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Article

Variations of Carbon Monoxide Concentrations in the Megacity of São Paulo from 2000 to 2015 in Different Time Scales

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Abstract: Air pollution is an important public health issue. High levels of carbon monoxide in the atmosphere are hazardous to human health. Studies regarding the concentration of this and other gases in the atmosphere allow political actions to manage and reduce the emission of pollutants. In this context, this paper studied the annual, seasonal and daily variations of carbon monoxide (CO) concentration for the Metropolitan Region of São Paulo (MRSP). We studied three sites in the MRSP, chosen due to the longer time series and the localities. Two of them are located in areas under the influence of heavy vehicle traffic (Osasco and Congonhas) and the third one in a city park (Ibirapuera Park). The results showed high influence of gasoline vehicles on CO emission. In the annual scale, instead of following the increasing number of vehicles, CO emission and concentration decreased due to improvements in emission technology. CO emission showed a seasonal, weekly and diurnal cycle. The highest values of mean concentration were observed in June/July for Osasco (2.20 ppm), Congonhas (2.04 ppm) and Ibirapuera (1.04 ppm), during the morning, due to weak dispersion of the polluting gases.

Keywords: carbon monoxide; diurnal cycle; seasonal cycle; urban pollution; pollution trends

1. Introduction

Urban atmospheric pollution has increased due to an increment in automobiles and industrial emissions, which worsen air quality and promote hazardous conditions for people, plants and animal life. The Metropolitan Region of São Paulo (MRSP), with 21 million of habitants and 39 cities, including the capital São Paulo with 11 million of habitants, is the sixth largest human conglomeration in the word [1]. According to the Environmental Agency of the State of São Paulo, about 97% of Carbon Monoxide (CO) concentrations are originated by vehicle emissions [2].

CO is a colorless, tasteless and odorless gas, flammable and dangerous to human health due to its toxicity and for promoting chemical asphyxiation. The main CO sources are combustion processes related to energy, warming, vehicle transport, biomass burning and the oxidation of methane and volatile organic compounds (VOCs). CO is produced by chemical reactions in the atmosphere between the hydroxyl radical (OH) and methane (CH_4) and other hydrocarbons, besides reactions between alkenes and ozone (O_3), and reactions from isoprene and terpenes with OH and O_3 [3,4]. The major sink of CO is its reaction with OH, while dry deposition and stratospheric flux

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are considered minor sinks [5,6,7,8]. At the troposphere, the hydroxyl free radical (OH) oxidizes carbon monoxide (CO) producing hydroperoxide radicals (HO_2) [9]:

$$CO + OH \rightarrow CO_2 + H \quad \text{(R1)}$$

$$H + O_2 + M \rightarrow HO_2 + M \quad \text{(R2)}$$

According to [10], excess NOx (NOx = NO + NO_2), as in the Megacity of São Paulo atmosphere with a NO mixing ratio higher than 10 pptv, promote O_3 production following reactions R1 and R2. Otherwise, O_3 is destroyed by hydroperoxylate radical. However, any chain reaction dissipates CO, producing carbon dioxide. R1 is a fast reaction, independent of temperature [11]. It implies a CO global lifetime of two months and is the most significant OH sink in the troposphere [12,10,13,14]. In the atmosphere, the main CO source is the methane oxidation by OH, which produces formaldehyde (CH_2O) and then carbon monoxide. This reaction, together with the R1 reaction, consume most of the OH in the troposphere. For this reason, CO and CH_4 tropospheric concentrations are very important indicators of the tropospheric oxidizing capacity, represented specifically by ozone and hydroxyl radical concentrations. CO is not considered a greenhouse gas because it does not have the capacity to absorb infrared radiation. The atmospheric CO balance shows the destruction of methane and the production of CO_2, O_3 and sulfate aerosols, which might affect the climate. These reactions modify the balance CO-CH_4, affecting water and temperature [15]. The bi-directional interaction between chemistry and the climate over CO is evident. The main CO sources are anthropogenic, such as fuel burning, heat systems, thermoelectric plants and biomass burning. Its natural sources are volcanic activity, electrical discharge and natural gas emissions. From the industrial revolution to 1980 decade, global CO concentration presented a marked increase; however, since 1980, this concentration has decreased [16,17], probably due the use of catalytic converters in cars [8]. Studies suggest that a decrease on global CO concentration would increase the OH radical, and consequently, the sink rate of CH_4. This would modify the oxidizing capacity of the troposphere [18,12,19,10,20]. As a policy measure to reduce the atmospheric loading of CH_4, a 50% reduction in the industrial emissions to 250 Tg-CO yr^{-1} would cause an increase by about 3.5% in OH concentrations leading to enhanced photochemical loss of CH_4. The photochemical production of CO, although quite uncertain, may account for 40–50% of the total CO source. According to three-dimensional global model calculations, CH_4 oxidation produces 700 Tg-CO yr^{-1}. Photochemical production of CO from the oxidation of naturally emitted NMHC is calculated to be equal to about 450 Tg-CO yr^{-1}, close to one third of the total photochemical source of CO. Anthropogenic NMHC oxidation forms 110 Tg-CO yr^{-1} [21].

