 mg/m^3, and 39.4 μg/m^3, respectively (Fig. 4b–e). Winter in the MAC is characterized by low temperatures due to the influence of polar air masses, predominance of high-pressure systems, calm winds, and low solar radiation dose (Table S3). These characteristics favor the formation of thermal inversions which, combined with a shallow mixing layer, hinder the dispersion of air pollutants [45,46]. Furthermore, the increase in NO_2, NOx, CO, and PM_{10} concentrations in winter can be attributed to limited oxidation potential (due to reduction of O_3 and the hydroxyl radical) and variability in emission sources [44,47]. For example, residential wood combustion has been identified as a significant source of particulates, increasing $PM_{2.5}$ and black carbon concentrations in Curitiba, particularly in the southern areas near the CIC and BOQ stations, during the winter of 2016 [48]. Moreover, low ambient temperatures can decrease the efficiency of vehicle engines and emission control systems during the first minutes of operation, causing increased emissions of NOx, CO and PM_{10} [49].

Most stations recorded their lowest NO_2, NOx, CO, and PM_{10} concentrations during the summer months, with mean values of 20.3 μg/m^3, 35.2 μg/m^3, 0.48 mg/m^3, and 17.7 μg/m^3, respectively. Summer is the rainiest season (534.2 mm) due to the prevalence of low-pressure and easterly winds (Table S3 and Fig. S6). Hence, the increased precipitation combined with a stronger atmosphere mixing might promote the cleansing of air by washing out and dispersing air pollutants in summertime [50].

O_3 showed a strong seasonal pattern (Fig. 4f), with the highest concentrations in spring (mean of 33.5 μg/m^3) and the lowest in autumn (22.5 μg/m^3). In the spring, persistent high-pressure systems lead to clear skies, increased sunlight and higher temperatures, which enhance photochemical reactions involving NOx and VOCs, resulting in higher O_3 concentrations, compared to other seasons. In addition to local factors, the region is affected by the long-range transport of smoke from Cerrado (tropical savanna) wildfires in spring, which has been shown to contribute to higher O_3 concentrations in several cities in the region [51,52].

3.3. Diurnal cycles of air pollutant concentrations

The SO_2 diurnal cycles differed considerably among the stations (Fig. 5a), with some stations exhibiting peaks at specific times of the day, while others showed small variations (e.g., STC). Highest concentrations were observed in the evening (19:00–21:00) for ASS, BOQ and CSN, while PAR and UEG peaked in the morning (09:00–10:00). These discrepancies might be related to the strong dependence of SO_2 on industrial and traffic sources (Section 3.1), their emission variability along the day and week and the interplay with the meteorological conditions. On average, reductions between 2% (STC) and 23% (PAR) were observed from weekdays to weekends, which can be explained by the decrease in traffic volume reported on weekends [48].

NO_2, NOx, and CO showed consistent patterns across all stations (Fig. 5b–d), peaking twice on weekdays and Saturdays (08:00–10:00 and 18:00–20:00), typical of traffic environments [44,53]. On Sundays, the highest concentrations occurred in the evening (19:00–22:00), with morning peaks varying across stations. These differences in peak times likely stem from variations in meteorological conditions (higher dispersion in the afternoon) [54], and in traffic share and volume. For example, NOx and CO are mainly related to emissions from heavy-duty diesel vehicles and light-duty vehicles (fueled with gasohol or ethanol), respectively [19]. On average, concentrations decreased by 20–34 % for NOx, 15–25 % for NO_2, and 4–25 % for CO between weekdays and weekends.

PM_{10} concentrations also showed a bimodal behavior (Fig. 5e), but peaks occurred 2 h later than the maxima for NO_2, NOx, and CO at most stations (11:00–12:00, and 22:00–23:00). This delay can be explained by several factors related to their sources, atmospheric behavior, and chemical transformations. NO_2, NOx, and CO are primarily emitted by combustion (i.e., vehicles and industrial processes) with immediate increases in concentrations. However, PM_{10} concentrations can also be influenced by resuspended particles from on-road vehicles and other sources [55,56], and secondary formation in which particles may form and grow over time through chemical reactions in the atmosphere [57]. Different from the gaseous species, the highest PM_{10} concentrations were recorded at night

and were associated with a more stable nocturnal boundary layer, as also found in previous studies [44,57]. Reductions in PM_{10} concentrations (11–19%) were also observed between weekdays and weekends.

