

Air pollutants associated with surface meteorological conditions in São Paulo's ABC region

Poluentes atmosféricos associados a condições meteorológicas de superfície na região do ABC em São Paulo

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ABSTRACT

Air pollution is one of the main environmental problems in urban areas like the Metropolitan Area of São Paulo (MASP) in Brazil, where millions of inhabitants are exposed to pollution concentrations above the standards, with potential health impacts. Exposure is unequal throughout MASP, relying on the dynamics of local emission sources interplaying with weather and climate in a regional scale. The ABC region — ABC standing for Santo André, São Bernardo do Campo and São Caetano do Sul, the cities the area originally comprised of — is MASP's largest industrial center, sitting in its southeast border, and encloses environmental protection areas. That leads to a unique emission profile that differ from the metropolis center. This study aims to characterize the variability of atmospheric pollutants in the ABC region in 2015, investigating possible sources and associations with surface meteorological conditions. Multivariate statistical analyses were applied to data from seven air quality monitoring stations and surface meteorological variables. Results show that São Bernardo do Campo stood out, with O_3 concentrations 20% higher ($43 \pm 19 \mu g.m^{-3}$) than the other sites, while São Caetano do Sul had the highest annual mean PM_{10} concentrations ($39 \pm 19 \mu g.m^{-3}$), mostly related to vehicular emissions. Relative humidity was negatively correlated with primary pollutants, while temperature and radiation correlated with O_3 . Unusually high O_3 concentrations were observed in January of 2015, concomitant with negative anomalies of precipitation and relative humidity, likely associated with the 2014/2015 summer drought event in Southeast Brazil. Overall, results show that local emission sources significantly impact air pollution loading and its diurnal variability, particularly in the case of primary pollutants. Climate modulates the seasonal concentration variability, and regional scale weather phenomena may impact air quality conditions. To reach concentration standards everywhere, policy makers must be aware of processes occurring in different spatial scales that determine air quality.

Keywords: air pollution; particulate matter; tropospheric ozone; multivariate analysis; Brazil.

RESUMO

A poluição atmosférica é um dos principais problemas ambientais em áreas urbanas como a Região Metropolitana de São Paulo (RMSP), no Brasil, onde milhões de habitantes estão expostos a concentrações acima dos padrões, com potenciais impactos à saúde. A exposição à poluição atmosférica é desigual na RMSP, dependendo da dinâmica de fontes emissoras locais e da influência do tempo e do clima em escala regional. A região do ABC — sigla originada a partir das iniciais de suas cidades originais: Santo André, São Bernardo do Campo e São Caetano do Sul — é o maior centro industrial da RMSP, localizada em sua fronteira sudeste, e inclui áreas de proteção ambiental. Essas características resultam em um perfil de emissões singular, que difere do centro da metrópole. Este estudo visa caracterizar a variabilidade na concentração de poluentes atmosféricos na região do ABC em 2015, investigando possíveis fontes e associações a condições meteorológicas de superfície. Análises estatísticas multivariadas foram aplicadas a dados de qualidade do ar de sete estações de monitoramento e variáveis meteorológicas de superfície. São Bernardo do Campo se destacou, com concentrações de O_3 20% maiores ($43 \pm 19 \mu g.m^{-3}$) do que as outras estações, enquanto São Caetano do Sul apresentou a maior média anual de PM_{10} ($39 \pm 19 \mu g.m^{-3}$), relacionada principalmente a emissões veiculares. A umidade relativa apresentou correlação negativa com os poluentes primários, enquanto a temperatura e a radiação se correlacionaram ao O_3 . Elevadas concentrações de O_3 foram atipicamente observadas em janeiro de 2015 ($59 \pm 19 \mu g.m^{-3}$), simultaneamente a anomalias negativas de precipitação e umidade relativa, possivelmente associadas ao evento de seca no Sudeste do Brasil no verão de 2014/2015. Os resultados mostram que fontes emissoras locais podem impactar significativamente a carga de poluição e sua variabilidade diurna, especialmente no caso de poluentes primários. O clima modula a variabilidade sazonal das concentrações, e fenômenos meteorológicos de escala regional podem impactar a qualidade do ar. Para atingir os padrões de concentração em toda a parte, o poder público deve ficar atento aos processos que ocorrem em diferentes escalas espaciais e que determinam a qualidade do ar.

Palavras-chave: poluição do ar; material particulado; ozônio troposférico; análise multivariada; Brasil.

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Introduction

Megacities worldwide concentrate intense economic activity, high population density and high emission of air pollutants, with impacts to human health, climate and environment (Parrish and Zhu, 2009; Gurjar et al., 2010). In the Metropolitan Area of São Paulo (MASP), vehicular emission plays a major role on air quality, followed by industrial emissions (Andrade et al., 2017; CETESB, 2019). The ABC region — ABC standing for Santo André, São Bernardo do Campo and São Caetano do Sul, the cities the area originally comprised of —, located in the southeast of MASP, comprises 7 municipalities and 2.6 million inhabitants (SEADE, 2018). In the ABC region, areas of environmental protection and water reservoirs coexist with vehicular traffic and industrial activity, including the Capuava petrochemical pole, automobile, metallurgic and chemical industries, resulting on an emission profile distinct from the central areas of MASP. The combination of several air pollution sources, both anthropogenic and biogenic, results in physical and chemical interactions that lead to the formation of secondary pollutants like ozone (O_3) and secondary particulate matter.

