Atmósfera 36(2), 329-341 (2023)
https://doi.org/10.20937/ATM.53056

Patterns related to pollutant concentrations in the Metropolitan Area of Belo Horizonte, Brazil

Luiza Maria Marcos Cerqueira MENDES[1], Vanessa Silveira Barreto CARVALHO[1]*, Fabrina Bolzan MARTINS[1] and Taciana Toledo de Almeida ALBUQUERQUE[2]

[1] *Instituto de Recursos Naturais, Universidade Federal de Itajubá, Itajubá, 37500-903, Minas Gerais, Brazil.*
[2] *Departamento de Engenharia e Sanitária Ambiental, Universidade Federal de Minas Gerais, Belo Horizonte, 31270-010, Minas Gerais, Brazil.*
*Corresponding author; email: vanessa.silveira@unifei.edu.br

Received: March 23, 2021; accepted: August 20, 2021

RESUMEN

La contaminación del aire por actividades humanas e industriales ha sido una gran preocupación en los últimos años. Entre los diversos contaminantes que se encuentran en la atmósfera, el material particulado (PM) y el ozono (O_3) muestran ocurrencias significativas, con altas concentraciones en los centros urbanos frecuentemente asociadas con problemas ambientales y de salud pública. Por lo tanto, este trabajo utiliza la técnica de análisis de varianza (ANOVA) y la prueba de Tukey para investigar los patrones relacionados con la variabilidad de las concentraciones máximas diarias de O_3 y las concentraciones medias diarias de MP con diámetro menor a 10 µm (PM_{10}), registradas entre 2007 y 2012 en seis sitios de la región metropolitana de Belo Horizonte, Brasil. Para ello, los datos se analizaron mediante ANOVA dispuestos en un esquema factorial (6 × 4 × 2) con cuatro repeticiones por tratamiento, seguido de la prueba de Tukey. En el ANOVA y la prueba de Tukey, el primer factor (A) representa las seis estaciones de monitoreo de la calidad del aire, el segundo (B) representa las estaciones y el tercero (C) las mediciones realizadas durante los días hábiles y fines de semana. Los patrones de variabilidad estacional muestran concentraciones más altas de O_3 en la primavera y de PM_{10} en el invierno. Los valores fueron 22.9 y 35.32% superiores a los promedios anuales de concentraciones de O_3 y PM_{10}, respectivamente. Los valores medios para los días laborables y los fines de semana mostraron patrones diferentes para los dos contaminantes. Las concentraciones de PM_{10} fueron 11% más altas durante los días laborables en comparación con los fines de semana. El efecto de fin de semana de O_3 se encontró sólo en una de las estaciones. Los perfiles de emisiones vehiculares e industriales se han identificado como un factor potencial que conduce a estos resultados.

ABSTRACT

Air pollution from human and industrial activities has been a major concern in recent years. Among the various pollutants found in the atmosphere, particulate matter (PM) and ozone (O_3) show significant occurrences, with high concentrations in urban centers frequently associated with environmental and public health problems. Therefore, this study uses the analysis of variance (ANOVA) technique and Tukey's test to investigate patterns related to the variability of maximum daily O_3 concentrations and mean daily concentrations of PM with a diameter less than 10 µm (PM_{10}), registered between 2007 and 2012 through six sites in the Metropolitan Area of Belo Horizonte, Brazil. To this end, the data were analyzed using ANOVA arranged in a factorial scheme (6 × 4 × 2) with four repetitions per treatment, followed by Tukey's test. In the ANOVA and Tukey's test, the first factor (A) represents the six air quality monitoring stations, the second (B) represents the seasons, and the third (C), the measurements carried out during working days and weekends. Seasonal variability patterns show higher concentrations of O_3 in spring and of PM_{10} in winter. The values were 22.9 and 35.32% higher than the annual averages of O_3 and PM_{10} concentrations, respectively. The mean values for working days and weekends showed different patterns for the two pollutants. PM_{10} concentrations were 11% higher during working days when compared to weekends. The O_3 weekend effect was found only in one of the stations. The profiles of vehicular and industrial emissions have been identified as a potential factor leading to these results.

Keywords: ANOVA, Ozone, Particulate Matter.

1. Introduction

The Metropolitan Area of Belo Horizonte (MABH), located to the mid-west of Minas Gerais state, covers 33 municipalities (Gouveia et al., 2019) with a population of 5961 815 inhabitants, which represents about 40% of the population of the entire state (IBGE, 2018), and has a vehicle fleet of nearly three million (DENATRAN, 2018). The MABH is in a region with enormous mining potential, including the Iron Quadrangle. This characteristic, combined with the population cluster, the availability of skilled labor, and the proximity to a consumer market, developed numerous industrial activities with high polluting potential (Radicchi, 2012), negatively impacting air quality (Miranda et al., 2011; FEAM, 2016; Gouveia et al., 2019; Peláez et al., 2020). In addition to high emission rates, air quality in the MABH is impacted by topography, which affects the distribution of rain, temperature variation, and wind speed and direction (Prudente et al., 2006; Santos et al., 2019).

The MABH registered an increase in concentrations of pollutants over the last two decades (Miranda et al., 2011; Pacheco et al., 2017; Peláez et al., 2020), and according to the Fundação Estadual do Meio Ambiente (State Environmental Foundation, FEAM) (FEAM, 2016), the main problem facing the MABH refers to high concentrations of particulate matter with a diameter less than 10 μm (PM_{10}) and ozone (O_3). For example, Pacheco et al. (2017) showed an increase in the average annual concentration of PM_{10} from 21.5 μg m^{-3} in 2005 to 31.3 μg m^{-3} in 2010. Sicard (2021) showed worldwide O_3 levels decreased in rural areas and increased in urban areas with an average increase for Brazil, between 2005 and 2014, of 0.56 ppb per year (approximately 1.1 μg m^{-3}). Paláez et al. (2020) identified frequent O_3 (8 h average concentrations) exceedances of the Brazilian National Air Quality Standards (NAQS) established by Resolution No. 491 (CONAMA, 2018) as safe for human health. The current NAQS in Brazil adopts the model of successive targets recommended by the WHO (2006) for reducing air pollution and ensuring the well-being and health of the population. Brazil is currently in the first stage; however, there is no timetable established for the implementation of the next targets nor indication of how they will be achieved.