The highest O_3 concentrations occurred in the afternoon (14:00–15:00, Fig. 5f) in response to production via photochemical reactions. Concentration decline followed, due to the increase in loss mechanisms —such as dry deposition and scavenging by NO titration— and reached a minimum at sunrise [43]. A secondary maximum was observed in the early hours (02:00–04:00) and can be attributed to horizontal advection or vertical transport of ozone-enriched air [52,58]. Additionally, all stations exhibited the so-called "ozone weekend effect" [52,59,60], with O_3 concentration increases by 5–13% (Saturday) and 8–24% (Sunday) compared to weekdays. This increase was more evident (5.6 $\mu g/m^3$) on Sundays compared to weekdays at PAR station, which is highly impacted by traffic emissions. This behavior is attributed to changes in precursors, mainly due to the reduction of NOx emissions in a VOC-limited chemical regime, decrease in traffic volume and distances traveled on weekends [59].

3.4. Correlation analysis of pollutant concentrations

The correlation analysis revealed that SO_2 was the most heterogeneously distributed pollutant (COD: 0.47−0.89) and with the lowest intersite temporal correlation ($R \leq 0.33$) (Fig. S7). This is in line with the results from the previous sections that discussed the local influence of industrial and vehicle emissions on SO_2 concentrations.

PM_{10} concentrations showed the least variability across the city (COD: 0.26−0.46), and were moderately correlated between stations (R: 0.60−0.79). Pérez et al. [61] found that the variability of PM_{10} was less affected by direct road traffic emissions when compared to NOx, CO and SO_2 in a study carried out in Barcelona, Spain. This means that other sources than traffic exhaust might have important contributions to PM_{10} over MAC, causing less spatial variability and a lower temporal correlation with NOx (R: 0.43−0.58) and CO (R: 0.25−0.69).

In general, O_3 concentrations showed a moderate spatial variability (COD: 0.33−0.48), but presented the highest temporal correlations between sites (R: 0.67−0.88), except for CIC station. The combination of shared sources of O_3 precursors, similar weather patterns, and a limited spatial scale (similar topography/vegetation) leads to a high correlation in O_3 concentrations within the city.