In the ABC region, the predominant winds are from southeast (IAG-USP, 2015a), with great influence of the sea breeze and mountain-valley circulation (Ribeiro et al., 2018; Valverde et al., 2020). The southeastern winds can transport region atmospheric pollutants produced at coastal cities (such as Cubatão and Baixada Santista), marine emissions and biogenic emissions from Mata Atlântica rainforest fragments (Carvalho et al., 2012; Ribeiro et al., 2018) to the ABC. Furthermore, the southeastern winds can transport pollutants generated at the ABC region to the center of the São Paulo metropolis. Occasionally, the preferred wind direction suffers an inversion, in a way that atmospheric emissions from agricultural areas at northwest São Paulo state may be transported to the MASP, and, consequently, to the ABC region (Sánchez-Ccoyllo et al., 2005). These elements make the ABC region a unique location for the study of the dynamics of atmospheric pollutants, the contribution of various pollutants sources and the influence of meteorological conditions.

Among CETESB's (Companhia Ambiental do Estado de São Paulo, São Paulo State Environmental Agency) 24 air quality monitoring stations located at MASP in 2018, the ABC municipalities of São Caetano do Sul, Santo André and Mauá figured among the 10 stations with highest PM_{10} (inhalable particulate matter) annual mean concentrations (CETESB, 2019). In the same year, the ABC municipality of São Bernardo do Campo counted nine exceedances of the O_3 state air quality standard ($140 \mu g m^{-3}$, 8 h moving average), the highest among the MASP monitoring stations (CETESB, 2019). This is an indication that air quality conditions in the ABC region may differ from other parts of MASP, being influenced by local sources and regional transport of pollutants.

Studies about air pollution dynamics, variability and concentration ranges are profuse for the MASP as a whole (e.g., Carvalho et al., 2015; Kumar et al., 2016; Andrade et al., 2017; and references therein).

However, despite the particularities of air pollution sources and dynamics, few atmospheric studies were dedicated to the ABC region. Most of them focused on air pollution health impacts (e.g., Chiarelli et al., 2011; Negrete et al., 2010; Silva et al., 2017), on urban climate (Valverde, 2017; Valverde et al., 2020), and a few on ambient air pollution measurements (Saiki et al., 2007; Savóia et al., 2009; Caumo et al., 2017; Guimarães et al., 2019). This study contributes to the filling of this gap, describing the variability of air pollutant concentrations in the ABC region, accounting for its particularities on pollution sources and atmospheric conditions.

In this way, the main objective of this study is to characterize the temporal and spatial variability of atmospheric pollutants at the ABC region in the year of 2015, exploring the associations with surface meteorological conditions, as well as investigating the main pollutant sources and atmospheric processes that explain the observed concentration variability.

Methodology

Characterization of the study area

The ABC region covers an area of 829 km² within MASP, in the Southeast region of Brazil (Figure 1). It is an urban area in the periphery of MASP, where intense vehicular traffic and industrial activity coexist with water reservoirs and areas of environmental protection. MASP is located on a 700 m plateau above mean sea level, and approximately 50 km inland from the coast. The predominant winds are from the southeast (IAG-USP, 2015a), and low level circulation is dominated by the sea breeze entrance, mountain-valley circulation and urban effects (Oliveira et al., 2003; Ribeiro et al., 2018; Valverde et al., 2020). While the sea breeze may contribute to the dispersion of the urban plume, the transport of air pollutants from industrial areas in the coastal region cannot be discarded.

The climate at MASP, including the ABC region, is classified as high elevation subtropical humid (Cwb), according to the Köppen classification (Piñero Sánchez et al., 2020). The winter at the ABC region is dry and mildly cold, with a mean temperature of 16.7°C and 74.5% relative humidity (RH) in July. The summer is wet and warm, with mean values of temperature and RH of 23.2°C and 78.8% in January. The highest monthly rainfalls occur in the summer, reaching 242 mm.month⁻¹ in January on average, while August is typically the month with the lowest amount of rainfall, 26 mm.month⁻¹ (Valverde et al., 2020). The planetary boundary layer (PBL) height at MASP shows a daytime maximum of about 1,500 m in the summer and 1,100 m in the winter, related to seasonal variations in the heat fluxes at surface (Piñero Sánchez et al., 2020). The seasonality of large-scale circulation at MASP is influenced by the dynamics of the South Atlantic Subtropical Anticyclone (SASA), which is zonally wider and closer to the continent in the austral winter and retracted to the east during the summer (Reboita et al., 2019). SASA spatial configuration can be