Air quality depends directly on the emission of pollutants and is subjected to weather variability, which plays an important role in the transport, transformation, and dispersion of pollutants into the atmosphere. Several studies have been carried out worldwide, including Brazil, to relate ambient pollutant concentrations and their variability to local weather conditions. As an example, Sánchez-Ccoyllo and Andrade (2002) studied the influence of weather conditions on the behavior of pollutants in the Metropolitan Area of São Paulo (MASP) and found that the high relative humidity and the occurrence of cold fronts favors the dispersion and dilution of pollutants in the area. On the other hand, strong thermal-inversion conditions in the low atmosphere were associated with high pollutant concentrations at the surface. Similar results were found by Carvalho et al. (2015) and Santos et al. (2016), showing higher concentrations of most pollutants in the MASP during winter, when low rainfall rates, low winds, the predominance of the South Atlantic Subtropical High (SASH), and thermal inversions in the lower atmosphere inhibit dispersal of pollutants. However, higher O_3 concentrations were registered during spring and summer, when clear sky conditions, high temperatures, low relative humidity, and no precipitation dominate (Carvalho et al., 2012, 2015; Santos et al., 2018).

It is important to point out that several statistical techniques have been used to analyze the patterns associated with the concentration of pollutants, as well as to verify the seasonal and weekday-weekend influence (Mansouri et al. 2011; Aenab et al., 2013; Mohamad et al., 2015; Govender and Sivakumar, 2020; Carvalho et al., 2020). Among those techniques, the Analysis of variance (ANOVA) allows investigating the influence of preponderant factors on pollutant concentrations and whether there is a relationship between them (Storck et al., 2011; Aenab et al., 2013; Mohamad et al., 2015; Carvalho et al., 2020; Tyubee et al., 2020). Within the preponderant factors, the following can be listed: (*i*) seasonal effects (Carvalho et al., 2015; Santos et al., 2016; Tyubee et al., 2020); (*ii*) effect of the day of the week, related to weekdays vs. weekends (Brönnimann and Neu, 1997; Carvalho et al., 2020); and (*iii*) monitoring sites (Carvalho et al., 2020). In other words, ANOVA allows grouping these factors (*i*, *ii*, and *iii*) with similar patterns of pollutant concentrations, in addition to assessing the individual influence of each factor on the observed patterns. Nevertheless, despite the potential and possibilities of ANOVA, studies applying this technique to air pollution data are still scarce. Some examples of studies that use the ANOVA technique are: (*i*) Aenab et al. (2013) evaluated Baghdad's air quality by analysis of heavy metals; (*ii*) Fang et al. (2017) tested mean concentration variance differences for metallic elements (PM, Hg(p), Mn, Fe, Zn, Cr, Cu, and Pb) through the seasons at Taiwan; (*iii*) Tyubee et al. (2020) assessed the influence of factors such as land use/land cover and climate have on the spatial and seasonal variation in pollutants concentrations in Gboko, Nigeria; and (*iv*) for Brazil, the most recent work was performed by Carvalho et al. (2020) to evaluate O_3 concentration behavior and variability throughout the State of São Paulo.

Although some studies have been carried out for the MABH (Miranda et al., 2011; Pacheco et al., 2017; Peláez et al., 2020), none looked in-depth at the patterns associated with PM_{10} and O_3 concentrations, nor applied the ANOVA technique. We should add that this type of analysis provides effective information for developing public policies to control air pollution. Therefore, this study aims to verify, using the ANOVA technique, the patterns associated with PM_{10} and O_3 concentrations considering the following effects: seasonal variability, weekday-weekend concentration patterns, and similarities and differences of MABH air quality monitoring sites. Since O_3 is a secondary pollutant formed from photochemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs), NO_x patterns were also analyzed to complement the analyses. VOCs data were not available for the region.

2. Methodology

2.1 Data source

To carry out this study, 1-h mean concentrations of O_3 and PM_{10} monitored by FEAM between 2007 and 2012 were used. Overall, six automatic monitoring stations, whose location, mean (Mean), and maximum (Max) values within the analyzed period are listed in Table I. The spatial distribution can be observed in Figure 1.

From the 1-h mean data, the daily maximum O_3 concentrations and the daily mean concentration of PM_{10} were obtained for each site. At least 75% of valid data was required to calculate this data. Then, the data were classified according to the seasons

Table I. Location, parameters, and mean and maximum values of the pollutants (PM_{10} and O_3) in $\mu g\ m^{-3}$, monitored by the network of air quality monitoring stations in MABH.

Municipality	Monitoring stations	Monitored parameters			
		PM_{10}		O_3	
		Mean	Maximum	Mean	Maximum
Belo Horizonte	Praça Rui Barbosa (RB)	32.4	613.0	29.7	228.8
	Bairro Jardim das Alterosas (JA)	40.3	659.5	29.0	239.4
Betim	Bairro Petrovale (BP)	33.9	627.0	38.4	284.1
	Centro Administrativo (Safran)	50.9	688.2	31.0	313.1
Ibirité	Bairro Cascata (BC)	23.2	637.0	38.5	314.4
	Bairro Piratininga (Ibiritermo)	29.0	354.0	43.68	257.0

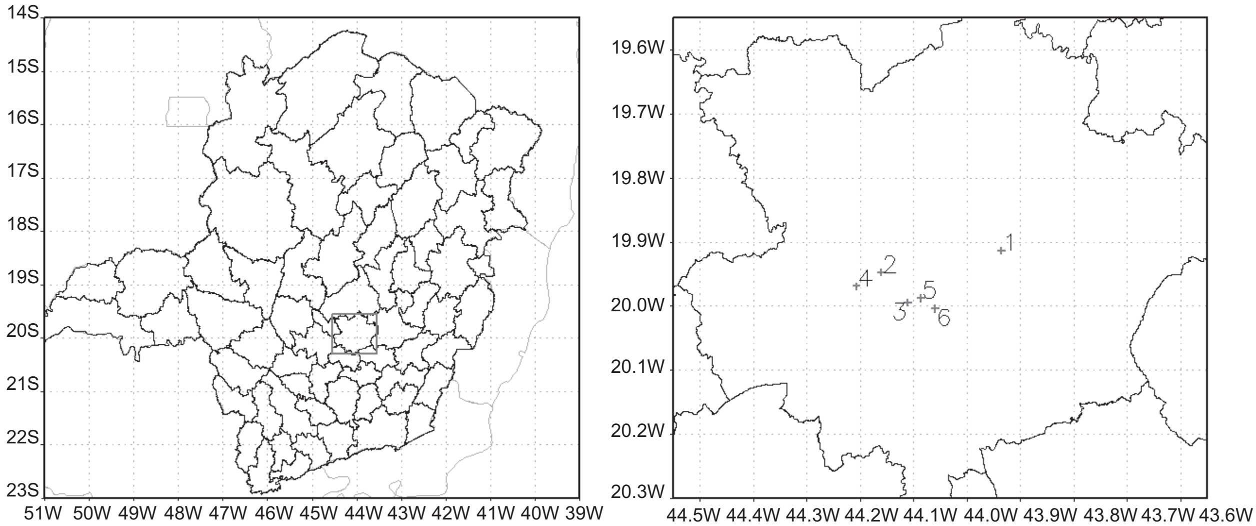

Fig. 1. State of Minas Gerais, Brazil (left) and spatial distribution of the air quality monitoring stations through Belo Horizonte Metropolitan Area (right), where: (1) Rui Barbosa, (2) Jardim Alterosa, (3) Bairro Petrovale, (4) Safran, (5) Cascata, and (6) Ibiritermo.