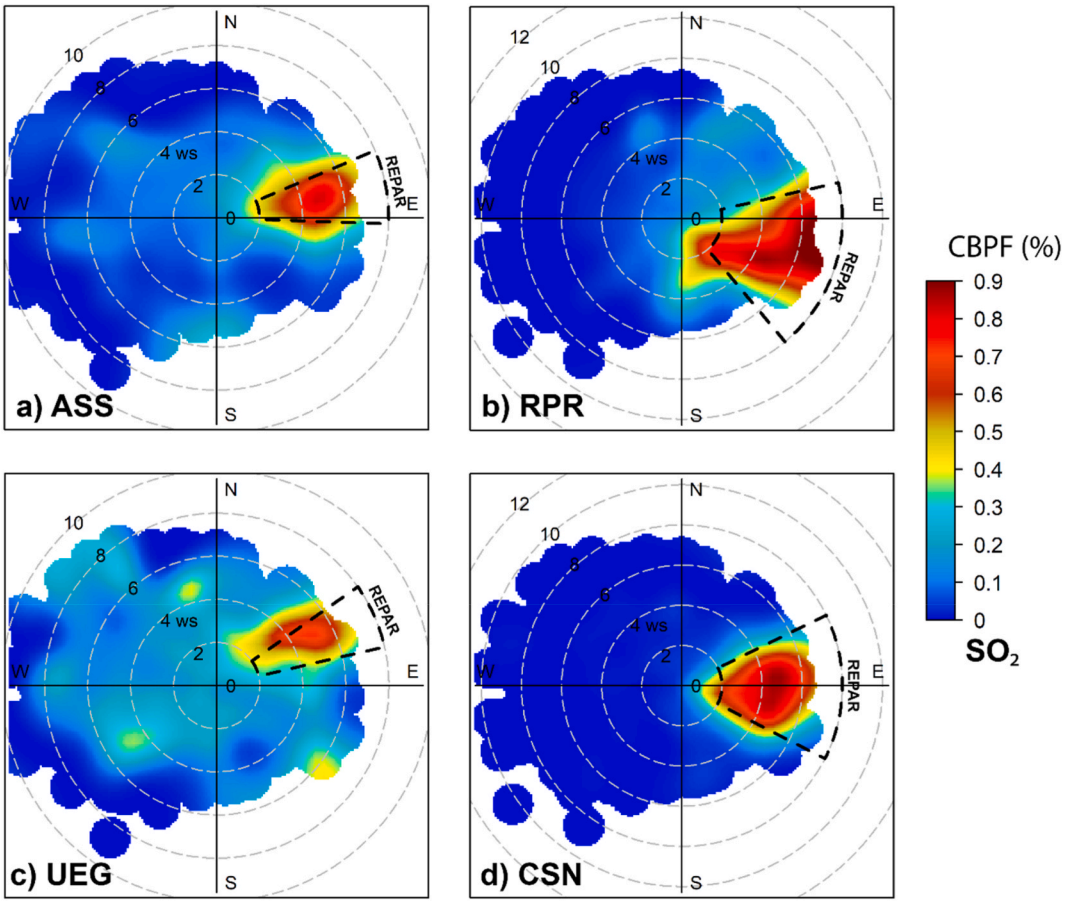

Fig. 6. CBPF plots for SO_2 concentrations in the higher quartile at the sites in Araucária municipality in the period 2003–2017. The dashed lines show the direction of potential known sources (Repar refinery and other nearby industries).

Intrasite temporal correlations were highest between NO_2 and NOx concentrations (R: 0.69−0.82), and particularly at two stations (ASS and STC, Fig. S8). The correlation between NO_2 and NOx is highest far from traffic stations due to: i) the broader range of emission sources that tend to yield more stable and consistent levels of pollution, ii) longer reaction times for the conversion of NO to NO_2, and iii) more uniform mixing and dilution of pollutants than at traffic sites [62,63].