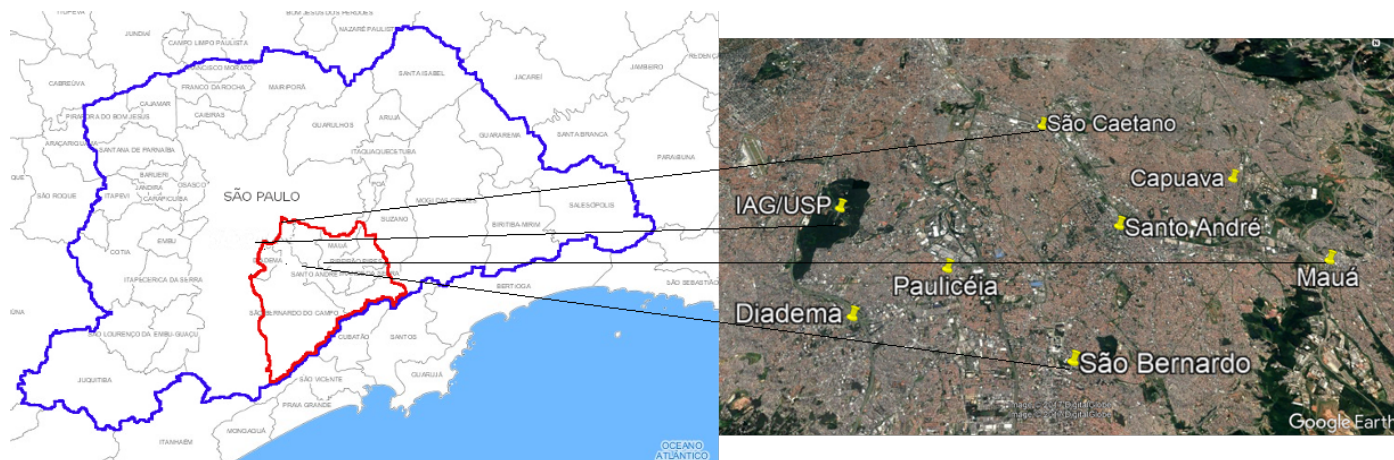


Figure 1 – Map showing the Metropolitan Area of São Paulo contoured in blue and the ABC region in red. The location of the seven Companhia Ambiental do Estado de São Paulo's air quality monitoring stations at the ABC region and the Instituto de Astronomia, Geofísica e Ciências Atmosféricas (Universidade de São Paulo) meteorological station are shown in a zoomed image (Google Earth). The distances between this ensemble of air quality and meteorology monitoring stations are in the range of 4 to 15 km.

disrupted by the influence of transient systems like cold fronts and extratropical cyclones, which are more frequent in the winter (Foss et al., 2017). Low-level jets intensify the moisture transport from equatorial South America to southeastern Brazil during the summer (Marengo et al., 2004). In the winter, surface anticyclonic circulation predominates at MASP, and postfrontal high-pressure systems moving northeast typically merge with SASA. This winter synoptic pattern inhibits cloud formation and provides increased atmospheric stability, leading to a higher frequency of thermal inversions and restrictions on the air pollutant dispersion at MASP (Piñero Sánchez et al., 2020; Gozzo et al., 2021; Oliveira et al., 2021).

Datasets of air pollution and surface meteorological variables

Hourly concentration data for ozone (O_3), inhalable particle matter (PM_{10}), carbon monoxide (CO), sulfur dioxide (SO_2) and nitrogen oxides (NOx) for the year of 2015 was obtained from seven CETESB air quality monitoring stations distributed in the ABC Region (Figure 1). Since the CETESB stations do not monitor meteorological variables continuously, surface meteorological data was obtained from IAG-USP's (Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo – Astronomy, Geophysics and Atmospheric Sciences Institute, University of São Paulo) meteorological station (World Meteorological Organization (WMO) station #83004). This is the closest available WMO meteorological station, with distances to the air quality monitoring stations ranging from 4 to 15 km (Figure 1). Previous studies have shown that measurements of temperature, precipitation and relative humidity at IAG-USP station are representative within this spatial scale (Sugahara et al., 2012; Piñero Sánchez et al.,

2020). The following surface variables were used in this study: air temperature (T), relative humidity (RH), wind speed (WS), global radiation (RAD) and precipitation. The time series of pollutants and meteorological data since 1998 were used for historical data analysis. Months with less than 50% data coverage were not included in monthly statistics. Table 1 shows the configuration of the air quality stations, including its spatial representability and whether they are directly influenced by stationary sources, according to CETESB (2014, 2016a). All stations were influenced by vehicular emissions to some extent.

Data analysis procedures

For investigation of the similarity between concentrations measured at different stations, multiple comparisons of group means were performed using one-way analysis of variance (ANOVA), which has been used before in air quality spatial variability studies (e.g., Estévez-Pérez and Vilar, 2013). The assumptions for ANOVA are normality and homoscedasticity, but previous studies show that ANOVA is robust even if normality is violated (e.g., Schmider et al., 2010). Although the time series of pollutant concentration daily averages did not completely fulfill the ANOVA requirements, tests with Kruskal-Wallis and Welch-ANOVA showed similar results, and all tests rejected the null hypothesis of equal means or ranks, with 95% significance and $p < 0.05$.

Principal component analysis (PCA) was applied to daily datasets of meteorological variables and pollutant concentrations at São Caetano do Sul and São Bernardo do Campo, aiming to identify pollution sources and processes that influence air quality at these sites. The choice of the stations was based on the variety of monitored parameters, as well as in the contrasting character of the stations con-

Table 1 – Characteristics of air quality stations and location of the the Instituto de Astronomia, Geofísica e Ciências Atmosféricas (Universidade de São Paulo) meteorological station. Representability scale was based on Companhia Ambiental do Estado de São Paulo (2014, 2016a) reports. The influence of fixed sources was based on the same reports, when available, and on visual inspection of aerial images in a radius of 1000 m around the stations of Santo André, São Bernardo do Campo and Pauliceia.

Name	Altitude	Coordinates	Fixed sources	Scale (km)	Variables monitored
Diadema	789 m (complex/top)	23.685 S 46.610 W	No	0.5–4	PM ₁₀ , O ₃
Capuava (Santo André)	815 m (complex/top)	23.637 S 46.488 W	Yes	0.5–4	PM ₁₀ , O ₃ , SO ₂
Mauá	775 m (complex/top)	23.669 S 46.466 W	Yes	0.5–4	PM ₁₀ , O ₃ , NOx
Santo André (Paço Municipal)	764 m (complex/valley)	23.657 S 46.530 W	Yes	0.1–0.5	PM ₁₀ , CO
São Bernardo do Campo (Centro)	781 m (plane/valley)	23.698 S 46.546 W	No	0.5–4	O ₃ , NOx, CO
Pauliceia (São Bernardo do Campo)	761 m (plane/valley)	23.670 S 46.584 W	Yes	0.5–4	PM ₁₀
São Caetano do Sul	745 m (plane/valley)	23.603 S 46.572 W	Yes	0.1–0.5	PM ₁₀ , O ₃ , NOx, CO, SO ₂
Instituto de Astronomia, Geofísica e Ciências Atmosféricas (Universidade de São Paulo)	800 m (complex/top)	23.651 S 46.622 W	–	–	T, RH, WS, RAD, rain