and day of the week corresponding to each of these registers. As a complement to the analysis related to the patterns of O_3 observed in MABH, the 1-h mean data for nitrogen dioxide (NO_2), nitrogen monoxide (NO), and the ratio between the concentrations of NO_2/NO were also used. The NO_2/NO ratio was used by Carvalho (2010) as an indicator of O_3 potential production in a region once its troposphere formation depends on the NO_2 photodissociation and that the NO acts on the consumption of the O_3 molecules. So, higher ratios are expected to be associated with higher concentration values of O_3.

2.2 Analysis of variance

Before proceeding to the ANOVA, the data of daily maximum and mean concentrations of the pollutants (O_3 and PM_{10}) were submitted to verify the assumption of normality and homogeneity of variance with the Shapiro-Wilk test ($\alpha = 0.05$). This procedure was performed to verify whether the data follow the normal distribution and have homogeneous variance ($p \geq 0.05$) or if the data do not follow the normal distribution and have heterogeneous variance ($p < 0.05$) (Mohamad et al., 2015). After this procedure, the data were analyzed using the three-factor ANOVA, organized in a factorial scheme ($4 \times 2 \times 6$) with four replicates per treatment. This procedure was adopted to evaluate the effect of the sources of variation (seasonal, day of the week, and monitoring site) at a 5% probability (Mohamad et al., 2015; Carvalho et al., 2020; Tyubee et al., 2020). The null hypothesis for ANOVA is that the factors are independent of each other, i.e., there is no interaction between them ($p \geq 0.05$) against the alternative hypothesis that the factors are dependent, meaning that there is an interaction between the sources of variation ($p < 0.05$). In this study, factor 1 refers to the seasons (four levels of factor 1: summer, autumn, winter, and spring); factor 2 refers to the weekday effect (2 levels of factor 2: weekday = data grouped from Monday to Friday; and weekend = data grouped from Saturday and Sunday); and factor 3 refers to the monitoring stations (six levels of factor 3: each of the six monitoring sites: Rui Barbosa (RB), Jardim das Alterosas (JA), Bairro Petrovale (BP), Safran, Bairro Cascata (BC), and Ibiritermo. Each repetition was considered the mean value of the maximum concentrations of O_3, and the mean value of the average concentrations of PM_{10}, totaling 576 data for each pollutant. Each treatment was the combination of the data among the three factors. Finally, a comparison of means was performed for the maximum concentration values of O_3 and the average concentration of PM_{10} using Tukey's test ($\alpha = 0.05$). All the tests were performed using the

Sisvar software (Ferreira, 2011) and followed the methodology analogous to Carvalho et al. (2020).

To complement the analysis of O_3 patterns, the same procedure (Shapiro-Wilk, ANOVA, and Tukey's test) was performed with the daily mean concentrations of NO_x and NO_2/NO ratio.

3. Results and discussion

3.1 Patterns associated with ozone concentration and its precursors

Using the Shapiro-Wilk test ($\alpha = 0.05$), the daily maximum O_3 concentrations, it was found that the daily mean NO and NO_2 concentrations and the daily mean NO_2/NO ratio violated the assumption of normality and homogeneity of variance. Therefore, they were transformed by (Ln(x)), following the recommendations of Storck et al. (2011) and Carvalho et al. (2020).

Regarding the ANOVA, daily maximum O_3 concentrations showed a significant interaction between the sources of variation: (*i*) seasons × monitoring stations, and (*ii*) day of the week × monitoring stations. Also, the factors monitoring stations (sites) and seasons were significant ($p < 0.05$) (Table II). This behavior means there is a differentiated pattern of maximum O_3 concentrations between monitoring stations, seasons, and days of the week. In other words, depending on the site, there are higher concentrations of O_3 in a given season, and there will be variations between weekdays and weekends. This result agrees with those presented by Carvalho et al. (2020), in which the ANOVA technique was applied to O_3 concentration data in the state of São Paulo. Also, the factors that contributed most to explain the pattern associated with O_3 concentrations were (in order of magnitude): season (F test = 169.5), monitoring station (F test = 81.8), the interaction between the levels of factors: season and monitoring station (test F = 7.1), and the interaction between the levels of factors: monitoring station and day of the week (F test = 3.1).

Once the interactions between (*i*) seasons × sites, and (*ii*) day of the week × sites were verified, it was necessary to analyze which monitoring stations differ and if/how the seasonal and weekend effects occur (Tables III and IV). For this purpose, the combined effects of each level of both factors were unfolded through Tukey's test. It is important to highlight that the coefficient of variation of 3.56% (less than 10%) indicates high precision in the analysis (Storck et al., 2011). Considering the results of the Tukey test

Table II. Analysis of variance of maximum daily O_3 concentrations ($\mu g\ m^{-3}$).

SV	DF	MS	F-test	P-value
Seasons*Week*Sites	15	0.0036	0.157	0.9999
Seasons*Week	3	0.0452	1.975	0.1167
Seasons*Sites	15	0.1623	7,086	0.0000*
Week*Sites	5	0.0698	3.046	0.0101*
Seasons	3	3.8820	169.463	0.0000*
Week	1	0.0872	3.805	0.0516
Sites	5	0.0229	81.772	0.0000*
Error	528	0.0229		
Total	575			
CV (%) =	3.56			
Overall mean	4.2551	Number of data:	576	

*Interaction between variation factors; **significant values by the F-test ($\alpha = 0.05$).

SV: sources of variation; Seasons: seasons of the year; Week: day of the week; Sites: monitoring stations; DF: degrees of freedom; MS: mean square; Fc: test F, given by the ratios of MS to the MS of the error; CV: coefficient of variation, given by equation (cv= ± 100 × σ/ mean); P: probability value of the F-test.