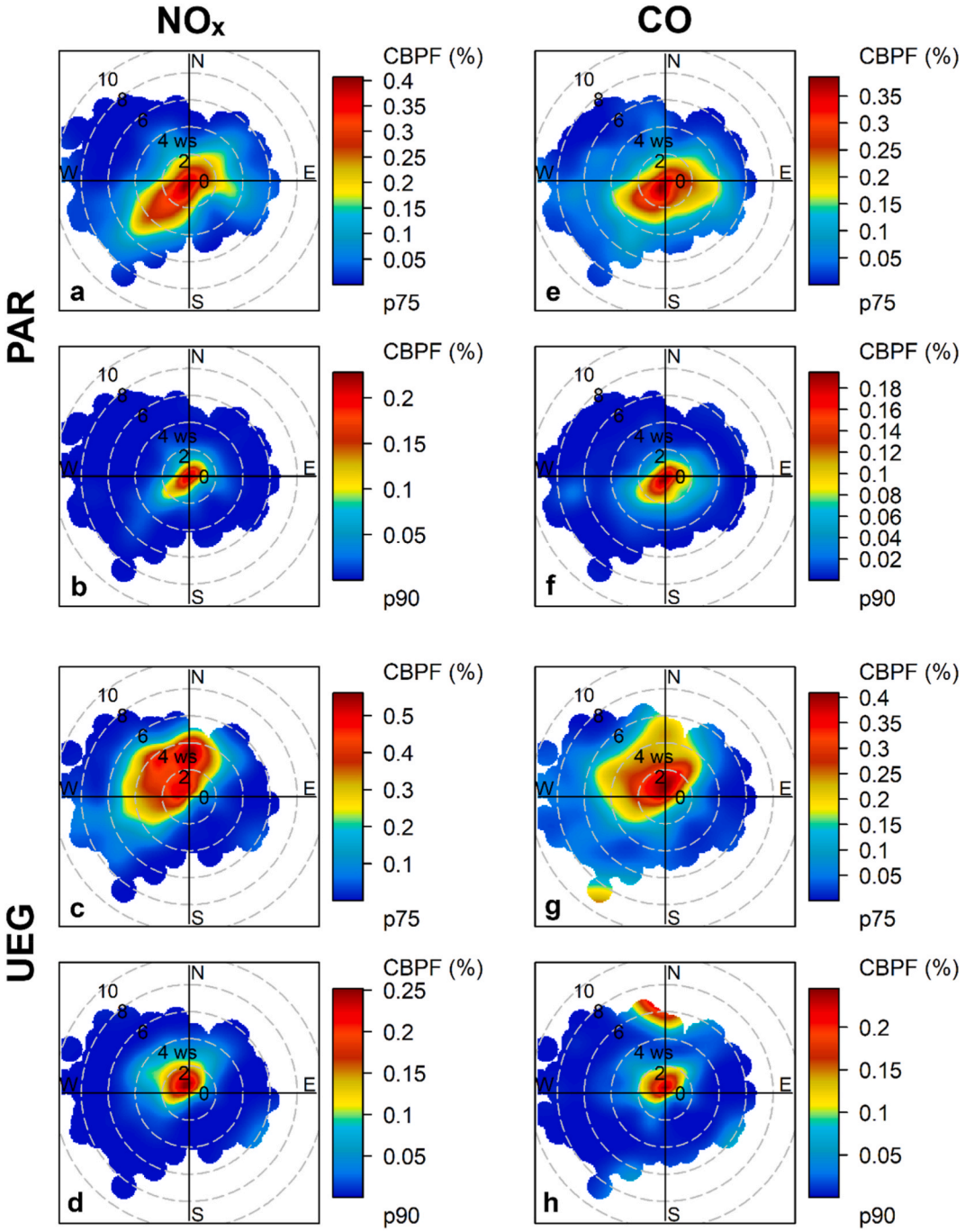

Fig. 7. CBPF plots for NOx and CO concentrations for the 75th and 90th percentiles at PAR (a,b,e,f) and UEG (c,d,g,h) stations in the period 2003–2017.

3.5. Identification of major air pollution sources

3.5.1. SO_2 concentrations

Stations ASS, CSN, RPR, and UEG exhibited high probabilities (60–90%) of elevated SO_2 concentrations (above the 75th percentile) under easterly and southerly winds, depending on the station. The highest probabilities were found for the CSN and RPR stations at wind speeds of 1–6 m/s (Fig. 6b–d). These stations showed the highest annual mean SO_2 concentrations (Section 3.1) and are closest (1.3–1.6 km) to the Repar refinery, the region's largest SOx emitter in 2017. Similarly, ASS and UEG stations also showed high probabilities of elevated SO_2 concentrations (>6.8 μg/m³ and >1.8 μg/m³) with wind speeds above 3 m/s (Fig. 6a–c), situated 4.0–4.4 km from the refinery.

On the other hand, the four stations in Curitiba municipality showed lower probabilities of elevated SO_2 concentrations from either industrial or vehicular sources. For instance, SO_2 concentrations exceeding 5.4 μg/m³ (90th percentile) at CIC station (Fig. S9) were associated with plumes from an asphalt production facility located less than 1 km to the south (Fig. S3), which operates heaters and boilers fueled by high-sulfur shale oil. Furthermore, vehicle emissions from the adjacent BR-376 highway (Curitiba's ring road) likely contributed to median SO_2 concentrations (2.6 μg/m³), with a 40–50% probability. Traffic on major avenues near PAR station (e.g., Presidente Getúlio Vargas Ave., Iguaçu Ave., Fig. S4) was responsible for high SO_2 concentrations (>8.6 μg/m³), with 20% probability.

3.5.2. NOx and CO concentrations

In general, NOx concentrations below the 50th percentile were associated with probabilities between 70 and 100% across all monitoring stations in the four quadrants and for different wind speeds, indicating urban background concentrations. As the concentration percentile increased, the highest probabilities (25–50 %) were observed at lower wind speeds.