High CO concentration is considered very toxic to humans because it can cause acute intoxication, leaving sequels or promote death by asphyxiation. The interaction of hemoglobin with CO is 240 times greater than with oxygen (O_2), so, carboxyhemoglobin is formed instead of oxyhemoglobin [22]. When the atmosphere is rich in CO, O_2 has difficulty to reach the tissue, causing death by suffocation. It was demonstrated statistically that maternal exposure to air pollution in the first trimester of gestation may contribute to lower fetal weight gain. Although it is difficult to isolate the influence of each pollutant, it was possible to show the greater influence of CO on newborn weight. Due to these and other factors, the monitoring and prevention of this gas is extremely important [23].

In the MRSP, mobile and stationary sources were responsible for the emission of about 165 thousand tons $year^{-1}$ of CO to the atmosphere, but 97% from this total are emitted by vehicles. Light-duty vehicles are the main CO source, from which gasoline vehicles respond for 44% of emissions. Even though there are less gasoline vehicles than flex ones, gasoline vehicles emit more CO because they are older. The motorcycles are significant sources due to their more polluting engine and increasing number in the MRSP [2].

Since 2008, the air quality standard of 8 hours for carbon monoxide (9 ppm) has not been exceeded in any of the stations of the Megacity of São Paulo. Current concentrations, despite the increase of personal vehicles, are lower than those observed in the 1990s. This fact is mainly due to the decrease in new light-duty vehicles emissions, in compliance with the increasingly strict limits of the Air Pollution Control Program for Light-Duty Vehicles (PROCONVE, original acronym) and the Program for the Control of Air Pollution by Motorcycles and Similar Vehicles (PROMOT, original

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acronym), associated with the renewal of existing vehicles. The decrease in emissions was more intense in the 1990's. Lately it has been less intense and tends to stabilize [2].

This paper addresses the temporal variability of CO concentrations monitored in three sites located in the in the Megacity of São Paulo (Osasco, Congonhas and Ibirapuera), considering its time series in terms of the annual, monthly, weekly and diurnal cycle. The results of this work can contribute to the definition of public policies to promote improvements in environmental management and public health in cities in general.

2. Data and Method

The MRSP was chosen due to its economic importance, as well as the high vehicular and industrial pollution rates. There are 27 automatic air quality-monitoring stations, and we analyzed the three stations with the most complete time series. Two (Osasco and Congonhas) are located close to the regions with intense vehicle traffic, while the third (Ibirapuera) is inside a city park.

2.1 Characterization of monitoring stations

Osasco station (Figure 1a) is in the western portion of the MRSP, in a residential, commercial and industrial area. This station is located approximately 20 meters from Autonomistas Avenue, and 45 meters from Visconde de Nova Granada Avenue. Both avenues have intense traffic of light and heavy-duty vehicles. So, this station is directly influenced by vehicular emissions.

Congonhas station is located in the south of MRSP, in a commercial and residential area (Figure 1b). This station is approximately 6 meters from Avenida dos Bandeirantes and 400 meters from Congonhas National Airport. It is also strongly affected by heavy-duty vehicle traffic.