Table III. Comparison of means for the average maximum O_3 concentrations (μg m^{-3}) considering the interaction between the Monitoring Stations (6 levels) and Seasons (4 levels).

Monitoring stations	Season			
	Summer	Autumn	Winter	Spring
Alterosa	63.35 Bb	49.79 ABa	65.26 ABb	85.24 ABc
Cascata	69.95 Ba	71.13 Ca	76.32 Ca	93.58 BCb
Ibiritermo	69.94 Ba	64.03 Ca	70.76 BCa	92.06 BCb
Petrovale	85.60 Ca	81.76 Da	77.72 Ca	97.16 Cb
Rui Barbosa	48.75 Aa	46.53 Aa	62.88 Ab	76.20 Ac
Safran	67.18 Bb	55.98 Ba	81.09 Cc	91.60 BCd

Note: Different uppercase letters in the column (monitoring stations) and different lowercase letters in the row (seasons) differ by the Tukey test at 5% probability. Letters A to C and a to c were set in ascending order of O_3 concentrations.

Table IV. Comparison of means for the average maximum O_3 concentrations (μg m^{-3}) considering the interaction between day of the week (two levels) and monitoring stations (six levels).

Monitoring stations	Day of the week			
	Monday-Friday		Saturday-Sunday	
Alterosa	64.69	Ba	67.13	Aa
Cascata	78.28	Da	77.21	Ba
Ibiritermo	75.00	CDa	73.40	Ba
Petrovale	85.86	Ea	85.26	Ca
Rui Barbosa	54.98	Aa	62.20	Ab
Safran	72.12	Ca	75.81	Ba

Note: Different uppercase letters in column (monitoring stations) and different lowercase letters in the row (seasons) differ by the Tukey test at 5% probability. Letters A to E and a or b were set in ascending order of O_3 concentrations.

($\alpha = 0.05$) for the interaction between the sources of variation seasons and sites (Table III), it is verified that the highest mean of maximum O_3 concentration was registered during spring (mean: 89.30 μg m^{-3}), significantly differing for the other seasons in all monitoring stations, followed by winter (72.34 μg m^{-3}), summer (67.46 μg m^{-3}), and autumn (61.54 μg m^{-3}). This pattern of higher concentrations during spring was also verified by Carvalho et al. (2015, 2020) for the state of São Paulo. In general, during spring, higher ozone concentration values are observed, mainly because of the combination of increased incidence of solar radiation and lower cloud cover (compared to summer), particularly in the afternoon (Fig. 2). This combination favors photochemical reactions responsible for forming the O_3 molecule (Carvalho et al., 2015). Furthermore, the highest mean values of the maximum daily O_3 concentrations were registered at Petrovale (97.16 μg m^{-3}) and Cascata (93.58 μg m^{-3}), both located near the Gabriel Passos refinery, a region influenced by industrial and vehicular sources (FEAM, 2016). It is also observed that, except for the Cascata and Petrovale stations, the lowest mean values relative to maximum concentrations of O_3 were recorded during autumn, a similar pattern observed by Alvim (2013) for the main O_3 precursors in the Metropolitan Area of São Paulo. Alvim (2013) showed that more compounds contribute to the formation of O_3 in the winter than in autumn, mainly due to higher VOC concentrations in the atmosphere. Although the ratio between VOC and NO_x concentrations for the MABH is unknown, by applying ANOVA for NO (Table V), it was observed that mean concentrations for all monitoring stations were higher in winter (17.46 μg m^{-3}), followed by autumn (12.55 μg m^{-3}), summer (7.63 μg m^{-3}), and spring (7.45 μg m^{-3}). Higher concentrations of NO during winter would result in lower concentrations of O_3 in that season. However, only for JA, RB, and Safran there was a pattern opposite to the expected, indicating higher concentrations of O_3 in the winter when compared to

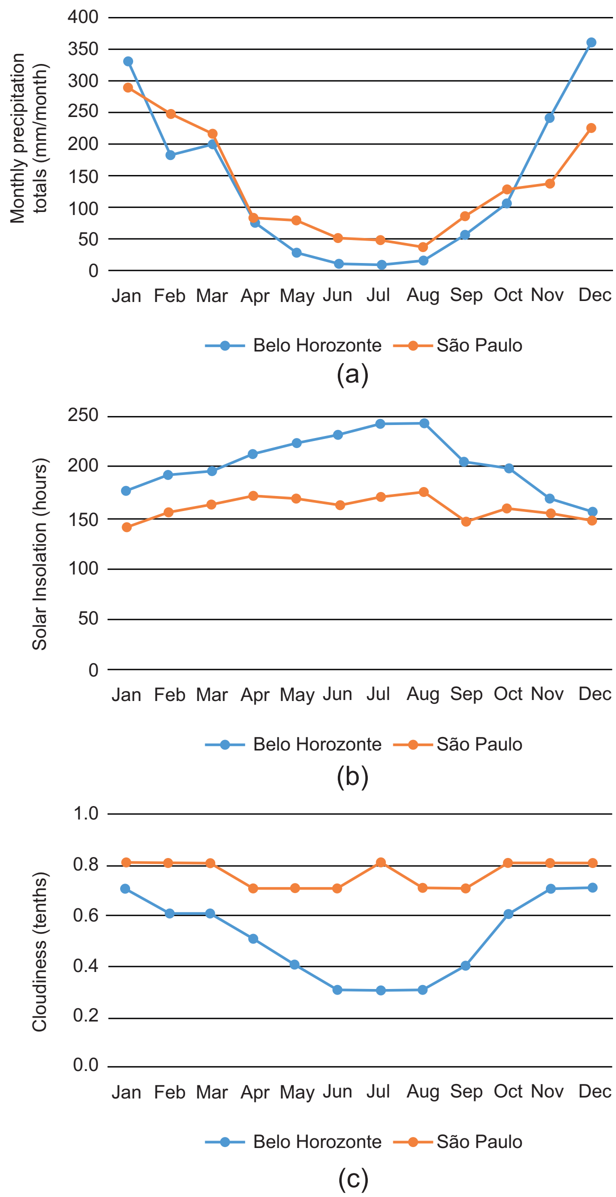

Fig. 2. Climatological normals (1981-2010) referring to the stations Belo Horizonte and São Paulo (Mirante de Santana) for (a) monthly precipitation totals (mm), (b) solar insolation (hours), and (c) cloudiness (tenths). Source: https://portal.inmet.gov.br/normais

autumn. The profile with higher mean concentrations in winter when compared to summer differs from that observed by Carvalho et al. (2015) for the MASP, probably due to the different climatic conditions registered between the two regions. As shown in Figure 2, during winter the climatological normals

Table V. Comparison of means for average NO concentrations ($\mu g\ m^{-3}$), NO_2/NO ratio, and O_3 concentrations ($\mu g\ m^{-3}$) between monitoring stations.