For example, Fig. 7a–d displays the NOx CBPF plots for PAR and UEG stations at the 75th (p75) and 90th (p90) percentile concentrations. According to Uria-Tellaetxe and Carslaw [35], high concentrations under low wind speeds are related to non-floating sources at ground level, such as traffic emissions. At PAR station, NOx concentrations had probabilities of 42% (p75) and 25% (p90) in the direction of the busy Presidente Getúlio Vargas Ave [64]. (Fig. 7a–b). Given the high correlation between NO_2 and NOx concentrations in traffic environments (Section 3.4), CBPF plots for both pollutants are rather similar, and we opted to show NOx only.

The CBPF plots for CO (Fig. 7e–f) are very similar to the NOx plots (Fig. 7a–b) for PAR station, likely due to their common emission sources. At UEG station, the highest NOx (Fig. 7c–d) and CO (Fig. 7g–h) concentrations were associated with traffic on the BR-476 highway (WS < 4 m/s). Additionally, industrial sources in the Araucária municipality to the north contributed to CO levels, especially during higher wind speeds.

3.5.3. PM_{10} concentrations

Stations exhibited relatively high probabilities for both low and high PM_{10} concentrations at high winds speeds, suggesting contribution from industrial stacks [35], and aligning with the emission inventory that identified industrial activities as main PM_{10} emitters [27]. Some stations near road traffic also showed the influence of vehicle emissions on the particle load.

As an example, Fig. 8a–b displays the CBPF plots for PAR and UEG stations for elevated PM_{10} concentrations (above the 85th percentile). High concentrations (28–39 μg/m³) at PAR were linked to industrial sources in the Cascatinha neighborhood, located to the northwest (Fig. 1b). These sources primarily consist of combustion processes using wood and oil boilers. High concentrations at UEG station (>52 μg/m³) were linked to industrial sources in Araucária and Campo Largo municipalities (Fig. 1b), located in the N and NE directions. Both stations also showed contributions from local traffic at low wind speeds (<2 m/s), with 10–20 % probability.

3.5.4. O_3 concentrations

The probability of O_3 concentrations was high (>80 %) for the top quartile across all stations, and was influenced by wind speed and direction. For instance, Fig. 9 displays the CBPF for O_3 in the higher quartile for STC station, which presented the highest annual

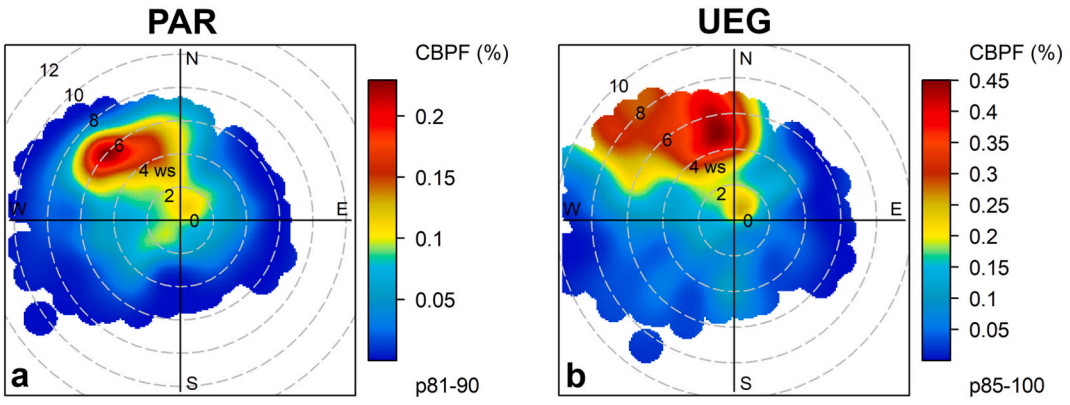

Fig. 8. CBPF plots for high PM_{10} concentrations (above the 85th percentile) at PAR (a) and UEG (b) stations in the period 2003–2017.