cerning air quality conditions. PCA is a multivariate analysis that identifies associations between variables in a dataset, resulting on a group of so called Principal Components (PCs), which consist of linear combinations of the original variables, reducing the complexity of the original dataset (Correia and Ferreira, 2007). PCA has been successfully applied to environmental data before (Guardani et al., 2003; Santos et al., 2018; Corrêa et al., 2019). The analysis was performed using the “principal” function in the R software, with the option of Varimax rotation. Six outliers were replaced by averages, being identified as values outside the interval $[Q1 - 3IQ; Q3 + 3IQ]$, where Q1 and Q3 are the 1st and 3rd quartiles and IQ is the interquartile range. The time series of CO, NO and SO₂ were log-transformed to get conformity with normal distribution, which is a requirement for PCA. Concentration and meteorological variables were normalized by their arithmetic mean and standard deviation. The Kaiser-Meyer-Olkin (KMO) test was applied to the datasets, obtaining the values of 0.68 for São Bernardo and 0.79 for São Caetano, attesting that the data is suited for PCA. Eigenvalues above 1.0 were used as criteria to define the number of PCs.

Results and Discussion

Spatial and temporal variation of pollutant concentrations

Analysis of air pollutant concentration time series at seven sites in the ABC region in 2015 revealed similarities and discrepancies, despite the proximity of the sites. Analysis of variance (ANOVA) was applied to daily concentration averages to investigate differences in the mean

concentration values and its variability among the sites. In Figure 2, circles indicate the mean concentration values for each pollutant at each site, and the error bars represent the overall variability. Differences between pairs of stations are statistically significant ($p < 0.05$) when the error bars do not overlap.

São Caetano do Sul showed significantly higher concentrations for PM₁₀, CO and NOx when compared to the other sites. In 2015, the annual mean PM₁₀ concentration at São Caetano do Sul was the second highest considering the whole MASP region (CETESB, 2016b). SO₂ concentrations were similar in São Caetano do Sul and Capuava, with typical concentrations in the range of 4 to 5 µg.m⁻³. According to CETESB (2016b), in 2015, CO in the MASP was mostly emitted by light duty vehicles and motorcycles (94%), while PM₁₀, NOx and SO₂ had a significant contribution of heavy duty vehicle emissions (respectively 31%, 44% and 10%). NOx and SO₂ also had a significant contribution from industrial sources (respectively 32% and 78%). The abundance of these pollutants in São Caetano suggest greater influence of local air pollution sources at this site, both vehicular (Valverde et al., 2020) and industrial. In fact, São Caetano do Sul is surrounded by five industries within a 1.5 km radius, and sits downwind of avenues with intense vehicular traffic — Goiás Avenue and Do Estado Avenue, respectively at ~0.8 and 1.4 km eastern to the site (CETESB, 2002). Even though Mauá and Capuava are located in the vicinity of petrochemical plants, the observed PM₁₀ concentrations there were significantly smaller in comparison to São Caetano do Sul. Conversely, O₃ in São Caetano do Sul was in the lower range of concentrations, similar to the Diadema and Capuava stations. Because of the prox-

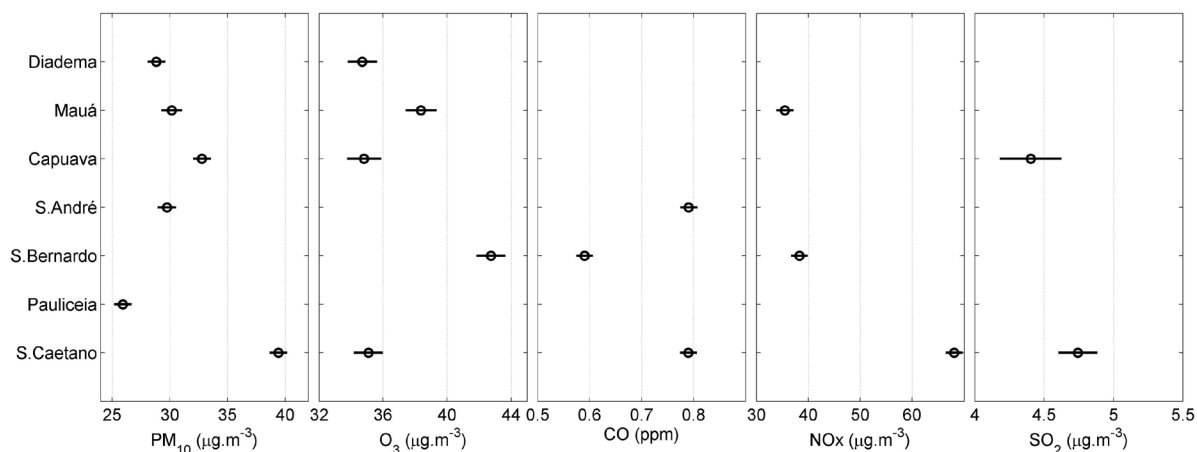


Figure 2 – Analysis of Variance (ANOVA) applied to daily mean concentrations of PM_{10} , O_3 , CO, NOx and SO_2 at seven air quality monitoring sites in the ABC region in 2015. Circles indicate the mean concentration values for each pollutant at each site. Error bars represent the overall confidence level for each pollutant, considering the variability at all sites. The difference in the mean concentration of a pollutant between pairs of stations is statistically significant ($p < 0.05$) when the error bars do not overlap. Note: SO_2 measurements at Capuava were available only between August and December.

imity of the stations, it is reasonable to assume that they had similar sky conditions on average, so that differences in annual mean O_3 concentrations may be explained by chemical factors related to the local availability of precursors.