Monitoring stations	NO	NO_2/NO	O_3
Alterosa	—	—	65.91 B
Cascata	5.74 B	4.71 AB	77.75 C
Ibiritermo	4.82 A	6.49 D	74.20 C
Petrovale	8.21 C	5.31 BC	85.56 D
Rui Barbosa	16.48 D	4.21 A	58.59 A
Safran	20.79 D	6.54 C	73.96 C

Different uppercase letters in column (monitoring stations) and different lowercase letters in the row (seasons) differ by the Tukey test at 5% probability. Letters A to D were set in ascending order of NO, NO_2/NO ratio, and O_3 concentrations.

(1981-2010) for the Belo Horizonte station show lower precipitation rates, higher solar insolation values, and lower cloudiness values, factors that contribute to the formation of O_3.

It is noteworthy that the BC and BP stations showed slightly lower values in summer and winter, respectively, but they did not differ from those found in summer. The lowest means were, in general, registered in the RB (46.53 $\mu g\ m^{-3}$) and JA (49.79 $\mu g\ m^{-3}$) monitoring stations. This fact may be associated with vehicular traffic, since both stations are in regions significantly influenced by vehicle emissions.

Considering the interaction between the factors site and day of the week (Table IV), it is observed that, except for the RB station, the other monitoring stations did not present significant differences between the concentrations on weekdays and weekends, confirming, therefore, the weekend effect only at the Rui Barbosa station. Except for RB, the others did not follow the pattern observed by Silva Junior et al. (2009) and Carvalho et al. (2015, 2020) for MASP, and Carvalho (2006) for the Metropolitan Area of Rio de Janeiro, where they found higher concentrations of O_3 during the weekend. As noted for RB, higher concentrations of O_3 during weekends may be related to the increase of the ratio between NO_2 and NO concentrations (NO_2/NO), which occurs due to a decrease in vehicle traffic during the weekend. This decreases the emission of NO, a compound that acts in the consumption of the O_3 molecule ($O_3 + NO \rightarrow NO_2 + O_2$. The weekend effect was also observed in studies conducted in France (Pont and Fontan, 2001), Turkey (Im et al., 2013), United States (Wolff et al., 2013), and Canada (Huryn and Gough, 2014). Sicard et al. (2020) showed a significant downward trend (–0.26 per year) for the weekend effect in Canada, United States, Japan, Germany and Italy and an upward trend (+1.15 ppb per year [approximately +2.2 µg m^{-3}]) in urban stations in France, South Korea, and the United Kingdom. It is important to point out that, between the six monitoring stations, only Rui Barbosa is located within the Greater Belo Horizonte, being the only site predominantly influenced by vehicle emissions. Sites predominantly influenced by vehicular emissions in the state of São Paulo also presented a significant weekend effect (Carvalho et al., 2020).

The highest concentration values of O_3 were observed in Cascata and Petrovale, located in the MABH industrial area. This result can be associated with lower NO levels, combined with lower vehicle traffic on these two stations (Table V). In all stations, mean NO concentrations showed higher values during weekdays (13.29 µg m^{-3}) compared with weekends (9.22 µg m^{-3}). Considering all the MABH, this represents an average reduction of 30% of weekend concentrations compared to working days. Additionally, considering only the RB station, an average reduction of 28.4% of NO was observed on weekends. The results of this study are similar to those found by Carvalho et al. (2015) for MASP, and Qin et al. (2004) for California (USA), with an average of NO_x reductions of 32 and 37% over the weekend, respectively.

Considering that NO acts on the consumption of the O_3 molecule, it is expected that in areas where NO levels are higher, O_3 levels will be lower, as in Rui Barbosa. This hypothesis is supported by the mean concentrations of NO found in all sites (Table V). Analyzing the average behavior of the ratio NO_2/NO, when compared to the average daily maximum O_3 concentrations, it can be noted that, in general, higher values of the ratio between nitrogen oxides (NO_2/NO) were followed by higher concentration values of O_3, matching the expected pattern, since the increase in O_3 concentrations is directly associated with the increase of the NO_2/NO ratio.

Additionally, the monitoring stations where no differences were found between O_3 concentrations during weekdays and weekends (Alterosa, Cascata, Ibirifero, Petrovale, and Safran) are close to industrial units, which supports the hypothesis that the vehicle emissions profile of Rui Barbosa station plays an important role in the occurrence of the weekend effect (Table IV).

When analyzing mean O_3 concentrations at the monitoring stations (Table V), it is observed that the highest concentration occurs at Petrovale, regardless of the factors season and day of the week, unlike the rest of the stations. Comparatively, the Rui Barbosa station presents the lowest O_3 concentrations (Tables IV and V). This result corroborates the results obtained by Mendes (2018), who identified that Petrovale station had the highest number of exceedances of 100 µg m^{-3} (suggested by the WHO as a safe value for the population) in an 8-h average. The study also found that although Rui Barbosa also exceeded this threshold in all years (except for 2009), it presented the lowest number of exceedances when compared with the other sites.

3.2 Patterns related to the concentration of PM_{10}

A violation of the assumption of normality and homogeneity of variance for the data of daily mean concentrations of PM_{10} was found by the Shapiro-Wilk test ($p < 0.05$). Therefore, the data were transformed into Ln(x) according to the recommendation by Storck et al. (2011) and Carvalho et al. (2020).

According to ANOVA, the factors that most contributed to explaining the pattern associated with PM_{10} concentrations were (in order of magnitude): season (F test = 169.5), monitoring stations (F test = 157.3), day of the week (F test = 43.5), and interaction between the levels of factors season and monitoring station (F test = 3.7) (Table VI).

Since there was a significant interaction between the sources of variation seasons × monitoring stations ($p < 0.05$) (Table VI), it was necessary to unfold the combined effects of each level of both factors (Table VII). Besides, it was necessary to verify the individual behavior of the sources of variation (*i*) sites, (*ii*) seasons, and (*iii*) days of the week.

In general, the highest values of PM_{10} daily mean concentrations were registered in winter in all sites, with an average of 45.78 µg m^{-3}, followed by spring

Table VI. Analysis of variance of daily average PM_{10} concentrations (µg m^{-3}).