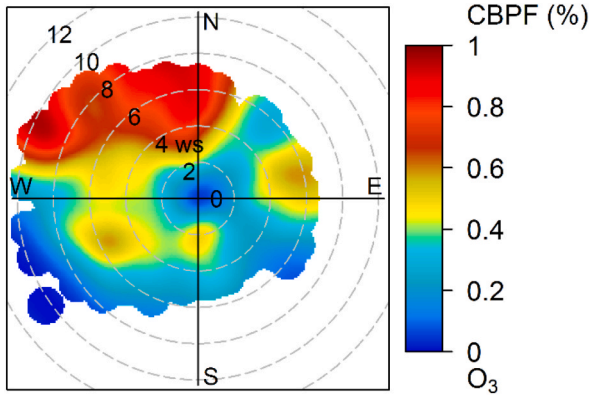

Fig. 9. CBPF plots for O_3 concentrations in the higher quartile (45–183 **µg/m³)** at STC station in the period 2003–2017.

mean O_3 concentrations (Section 3.1). The large probabilities observed for strong north and northwest winds (WS > 4 m/s), indicate regional transport contributions that add to the local sources. The transport effect was strongest from August to October (Fig. S10), as reported in other Brazilian regions and linked to the biomass burning in the Cerrado biome (Section 3.2).

3.6. Trends of air pollutant concentrations

3.6.1. SO_2 trends

SO_2 concentrations exhibited statistically significant declines over time at the six monitoring stations (ASS, BOQ, CSN, PAR, RPR, and UEG) with representative data (Table S4). The mean trend was −0.67 µg/m³/yr (−5.9%/yr), comparable to the trend (−0.82 µg/m³/yr) reported in the MASP in the period 1996–2009 [18].

The concentrations in Curitiba (BOQ and PAR stations) declined slower (both −0.17 µg/m³ yearly) and were influenced by weekday and time-of-day patterns, consistent with vehicular emissions as the primary SO_2 source in the city. The gradual decrease in sulfur content of transportation fuels (diesel and gasoline) observed nationwide contributed to this trend, as shown for PAR station (Fig. S11).

In contrast, Araucária's four monitoring stations experienced a more pronounced reduction (−0.93 µg/m³/yr; -**6**.3 %/yr), due to stringent emission controls for industries besides the benefit from cleaner transportation fuels. Industrial processes such as NH_3 production, sulfur recovery, and catalytic cracking, coupled with regulatory measures and control equipment (incinerators, scrubbers, and gas absorbers), contributed to these reductions. For instance, ASS station recorded a 37 % decline in SO_2 concentrations from 2007 since the implementation of regulations for fixed sources. We also found that the decline showed a directional dependence, with the greatest reductions towards major industrial facilities (east, southeast, northeast wind directions, depending on the station).

3.6.2. Nitrogen oxide trends

Three of the four stations with representative data (CSN, PAR and RPR) during 2003–2017 showed statistically significant decreases in NO_2 concentrations (Table S4), with a mean trend of −0.89 µg/m³/yr (−2.6%/yr). The same stations showed a significant reduction in NOx concentrations (Table S4) with a mean decline of −1.89 µg/m³/yr (−2.6%/yr). This trend was similar to results reported in the MASP (−1.82 µg/m³/yr) between 1996 and 2009, and was mainly attributed to the implementation of the PROCONVE program [18]. We found no studies on NO_2 trends in Brazil to contextualize our findings.

Despite the growth of the vehicle fleet (Fig. 3), most monitoring stations showed decreases in NO_2 and NOx concentrations. For example, PAR station showed the largest NOx decline (−3.17 µg/m³/yr), with the greatest reduction (−5.86 µg/m³/yr) towards Pres. Getúlio Vargas Ave. and other busy streets (south and southwest directions). This trend may be linked to technological improvements in engine design and after-treatment devices introduced by the PROCONVE program. Exhaust gas recirculation systems were implemented in light-duty vehicles during phase L2, and selective catalytic reduction was introduced in heavy-duty vehicles from 2012 (phase P7) to reduce NOx emissions. Regulation on industrial emissions might have also helped to reduce trends given that industries are the main sources of NOx in the Araucária municipality.

3.6.3. CO trends

CO concentrations significantly decreased at all stations, but trends are presented only for BOQ and RPR, with representative data spanning 2003–2017 (Table S4). The mean reduction was −0.04 mg/m³/yr (−5.4%/yr), which is similar to trends in the MASP. For example, Carvalho et al. [18] observed decreases of −0.10 mg/m^{-3}/yr between 1996 and 2009, while Ribeiro et al. [41] reported trends between −3.6 and −8.4%/yr during 1996–2013, which they associated with the implementation of the federal PROCONVE program and local traffic policies.