In general, stations with relatively low NOx concentrations showed significantly higher O_3 concentrations when compared to the others. This fact agrees with the hypothesis of a VOC (volatile organic compounds) limited regime for tropospheric O_3 production at MASP, in which an increase on NOx concentrations leads to a decrease on O_3 net production (Silva Junior et al., 2009; Madronich, 2014; Alvim et al., 2017). São Bernardo do Campo, for example, showed low concentrations for CO and NOx, and the highest mean for O_3 ($43 \pm 18 \mu\text{g.m}^{-3}$), above the national standard for O_3 (annual mean of $40 \mu\text{g.m}^{-3}$ Brasil, 2018). In 2015, São Bernardo do Campo figured as the MASP station with the second highest number of O_3 exceedances (CETESB, 2016b), demonstrating the need for a better understanding of the dynamics and emission of O_3 precursors at this municipality.

Figure 2 reflects the spatial distribution of air pollutants in 2015, but it is important to mention that this scenario evolved along the years. Carvalho et al. (2015) reported negative PM_{10} concentration trends in the ABC region between 1996 and 2009, ranging from -2 to $-3 \mu\text{g/m}^3$ per year. The year of 2015 showed one of the lowest annual mean PM_{10} concentrations in the ABC since 1998, attributed to the combination of continuous reduction of vehicular emissions (Andrade et al., 2017) and occurrence of favorable dispersion conditions in the austral spring of 2015, associated with the influence of the 2015–2016 El Niño episode (CPTEC, 2015; Kogan and Guo, 2017; Pereira et al., 2017).

The seasonal variability observed for PM_{10} and O_3 was similar at all sites in the ABC region (Figure 3). This is an indication that the variability of pollutant concentrations at this time scale is modulated by the climate, which reflects the seasonality of atmospheric circulation in regional and large scale. The variability of PM_{10} concentrations in 2015 was in agreement with previous reports at MASP, with highest concentrations during the austral winter (Figure 3D), when the atmosphere is typically more stable (Piñero Sánchez et al., 2020) and the accumulated precipitation is lower (Figure 3B), leading to a meteorological scenario that favors the retention of PM_{10} in the surface layer (Carvalho et al., 2015; Valverde et al., 2020). The concentration of NOx, CO and SO_2 , which are mostly of primary origin, followed the same seasonal pattern as PM_{10} , with higher concentrations during the winter. During the austral summer, PM_{10} and primary pollutant concentrations decreased, likely due to the influence of typical summertime convection systems that promote atmospheric instability, wind gusts and rainfall (Marengo et al., 2004; Valverde et al., 2020), favoring the dispersion and removal of aerosols.

PM_{10} concentrations peaked in August of 2015 at all ABC stations, and exceeded the 1998–2015 mean in São Caetano do Sul (Figure 3D). This month was characterized by surface wind velocities (not shown) and relative humidity (Figure 3C) below the 1998–2015 average. It is likely that these surface weather conditions were associated with the occurrence of a high pressure system that restrained frontal activity in the Brazilian southeast region (CPTEC, 2015), and resulted in the absence of precipitation at MASP between July 26 and August 19, 2015 (IAG-USP, 2015b). This meteorological scenario possibly inhibited the dis-