SV	DF	MS	F-test	P-value
Seasons*Week*Site	15	0.0139	0.205	0.9995
Seasons*Week	3	0.1044	1.538	0.2036
Seasons*Site	15	0.2538	3.739	0.0000**
Week*Site	5	0.0480	0.707	0.6183
Seasons	3	11.5036	169.481	0.0000**
Week	1	2.9518	43.488	0.0000**
Site	5	10.6806	157.355	0.0000**
Error	528	0.0679		
Total	575			
CV (%)	7.65			
Overall mean	3.4059	Number of data:	576	

*Interaction between variation factors; **significant values by the F-test ($\alpha = 0.05$). SV: sources of variation; Seasons: seasons of the year; Week: day of the week; Sites: monitoring stations; DF: degrees of freedom; MS: mean square; F-test: F-test value, given by the MS ratios; CV: coefficient of variation, given by equation CV= $\pm 100 \times \sigma$/mean; P: probability value of the F-test.

Table VII. Comparison of means for average PM_{10} concentrations (µg m^{-3}) considering the interaction between the monitoring stations (six levels) and seasons (four levels).

Monitoring stations	Seasons			
	Summer	Autumn	Winter	Spring
Alterosa	28.67 Da	44.99 Cc	62.41 Cd	37.15 Bb
Cascata	16.16 Ba	20.94 Ab	29.08 Ac	26.78 Ac
Ibiritermo	13.28 Aa	19.53 Ab	28.20 Ac	22.29 Ab
Petrovale	21.51 Ca	30.47 Bb	43.22 Bc	35.25 Bb
Rui Barbosa	25.91 CDa	30.22 Bab	37.40 Bc	35.05 Bbc
Safran	29.86 Da	48.18 Cb	74.35 Cc	51.00 Cb

Different uppercase letters in the column (monitoring stations) and different lowercase letters in the row (seasons) differ from each other by the Tukey test at 5% probability. Letters A to D and a to d were set in ascending order of particulate matter concentrations.

(34.59 µg m^{-3}), autumn (32.39 µg m^{-3}), and summer (22.56 µg m^{-3}). Similar results were found in several regions in Brazil, such as São Paulo and Rio de Janeiro (Castanho and Artaxo, 2001; Miranda et al., 2002, 2011; Carvalho et al., 2015; Santos et al., 2016).

Additionally, it was possible to verify, using Tukey's test, that the highest mean PM_{10} concentrations recorded during winter (Table VII) deffered from the other seasons in all monitoring stations, except for Cascata and Rui Barbosa, with no significant differences between winter and spring. Unfavorable atmospheric conditions of dispersion justify the pattern of occurrence of higher PM_{10} concentrations during winter and early spring, when the SASH position is closest to the continent (Santos et al., 2016), reducing cloudiness and precipitation in the MABH. Besides, the low wind speed also impairs the dispersion of pollutants during winter.

The highest mean value of PM_{10} concentrations was observed for Safran (50.85 µg m^{-3}), followed by

Alterosa (43.30 µg m^{-3}), Petrovale (32.61 µg m^{-3}), Rui Barbosa (32.14 µg m^{-3}), Cascata (23.24 µg m^{-3}), and Ibiritermo (20.82 µg m^{-3}) (Table VIII). These results corroborate those reported by the atmospheric emissions inventory for RMBH in 2003 (FEAM, 2003) since the highest concentrations of PM_{10} are observed in the vicinity of the Alterosa and Safran stations.

Table VIII. Comparison of means for average PM_{10} concentrations (µg m^{-3}) considering as source of variation the Monitoring Stations

Monitoring Stations	Concentrations
Alterosa	43.30 D
Cascata	23.24 B
Ibiritermo	20.82 A
Petrovale	32.61 C
Rui Barbosa	32.14 C
Safran	50.85 E

Different uppercase letters in the column (monitoring stations) differ by the Tukey test at 5% probability. Letters A to E were set in ascending order of particulate matter concentrations.

The sites Safran, Alterosa, and Rui Barbosa are influenced by the heavy vehicles traffic, which increases PM_{10} concentrations due to emissions and to road dust resuspension, which is an important PM_{10} source (Pant and Harrison, 2013). In addition to the local impact of vehicular emissions on air quality, atmospheric pollutants can also be transported to other regions, impacting areas without heavy traffic (Santos et al., 2016). Tavares et al. (2010) attributed the poor air quality in the central area of the MABH to traffic of diesel-powered vehicles (mainly buses) as the main PM emission source. The intense industrial activity related to the steel sector, namely, non-metallic minerals (cement and lime), oil, and the automobile industry in the vicinity of the MABH, was also identified as one of the main sources affecting PM_{10} concentrations (Brum, 2010). Through elemental composition analysis of PM_{10}, Moura (2016) also noted that mining activity at various locations of the MABH has a negative impact on the region's air quality.

Significant differences on PM_{10} concentrations through weekdays and weekends were also shown. The highest concentration of PM_{10} was observed during weekdays (35.77 µg m^{-3}) and the lowest in weekends (31.89 µg m^{-3}), with an average percentage reduction of 11% at the latter. Lower concentrations of PM_{10} at weekends were also found in the MASP (Carvalho et al., 2015) and Southern California (Qin et al., 2004), where average reductions of 15 and 14% were observed, respectively, regarding weekdays. In general, during weekdays (Monday to Friday), there is a greater flow of vehicles in large urban centers, which explains the higher concentrations of PM_{10}. According to the official local emissions inventory, this result is expected, since the largest source of PM_{10} in Belo Horizonte are vehicles (71%).

It is important to point out that the absence of valid data at several points in the data series and limited access to data undermine the available information regarding air quality in the MABH. Thus, we identified the importance of future improvements in the current air quality monitoring network of the MABH, including VOCs sampling, which is vital for the O_3 formation process. Also, it is necessary to perform regular maintenance of the existing monitoring network, besides its expansion, since the current stations are mainly located in traffic corridors and industrial areas, covering a small and unrepresentative number of municipalities of the MABH. Resizing the monitoring network, including the installation of stations in areas exposed to different types of emission, would also be important for a better diagnosis of air quality in the state of Minas Gerais.

4. Conclusions

The application of the ANOVA technique to data of daily maximum concentrations of O_3 and daily mean concentrations of PM_{10} registered between 2007 and 2012 in six monitoring stations of the MABH, was efficient to identify patterns associated to the variability of both pollutants' concentrations. It was possible to verify significant differences in the behavior pattern of the pollutants between the considered sources of variation (seasons, day of week, and monitoring stations). The O_3 concentration pattern was higher in the spring in all monitoring stations, while the PM_{10} concentration was higher during winter. There was a higher concentration of PM_{10} during weekdays when compared to weekends. Regarding O_3, the day of the week effect was identified only in the Rui Barbosa station, which is predominantly influenced by vehicle emissions. The other stations are located in industrial plants and showed no significant differences between the concentrations observed on working days and weekends. This shows that the vehicle emissions profile, which decreases during weekends, plays an important role in the weekend effect pattern associated O_3 concentrations in the MABH.