Also located in the south of the MRSP, and approximately 3000 meters from the Congonhas station, Ibirapuera station is located (Figure 1c) in a city park surrounded by urbanized areas where the predominant characteristics are residential. This station is approximately 500 meters from the Republica do Líbano Avenue and 750 meters from Ibirapuera Avenue, so it is not directly influenced by these sources. More information can be found in Table 1.

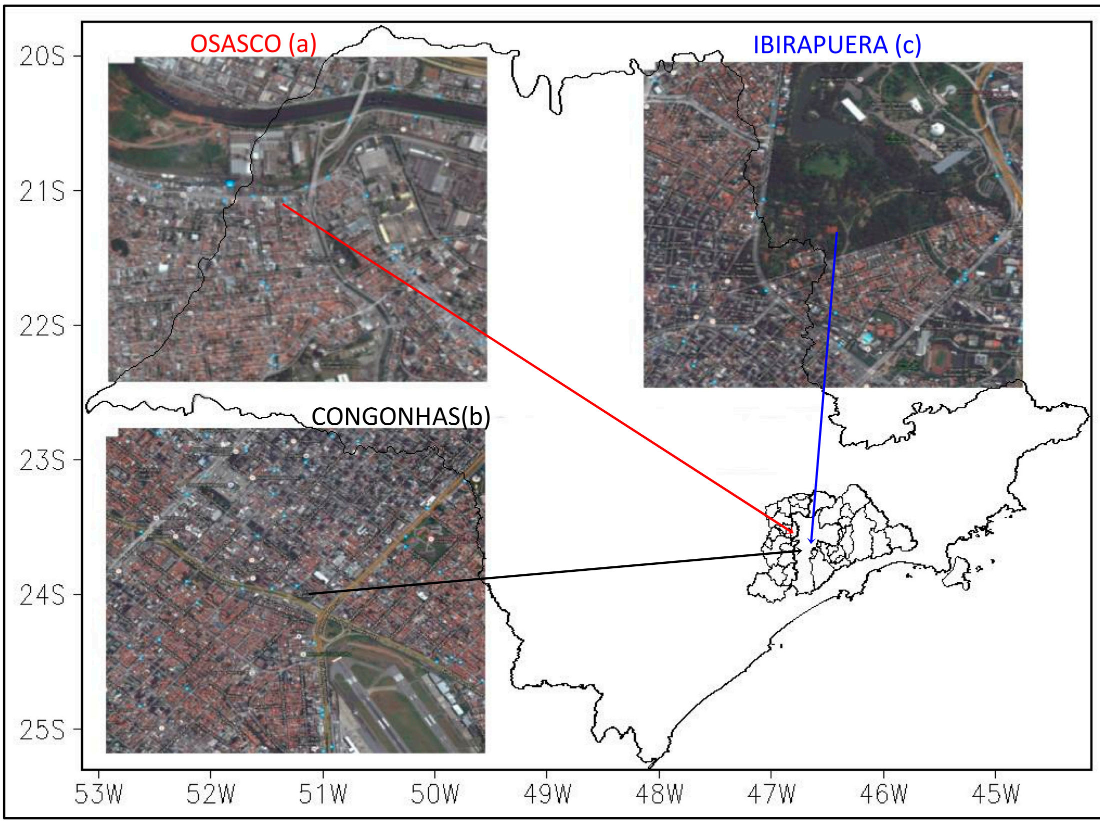

Figure 1. Location of the automatic air quality monitoring stations of this study.

Table 1. Additional information about the stations.

Station	Latitude (South)	Longitude (West)	Altitude (m)
Osasco	23º 31' 35"	46º 47' 31"	740
Congonhas	23º 36' 29"	46º 39' 37"	760
Ibirapuera	23º 34' 55"	46º 39' 25"	750

2.2 Data

In this study, 16 years of air quality data were used, from January 2000 to December 2015. The samples were averages of hourly frequency. Information on CO concentrations, in part per million (ppm), was obtained from the database of the São Paulo State Environmental Agency (CETESB), in the Air Quality Monitoring department (ar.cetesb.sp. Gov.br/qualar/). CETESB obtains the concentrations of this pollutant using an automatic monitoring network connected to a central computer through the telemetry system. Information, recorded on an uninterrupted basis, is processed based on the average established by legal standards and are made available every hour. At 5 o'clock in the morning (local time) there is an automatic calibration of the equipment, so there are no measurements for CO at this hour.