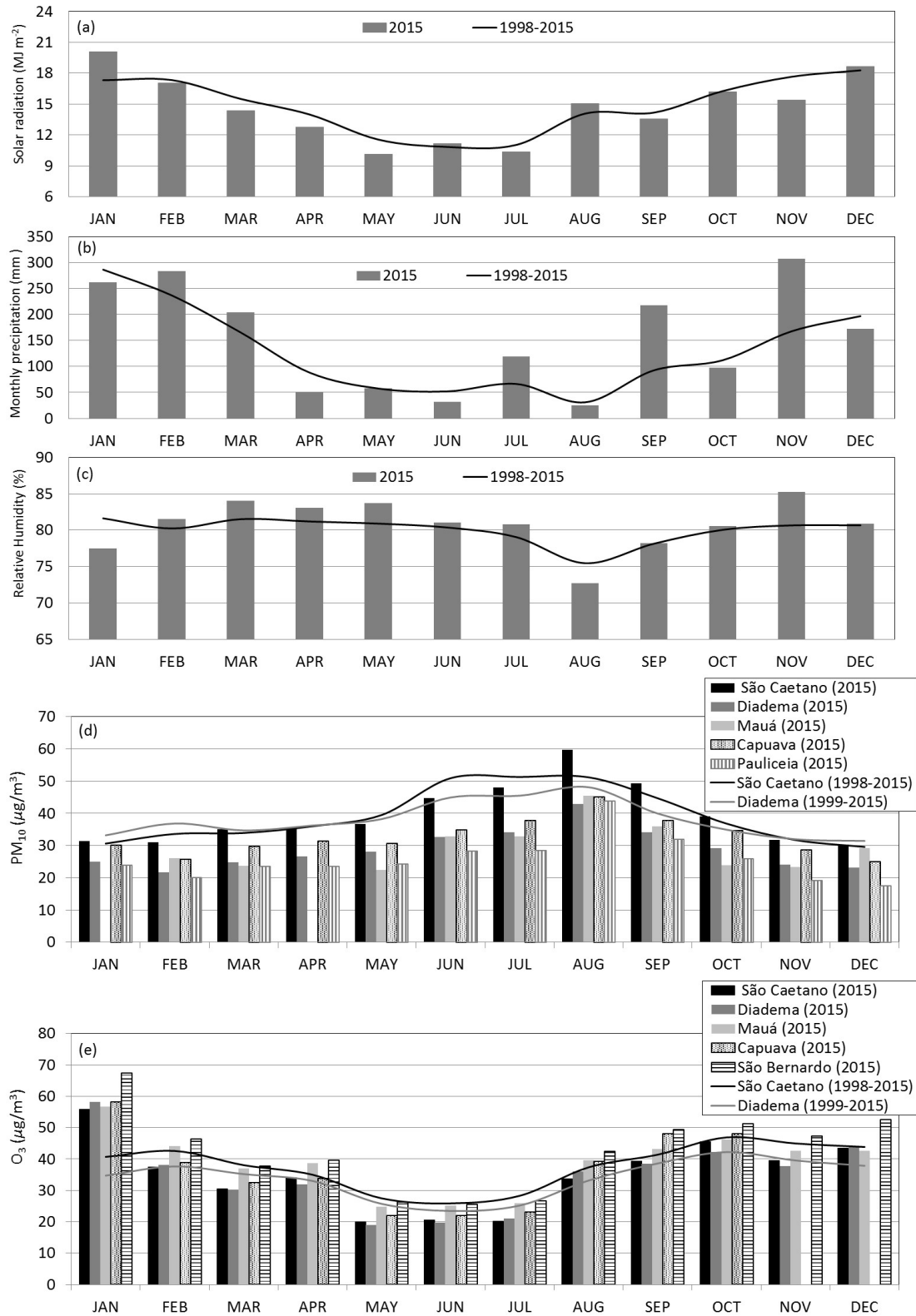


Figure 3 – Monthly means for 2015 and for the historical time series (1998–2015) for surface meteorological variables measured at the Instituto de Astronomia, Geofísica e Ciências Atmosféricas (Universidade de São Paulo) meteorological station: (A) global solar radiation, (B) monthly accumulated precipitation, (C) mean relative humidity and pollutant concentrations: (D) PM_{10} , (E) O_3 .

persion of air pollutants at MASP, although a detailed characterization of the active synoptic systems and atmospheric thermodynamic conditions in August of 2015 would be necessary to support this hypothesis.

While the seasonal behavior was very similar for PM_{10} , significant concentration differences were observed between the stations. PM_{10} concentrations at São Caetano do Sul's station stood out throughout the year (Figure 3D), once more suggesting the influence of local sources of the pollutant at this site. At Diadema, PM_{10} concentrations were, most of the time, well below the 1999–2015 average, and the same holds for Mauá and Capuava. Particularly, the Pauliceia site showed an intense reduction in PM_{10} levels over the years, with concentrations 50% lower in 2015 when compared to 1998, when PM_{10} concentrations in Pauliceia used to be similar to the São Caetano site. The year of 2015 was relatively rainy (Figure 3B), with precipitation rates above the climatology, especially during the austral spring (IAG-USP, 2015a), possibly related to the influence of the 2015–2016 El Niño (CPTEC, 2015; Kogan and Guo, 2017; Pereira et al., 2017). This scenario certainly contributed to the dispersion and removal of PM_{10} at the ABC region, leading to the observed concentrations below the average at most stations, except in São Caetano do Sul.

Contrary to PM_{10} , O_3 concentrations peaked in the austral spring and summer (Figure 3E). São Bernardo do Campo stood out, with O_3 concentrations significantly higher when compared to other stations, in agreement with the ANOVA analysis (Figure 2). Observed O_3 concentrations in 2015 were similar to the 1998–2015 averages at all stations, except in January, when an anomalous concentration peak was observed. Previous studies at MASP report highest O_3 concentrations at austral spring, when the combination of increased solar radiation input and decreased nebulosity favors the production of this secondary pollutant (Silva Junior et al., 2009; Carvalho et al., 2015; Carvalho et al., 2020).

The high O_3 concentrations observed in January 2015 (Figure 3E) were concomitant with positive anomalies in global solar radiation (8% above the 1998–2015 mean value for January) and negative anomalies in precipitation and relative humidity (Figures 3A–3C). It is very likely that this meteorological pattern at the surface was associated to an atypical high pressure system established over Southeast Brazil at the end of December 2014. This episode is well documented in the literature, since it resulted in an extreme drought event, with shortages in water supply at MASP (CPTEC, 2015; Marengo et al., 2015; Coelho et al., 2016; Nobre et al., 2016; Cavalcanti et al., 2017). Based on detailed synoptic analysis for the austral summer of 2014/2015, the authors show that a mid-tropospheric blocking high inhibited the development of the South Atlantic Convergence Zone (SACZ) and of typical summertime rainfall events. Changes in circulation were associated with a large-scale teleconnection wave train (Coelho et al., 2016).

The unusual high O_3 concentrations observed at the ABC region in January 2015 were also reported for other CETESB stations

at the MASP (CETESB, 2016b). On 17 January 2015, 14 out of 19 CETESB monitoring stations at MASP had maximum O_3 (8 h moving average) above the state standard ($140 \mu\text{g m}^{-3}$), including all stations at the ABC region. Particularly, three ABC stations, Diadema, Mauá and São Bernardo do Campo, reached the attention level for O_3 ($>200 \mu\text{g m}^{-3}$, 8 h moving average) between January 13 and 20. Since this air pollution event was observed in a regional scale, it is possible that the synoptic conditions during the 2014/2015 summer drought may have affected O_3 photochemical production at the ABC region in January of 2015. However, to confirm this hypothesis, further studies should be conducted, including a detailed case study on atmospheric circulation and thermodynamics in a synoptic scale. Also, since O_3 formation relies on the relative proportion of precursors in a non-linear way, the impact of possible changes in the emission patterns of NOx and VOCs cannot be ruled out. To investigate the role of atmospheric chemistry on the observed O_3 peak, monitoring of VOCs would be necessary at the ABC region, particularly for species with high O_3 yield, like aldehydes and isoprene (Alvim et al., 2017).