The significant reduction in CO concentrations in the MAC can be attributed to the implementation of the PROCONVE program, despite the growth in the light-duty vehicle fleet (Fig. 3), the primary CO emitter [27]. The first phases of PROCONVE (L2 and L3)

introduced three-way catalytic converters, electronic fuel injection, and electronic control modules to reduce CO emissions. Additionally, regulations on stationary sources likely played a role, especially at high wind speeds (Section 3.5.2).

3.6.4. PM_{10} trends

PM_{10} concentrations decreased significantly at all stations, but we only report trends for the stations with representative data in the period 2003–2017 (PAR, RPR, and UEG). These stations experienced a mean decrease of −1.29 μg/m³/yr (−3.7%/yr), aligned with studies in the MASP. Carvalho et al. [18] and Pérez-Martínez et al. [19] reported PM_{10} reductions of −1.97 and −1.08 μg/m³/yr in the periods 1996–2009 and 2000–2013, respectively. Both studies attributed these decreases to stricter vehicle emission standards (PROCONVE) and technological advancements in the road transportation sector.

Although the heavy-duty vehicle fleet increased by 70 % in the MAC between 2003 and 2017 (Fig. 3), the nationwide PROCONVE program likely contributed to reduced vehicle emissions, potentially influencing overall PM_{10} concentrations. While PAR station in Curitiba, largely influenced by traffic, showed a smaller reduction (−0.71 μg/m³/yr), Araucária's stations presented larger declines (−1.60 μg/m³/yr on average). This suggests that industrial emission controls were a primary driver of overall PM_{10} reductions in the study area. Major PM_{10} sources include industries involved in NH_3 production, catalytic cracking, and pulp and paper [27]. For instance, the Repar refinery has implemented several removal technologies such as bag filters, electrostatic precipitators, and multi-cyclones.

3.6.5. O_3 trends

Ozone concentrations increased significantly at four out of seven stations with representative data between 2003 and 2017 (ASS, BOQ, CSN, and STC; Table S4), with a mean rise of 0.82 μg/m³/yr (3.3 %/yr). Conversely, O_3 concentrations at RPR station declined significantly by 2.2% annually. These findings align with a study in the MASP in the period 1996–2009 [18], where O_3 increases were observed at five out of 10 stations and were attributed to VOC-limited O_3 formation.

Several factors influence O_3 trends, including precursor emissions, meteorology, and regional transport [42,68]. Despite declining NOx concentrations in the MAC, most stations in the study area may favor O_3 formation under VOC-limited conditions. The growing use of gasohol and hydrated ethanol in Paraná state [65] could have increased VOC emissions, contributing to O_3 production through direct acetaldehyde emissions and evaporation [21]. Moreover, regional transport of O_3 (Section 3.2) may have also contributed to the observed increases in the MAC.

Only RPR and UEG stations exhibited downward O_3 trends, with the latter being non-significant. The observed O_3 decline over time could be explained by a high hydrocarbon availability close to the RPR station, from nearby industries besides local traffic.

3.7. Comparison with air quality standards

The two monitoring stations most affected by industrial emissions (CSN and RPR) recorded annual mean SO_2 concentrations above the NAQS of 40 μg/m³. CSN reported exceedances in 2004, 2005, and 2013, while RPR exceeded the limit in 2005. Both stations also surpassed the daily values set by NAQS (125 μg/m³) and WHO (40 μg/m³). However, the frequency of exceedances decreased after 2007, when stricter regulations for industrial emissions were implemented. Additionally, ASS and BOQ exceeded the WHO-recommended daily value for SO_2 before 2008, and occurred only between 5 and 8 days per year.

Although no stations surpassed the national annual NO_2 standard of 60 μg/m³, all stations reported concentrations above the WHO-recommended annual concentrations of 10 μg/m³ between 2003 and 2017. The national hourly NO_2 standard (260 μg/m³) and the WHO guideline (200 μg/m³) were surpassed at all stations, except at STC. CIC recorded the highest number of hourly exceedances, particularly in 2011, followed by UEG and RPR. A general reduction in hourly NO_2 exceedances was observed at most stations starting in 2012, possible linked to the implementation of phase P7 of the PROCONVE program (Section 3.6.2).