Acknowledgments

To the Coordination of Improvement of Higher Education Personnel – CAPES (process number 1577748) for financial support and FEAM for the data, which allowed this study to be performed.

References

Aenab AM, Singh SK, Lafta AJ. 2013. Critical assessment of air pollution by ANOVA test and human health effects. Atmospheric Environment 71: 84-91. https://doi.org/10.1016/j.atmosenv.2013.01.039

Alvim DS. 2013. Estudo dos principais precursores de ozônio na Região Metropolitana de São Paulo. Ph.D. thesis. Instituto de Pesquisas Energéticas e Nucleares, Universidade de São Paulo.

Brönnimann S, Neu U. 1997. Weekend-weekday differences of near surface ozone concentrations in Switzerland for different meteorological conditions. Atmospheric Environment 31: 1127-1135. https://doi.org/10.1016/S1352-2310(96)00311-1

Brum DR. 2010. Estudo da composição química do material particulado fino ($MP_{2,5}$) em Porto Alegre e Belo Horizonte. M.Sc. thesis. Universidade de São Paulo, Brazil.

Carvalho VSB. 2006. Metodologia da qualidade do ar no que tange as concentrações de Ozônio e dos Óxidos de Nitrogênio na Região Metropolitana do Rio de Janeiro**.** M.Sc. thesis. Universidade Federal do Rio de Janeiro, Brazil.

Carvalho VSB. 2010. O impacto das megacidades na qualidade do ar em escala local e regional: os casos das Regiões Metropolitanas de São Paulo e do Rio de Janeiro. São Paulo, 2010. Ph.D. thesis. Universidade de São Paulo, Brazil.

Carvalho VSB, Freitas ED, Mazzoli CR, Andrade MF. 2012. Avaliação da influência de condições meteorológicas na ocorrência e manutenção de um episódio prolongado com altas concentrações de ozônio sobre a Região Metropolitana de São Paulo. Revista Brasileira de Meteorologia 27: 463-474. https://doi.org/10.1590/S0102-77862012000400009

Carvalho VSB, Freitas ED, Martins LD, Martins JA, Mazzoli CR, Andrade MF. 2015. Air quality status and trends over the Metropolitan Area of São Paulo, Brazil as a result of emission control policies. Environmental Science and Policy 47: 68-79. https://doi.org/10.1016/j.envsci.2014.11.001

Carvalho VSB, Martins FB, Silveira WW, Campos B, Simões JB. 2020. Variance analysis applied to ground-level ozone concentrations in the state of São Paulo, Brazil. Brazilian Journal of Chemical Engineering 37: 505-513. https://doi.org/10.1007/s43153-020-00045-7

Castanho ADA, Artaxo P. 2001. Wintertime and summertime São Paulo aerosol source apportionment study. Atmospheric Environment 35: 4889-4902. https://doi.org/10.1016/S1352-2310(01)00357-0

CONAMA. (2018). Resolução CONAMA 491 de 19 de novembro. Ministério do Meio Ambiente/Conselho Nacional do Meio Ambiente, Brasília. Available at: https://www.in.gov.br/web/guest/materia/-/asset_publisher/Kujrw0TZC2Mb/content/id/51058895/do1-2018-11-21-resolucao-n-491-de-19-de-novembro-de-2018-51058603 (accessed on September 22, 2022).

DENATRAN. 2017. Frota de veículos 2017. Departamento Nacional de Trânsito, Brazil. Available at: http://www.denatran.gov.br/estatistica/610-frota-2017 (accessed on February 22, 2018).

Fang GC, Lo CT, Zhuang YJ, Cho MH, Huang CY, Xiao YF, Tsai KH. 2017. Seasonal variations and sources study by way of back trajectories and ANOVA for ambient air pollutants (particulates and metallic elements) within a mixed area at Longjing, central Taiwan: 1-year observation. Environmental Geochemistry and Health 39: 99-108. https://doi.org/10.1007/s10653-016-9810-8

Ferreira DF. 2011. Sisvar: A computer statistical analysis system. Ciência e Agrotecnologia. Lavras 35: 1039-1042. https://doi.org/10.1590/s1413-70542011000600001

FEAM. 2003. Inventário de Fontes Emissoras de Poluentes Atmosféricos. Estudos de Dispersão Atmosférica e

Projeto de Rede Otimizada para a Região Metropolitana de Belo Horizonte/2003. Fundação Estadual do Meio Ambiente. Available at: http://www.feam.br/qualidade-do-ar/relatorios-artigos-e-publicacoes (accessed on: October 1, 2020).

FEAM. 2016. Relatório Anual de Qualidade do Ar – Ano Base 2015. Fundação Estadual do Meio Ambiente. Available at: http://www.feam.br/qualidade-do-ar/relatorios-artigos-e-publicacoes (accessed on October 1, 2020).

Gouveia N, Leon AP, Junger W, Lins JF, Freitas CU. 2019. Poluição do ar e impactos na saúde na Região Metropolitana de Belo Horizonte – Minas Gerais, Brasil. Ciência & Saúde Coletiva 24: 3773-3781. https://doi.org/10.1590/1413-812320182410.29432017

Govender P, Sivakumar V. 2020. Application of k-mean and hierarchical clustering techniques for analysis of air pollution: A review (1980-2019). Atmospheric Pollution Research 11: 40-56. https://doi.org/10.1016/j.apr.2019.09.009

Huryn SM, Gough WA. 2014. Impact of urbanization on the ozone weekday/weekend effect in Southern Ontario, Canada. Urban Climate 8: 11-20. https://doi.org/10.1016/j.uclim.2014.03.005

Im U, Incecik S, Guler M, Tek A, Topcu S, Unal YS, Yenigun O, Kindap T, Odman MT, Tayanc M. 2013. Analysis of surface ozone and nitrogen oxides at urban, semi-rural and rural sites in Istambul, Turkey. Science of the Total Environment 443: 920-931. https://doi.org/10.1016/j.scitotenv.2012.11.048

IBGE. 2018. População. Instituto Brasileiro de Geografia e Estatística. Available at: http://www.ibge.gov.br/home/estatistica/populacao (accessed on July 18, 2018).