While the seasonal variability of pollutant concentration was very similar between the monitoring stations, the diurnal pattern showed significant differences from one station to another (Figure 4), reflecting the influence of local emission sources and processes. O_3 diurnal cycle behaved as expected, with highest concentrations observed between 2 PM and 4 PM local time (LT) (Figure 4B), a period of high solar incidence and elevated temperatures, which favors the formation of the pollutant. The diurnal peak, considering all ABC stations in 2015, was $74 \pm 4 \mu\text{g/m}^3$ (average $\pm$ standard deviation), compatible with previous reports for the MASP (Carvalho et al., 2015; Schuch et al., 2019). The diurnal variability and O_3 concentrations were similar at most stations, due to the fact that it is a secondary pollutant and thus has a weaker dependence on local sources. São Bernardo do Campo was the only station that stood out, with higher O_3 concentrations when compared to the other sites. It is reasonable to assume that the average sky conditions were similar between the monitoring stations considered in this study, since they are up to 14 km apart from each other. So, the significantly higher O_3 concentrations at São Bernardo do Campo (Figure 2) are likely related to the relative proportion of the precursors NOx and VOCs near the site, favoring O_3 photochemical production (Alvim et al., 2017).

The diurnal pattern of PM_{10} (Figure 4A), NOx (Figure 4C) and CO (not shown) showed concentration peaks in the morning (between 7 AM and 10 AM LT) and evening (between 5 PM and 8 PM LT), associated with periods of intense vehicular traffic and low mixing layer height, in accordance with previous observations at MASP and other cities worldwide (Laakso et al., 2003; Zhao et al., 2009; Muñoz and Alcañiz, 2012; Carvalho et al., 2015; Valverde et al., 2020). The morning peaks were usually concomitant, while, in the evening, PM_{10} peaks typically occurred two hours earlier than CO and NOx

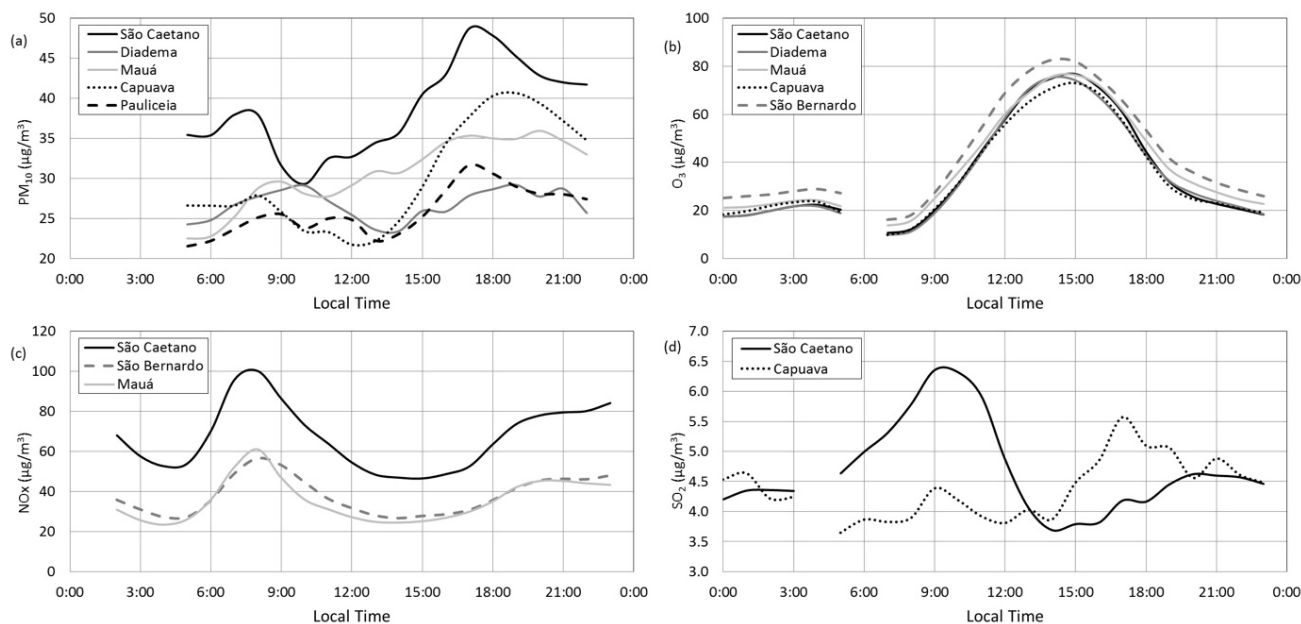


Figure 4 – Mean diurnal cycle for (A) PM_{10} , (B) O_3 , (C) NO_x and (D) SO_2 at five ABC stations in 2015. There is a lack of data at certain hours of the day because of automated instrumental checks in the monitoring stations. Note: SO_2 measurements at Capuava were available only between August and December.

peaks. The similar diurnal variability of PM_{10} , CO and NO_x in São Caetano suggest common emission sources, as will be discussed in the next section.

Another aspect shown in Figure 4A is that the PM_{10} diurnal pattern differed between the stations. Around noon, PM_{10} concentrations decreased in most stations, in response to the dilution caused by the development of the mixed layer. Mauá station was an exception, with PM_{10} concentrations rising steadily between 10 AM and 8 PM LT. This station sits nearby industrial plants and at the top of complex topography landscape (Table 1), which can affect the local wind circulation (Valverde et al., 2020), influencing the PM_{10} diurnal variability. Different variability of pollutant concentrations at Mauá station has been reported in a previous study, although for O_3 (Guardani et al., 2003). Considering that about 75% of PM_{10} at MASP are of primary origin (CETESB, 2016b), its diurnal pattern can be strongly influenced by the variability and strength of local sources.

The diurnal variability of SO_2 (Figure 4D), which is considered a tracer for industrial emissions at MASP (CETESB, 2016b), also showed morning and late afternoon peaks, but they were not always concomitant with CO and NO_x . However, the analysis for SO_2 and the contribution of industrial emissions was undermined by the lack of observations, since it was monitored only at two stations.