The annual mean PM_{10} NAQS of 40 μg/m³ was exceeded at the three stations most affected by industrial emissions: CSN, RPR, and UEG. These exceedances occurred in 2003 for CSN, 2004 for RPR, and during 2006–2007 for UEG. All stations also surpassed the daily mean PM_{10} standard of 120 μg/m³. However, the frequency of exceedances declined over time, likely due to the introduction of fixed-source emission regulations, as industrial activities are a major source of PM_{10}. Across all stations, the proportion of exceedances decreased from 68% to 16% after 2007, when the new regulations were enforced. Despite these improvements, all stations exceeded the WHO-recommended annual mean PM_{10} limit of 15 μg/m³, and a similar trend was observed in relation to the daily WHO standard of 45 μg/m³.

The 8-hr O_3 national standard of 140 μg/m³ was exceeded at ASS, BOQ, CIC, and STC in some years with no defined pattern. Exceedances at ASS, BOQ, and STC were observed during the spring, a period associated with higher O_3 concentrations (Section 3.2). At CIC, all exceedances occurred in June 2011, a year that also saw NO_2 exceedances, suggesting that elevated NO_2 concentrations may have contributed to increased O_3 in that year. The WHO guideline for the 8-hr O_3 standard (100 μg/m³) was exceeded at all monitoring stations, though no clear trend was observed over the study period.

4. Summary and conclusions

This study analyzed air quality in the MAC region through measurements of various pollutants (SO_2, NO_2, NOx, O_3, CO, and PM_{10}) at eight monitoring stations from 2003 to 2017. The results showed distinct pollutant patterns influenced by location, season, and weather conditions. NO_2, NOx, CO, and PM_{10} concentrations were higher in winter due to poor dispersion and increased emissions from sources like wood burning and inefficient vehicle exhaust in cold temperatures. In contrast, O_3 concentrations peaked in spring,

driven by regional transport from biomass burning. SO_2 showed no clear seasonal pattern.

While most pollutants followed similar diurnal cycles across the stations, SO_2 exhibited different patterns. NO_2, NOx, and CO correlated strongly with road traffic emissions, peaking during rush hours, while O_3 peaked in the afternoon due to solar radiation and precursor emissions, with a secondary nocturnal peak linked to regional transport. PM_{10} concentrations typically rose at night, influenced by mixing layer dynamics and resuspended particles from road wear and vehicle activity.

CBPF analysis highlighted the impact of industrial emissions and local traffic. SO_2 concentrations in Araucária were strongly affected by the Repar refinery, especially at nearby stations. NOx and CO were influenced by local traffic, while PM_{10} was driven by industrial activity, with traffic playing a smaller role. O_3 concentrations depended on wind patterns and regional transport, exacerbated by biomass burning during certain months.

Most pollutants showed declining temporal trends (except for O_3), likely due to air pollution control measures in the transportation and industrial sectors. The increase in O_3 was linked to lower NOx concentrations, potential increases in VOC emissions, and regional O_3 transport.

The two stations most impacted by industrial emissions surpassed NAQS and WHO guidelines for SO_2 and PM_{10}, with exceedances declining after 2007 regulations. NO_2 concentrations exceeded WHO guidelines at all stations, with reductions seen post-2012 due to new vehicle emission standards. Daily PM_{10} exceedances also decreased but remained above WHO limits. The 8-hr O_3 standard was surpassed at multiple stations, especially in spring, with no clear trend over time.

The findings underscore the need for continued emission reduction efforts, such as cleaner transportation, improved industrial processes, and effective air quality management plans to mitigate pollution and protect public health. This study also emphasized the importance of long-term observations for tracking trends and evaluating air quality programs.

CRediT authorship contribution statement

Patricia Krecl: Writing – original draft, Visualization, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Lizeth Bibiana Castro:** Visualization, Software, Resources, Investigation, Formal analysis. **Admir Créso Targino:** Writing – review & editing. **Gabriel Yoshikazu Oukawa:** Writing – review & editing, Visualization, Formal analysis.

Data and code availability

All datasets used in this study are not publicly available; they were obtained from official institutions and cannot be directly shared. The codes supporting the findings are available from the corresponding author upon reasonable request.

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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e40651.

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