Mansouri B, Hoshyari E, Mansouri A. 2011. Study on ambient concentrations of air quality parameters (O_3, SO_2, CO and PM_{10}) in different months in Shiraz city, Iran. International Journal of Environmental Sciences 1: 1440-1447. https://doi.org/10.6088/ijessi.00107020005

Mendes LMMC. 2018. Diagnóstico da qualidade do ar na Região Metropolitana de Belo Horizonte, MG. M.Sc. tesis. Universidade Federal de Itajubá, Brazil.

Miranda RM, Andrade MF, Worobiec A, Van Grieken R. 2002. Characterization of aerosol particles in São Paulo Metropolitan area. Atmospheric Environment 36: 345-352. https://doi.org/10.1016/S1352-2310(01)00363-6

Miranda RM, Andrade MF, Fornaro A, Astolfo R, Andre PA, Saldiva P. 2011. Urban air pollution: A representative survey of $PM_{2,5}$ mass concentrations in six Brazilian cities. Air Quality, Atmosphere & Health 5: 63-77. https://doi.org/10.1007/s11869-010-0124-1

Mohamad ND, Ash'aari H, Othman M. 2015. Preliminary assessment of air pollutant sources identification at selected monitoring stations in Klang Valley, Malaysia. Procedia Environmental Sciences 30: 121-126. https://doi.org/10.1016/j.proenv.2015.10.021

Moura IFS. 2016. Avaliação de MP_{10} na Região Metropolitana de Belo Horizonte. M.Sc. thesis, Universidade Federal de Minas Gerais, Brazil.

Pacheco MT, Parmigiani MMM, Andrade MF, Kumar P. 2017. A review of emissions and concentrations of particulate matter in the three major Metropolitan Areas of Brazil. Journal of Transport and Health 4: 53-72. https://doi.org/10.1016/j.jth.2017.01.008

Pant P, Harrison RM. 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. Atmospheric Environment 77: 78-97. https://doi.org/10.1016/j.atmosenv.2013.04.028

Peláez LM, Santos JM, Albuquerque TTA, Reis Jr NC, Andreão WL, Andrade MF. 2020. Air quality status and trends over large cities in South America. Environmental Science & Policy 114: 422-435. https://doi.org/10.1016/j.envsci.2020.09.009

Pont V, Fontan J. 2001. Comparison between weekend and weekday ozone concentration in large cities in France. Atmospheric Environment 35: 1527-1535. https://doi.org/10.1016/S1352-2310(00)00308-3

Prudente CN, Raia A, Reis RJ. 2006. Comportamento do Vento na Região Metropolitana de Belo Horizonte. In: Anais do XIV Congresso Brasileiro de Meteorologia, Florianópolis.

Qin Y, Tonnesen GS, Wang Z. 2004. Weekend/weekday differences of ozone, NO_x, CO, VOCs, PM_{10} and the light scatter during ozone season in southern California. Atmospheric Environment 38: 3069-3087. https://doi.org/10.1016/j.atmosenv.2004.01.035

Radicchi ALA. 2012. A poluição na bacia aérea da região metropolitana de Belo Horizonte e sua repercussão na saúde da população. Revista Brasileira de Estudos de População 29: 195-198. https://doi.org/10.1590/S0102-30982012000100013

Sanchez-Ccoyllo OR, Andrade MF. 2002. The influence of meteorological conditions on the behavior of pollutants concentrations in São Paulo, Brazil. Environmental Pollution 116: 257-263. https://doi.org/10.1016/S0269-7491(01)00129-4

Santos TC, Carvalho VSB, Reboita MS. 2016. Avaliação da influência das condições meteorológicas em dias com altas concentrações de material particulado na Região Metropolitana do Rio de Janeiro. Engenharia Sanitária e Ambiental 21: 307-313. https://doi.org/10.1590/s1413-41522016139269

Santos TC, Reboita MS, Carvalho VSB. 2018. Investigação da Relação entre Variáveis Atmosféricas e a Concentração de MP_{10} e O_3 no Estado de São Paulo. Revista Brasileira de Meteorologia 33: 631-645, 2018. https://doi.org/10.1590/0102-7786334006

Santos FS, Pinto JA, Maciel FM, Horta FS, Albuquerque TTA, Andrade MF. 2019. Avaliação da influência das condições meteorológicas na concentração de material particulado fino ($MP_{2,5}$) em Belo Horizonte, MG. Engenharia Sanitaria e Ambiental 24: 371-381. https://doi.org/10.1590/s1413-41522019174045

Silva Júnior RS, Oliveira MGL, Andrade MF. 2009. Weekend/weekday differences in concentrations of ozone, NOx and non-methane hydrocarbon in the Metropolitan Area of São Paulo. Revista Brasileira de Meteorologia 24: 100-110. https://doi.org/10.1590/S0102-77862009000100010

Sicard P, Paoletti E, Agathokleous E, Araminienė V, Proietti C, Coulibaly F, De Marco A. 2020. Ozone weekend effect in cities: Deep insights for urban air pollution control. Environmental Research 191: 110193. https://doi.org/10.1016/j.envres.2020.110193.

Sicard P. 2021. Ground-level ozone over time: An observation-based global overview. Current Opinion in Environmental Science & Health 19: 100226. https://doi.org/10.1016/j.coesh.2020.100226

Storck L, Lopes SJ, Estefanel V, Garcia DC. 2011. Experimentação vegetal. 3rd ed. Editora da Universidade Federal de Santa Maria, Rio Grande do Sul, Brazil.

Tavares FVF, Barreto AA, Dutra EG, Jacomino VMF. 2010. Estudo do processo de dispersão de emissões veiculares em uma microrregião de Belo Horizonte (MG) utilizando simulação numérica. Engenharia Sanitária e Ambiental 15: 315-324. https://doi.org/10.1590/S1413-41522010000400004

Tyubee BT, Yiyeh GH, Onah MA. 2020. Assessment of air pollution in Gboko, Benue State, Nigeria. Urban Studies and Public Administration 3: 38-58. https://doi.org/10.22158/uspa.v3n4p38

Wolff GT, Kahlbaum DF, Heuss JM. 2013. The vanishing ozone weekday/weekend effect. Journal of the Air Waste Management Association 63: 292-299. https://doi.org/10.1080/10962247.2012.749312

WHO. 2006. Air quality guidelines. Global update 2005: Particulate matter, ozone, nitrogen dioxide, and sulfur dioxide. World Health Organization, Geneva. Available at: https://apps.who.int/iris/handle/10665/69477 (accessed on September 9, 2021).