Air pollution sources and processes

Aiming to identify air pollution sources, processes, and their relative importance, PCA was applied to daily databases of pollutant con-

centrations and meteorological variables at São Bernardo do Campo and São Caetano do Sul. These stations were chosen based on data availability and diversity of local conditions. In São Bernardo do Campo, three principal components (PCs) were found, responding for 84% of total variance (Table 2). The first component was identified as photochemical production of pollutants, since it includes O_3 , temperature and radiation, while the second component was associated with vehicular emissions due to the presence of CO, considered a tracer for light duty vehicle emissions (Guardani et al., 2003; CETESB, 2019). PC1 and PC2 showed similar contributions to the total variance, explaining 36% and 35%, respectively. Relative humidity had negative loadings split between the PCs 1 and 2, indicating a negative correlation with pollutant concentration. Previous studies reported associations between increased O_3 concentrations, high temperatures and low relative humidity at MASP (Santos et al., 2018). A third component, less relevant in terms of explained variance, had only wind speed as a main variable, isolated from the other variables.

In São Caetano do Sul, PCA resulted in three components, explaining 78% of total variance (Table 3). Contrary to São Bernardo do Campo, the first PC, which explained 37% of the variance, was associated with vehicular emissions. PC2 explained 30% of the variance, being associated with photochemical formation of pollutants, similarly to São Bernardo do Campo. Once again, relative humidity had negative loadings split between the PCs 1 and 2 and wind speed was isolated in the third PC. The fact that PM_{10} had a high positive loading in PC1 suggests that, in São Caetano do Sul, most of PM is from primary ve-

Table 2 – Principal component analyses applied to São Bernardo do Campo's daily dataset of pollutant concentrations (CO, NO, NO₂ and O₃) and surface meteorological variables in 2015: RAD (global radiation), T (air temperature), RH (relative humidity) and WS (wind speed).

Principal Components (PCs)			
Variables	1	2	3
CO	0.11	0.86	0.34
NO	-0.28	0.88	0.08
NO ₂	0.05	0.94	0.13
O ₃	0.87	-0.23	0.04
RAD	0.90	0.04	-0.02
T	0.86	-0.01	0.15
RH	-0.69	-0.52	0.27
WS	-0.06	-0.29	-0.92
Eigenvalues	2.87	2.8	1.07
% variance	36%	35%	13%

Table 3 – Principal component analyses applied to São Caetano do Sul's daily database of pollutant concentrations (CO, NO, NO₂, O₃, SO₂, PM₁₀) and surface meteorological variables measured at the Instituto de Astronomia, Geofísica e Ciências Atmosféricas (Universidade de São Paulo) meteorological station in 2015: RAD (downward global radiation), T (air temperature), RH (relative humidity) and WS (wind speed).

Principal Components (PCs)			
Variables	1	2	3
CO	0.85	-0.07	0.14
NO	0.87	-0.33	-0.06
NO ₂	0.93	-0.03	0.06
SO ₂	0.52	0.29	0.24
PM ₁₀	0.83	0.27	0.24
O ₃	-0.19	0.85	0.24
RAD	0.09	0.90	-0.08
T	-0.02	0.83	-0.06
RH	-0.57	-0.67	0.27
WS	-0.24	0.05	-0.92
Eigenvalues	3.72	2.95	1.14
% variance	37%	30%	11%

hicular emissions. The presence of SO₂ in PC1 suggests an influence of heavy duty vehicle emissions at this station. Nevertheless, the relatively low SO₂ loadings in the PCs 1 and 2 indicate that this pollutant has a distinct behavior when compared to the others, and possibly a different source, likely related to industrial emissions. Unfortunately, no other

tracers for industrial emissions were available in a daily timescale for inclusion in the PCA analysis.

Conclusion

This study described the spatial and temporal variability of atmospheric pollutants at MASP's ABC region in 2015, and its associations with meteorological conditions. Climate regulated the seasonal variability of pollutant concentrations at all monitoring stations. Local processes influenced the loading of primary pollutants like PM₁₀, CO and NO_x and their diurnal cycles, which were different across the monitoring stations. Higher PM₁₀ concentrations were observed at the São Caetano and Capuava sites, reflecting the proximity to industrial areas and traffic of heavy duty vehicles. In the case of O₃, which is a secondary pollutant, local processes had a weaker influence, and only the station of São Bernardo stood out with significantly higher concentrations. Vehicular emissions and photochemical production were identified as the main processes explaining the observed concentrations. It is possible that insufficient data on industrial emission tracers prevented the identification of fixed sources as a major contributor.

Overall, results have shown that air quality is unequal in the ABC region, relying on the magnitude and dynamics of local emission sources. Expansion of the air quality monitoring network is important in order to improve knowledge on local processes, or, at least, increase the variability of atmospheric parameters monitored at the existing stations. In addition to the impact of local processes, weather events may lead to extreme events of air quality deterioration, with likely health impacts for the population. In order to attain air quality concentration standards at all parts of the ABC region, policy makers should consider the proximity to emission sources and be aware of the variability of atmospheric dispersion conditions. The development of policies and mechanisms for provisory restriction of emissions during episodes of unfavorable dispersion conditions are recommended to minimize impacts on human health and environment.

Future studies could expand the analysis for other years, investigating long term trends in air pollutant concentrations at the ABC regions and its spatial differences. Detailed case studies on synoptic meteorological conditions during extended periods of air quality deterioration are recommended to evaluate the direct impact of regional weather phenomena on air pollution at MASP. The investigation on local air pollution sources could be improved by the inclusion of other pollutant species in the analysis, as well as proxies to the emission strength of industrial and vehicular sources. Measurements of hydrocarbons would be crucial to unveil the relative roles of atmospheric chemistry and meteorological conditions in episodes of high O₃ concentrations.

Contribution of authors:

Silva, M.D.: Conceptualization, Methodology, Formal analysis, Writing – original draft. Oliveira, M.C.Q.D.: Validation, Visualization, Writing – original draft. Drumond, A.: Validation, Supervision, Writing – review & editing. Rizzo, L.V.: Conceptualization, Writing – original draft, Supervision, Project administration.

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