The method used to measure CO concentration is the non-dispersive infrared. It consists of the absorption of radiation by CO. The interaction of this gas with the incident radiation emits energy in the infrared region, so these interactions are detected electronically, amplified and, consequently, quantified.

The results are in simple average terms according to Equation (1). The analysis of the collected data was performed in terms of annual, monthly, weekly and diurnal cycles.

$$M = \sum_{i=ti}^{i=tf} \frac{[COi]}{tf} \qquad (1)$$

Where:

M = average;

[CO] = annual, monthly, weekly and diurnal CO concentration;

i = range index;

ti = initial time;

tf = final time.

3. Results and Discussions

3.1 Annual evolution and seasonal, diurnal cycle

The annual time series for Osasco, Congonhas and Ibirapuera Park stations, Figure 2a, were obtained by averaging all CO concentrations for each year. In general, a decrease in CO concentrations is perceived for the three studied localities. Osasco and Congonhas presented marked decreases, mainly in the first five years. For Ibirapuera, the decrease is smoother. The reductions in CO concentration over the years we also observed in other locations such as in Pt Barrow, Alaska; Cape Meares, Oregon; Cape Kumukahi and Mauna Loa Observatory, Hawaii; Cape Matatula, Samoa; Cape Grim, Tasmania; Palmer Station and South Pole, Antarctica [17]. This decrease is now found largely confined to the Northern Hemisphere, where dramatic reductions in fossil fuel emissions have reportedly occurred. In contrast, no significant trend is determined in the Southern Hemisphere between 1991 and 2001. Globally averaged CO exhibits large interannual variability, primarily reflecting year to year changes in emissions from biomass burning [24]. This behavior may be explained by the reduction of emissions from cars (and industrial sources) due to technological upgrades of vehicle emissions, since the number of vehicles in this region has grown considerably during these years (exemplified in appendix A1). The rate of decrease in CO concentration from 2000 to 2015 was about 63.7% for Congonhas; 56.5% Osasco; and 59.5% for

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Ibirapuera. Osasco and Congonhas stations had higher CO concentration because they are located close to very busy avenues, under daily direct influence of emissions from thousands of vehicles. Ibirapuera station had the lowest values in concentration over the years and also showed the lowest variation (except for the last year) because it is located in the middle of a park, and the majority of the concentrations measured are probably associated to advective processes which transport CO from adjacent neighborhoods. In the average for all 16 years, in percentage terms, Osasco presented the high CO concentration: 56% higher than Ibirapuera and 3% higher than of Congonhas.

Figure 2b shows the monthly average of CO concentrations for the three localities studied and the monthly cumulative precipitation. A well-defined seasonal cycle of CO concentration, also verified in many other studies, is clearly observed [25,26,27]. This cycle presents maximum CO concentrations during June, July and August, associated with the lowest precipitation ratios. The lowest CO concentrations occur in November, December, January and February. High precipitation contributes to remove CO from the atmosphere through wet scavenging and convective processes. This pattern is mainly associated with chemical reactions occurring in the troposphere, together with active meteorological conditions. In this context, the seasonal CO cycle is strongly modulated by the seasonal cycle of the hydroxyl (OH) radical present in the troposphere.

According to [28], hydroxyl concentration maximums were observed in the austral summer, which correspond to minimum CO concentration. Background OH is high in summer and low in winter, as a consequence of the solar radiation variation. The presence of OH radicals in the troposphere contribute to the removal of CO and other polluting gases. OH levels are much higher in the boundary layer than in the upper troposphere, and higher in summer than in winter. Thus, CO lifetime is shorter in the boundary layer during the summer than in the winter. These results corroborate with the results obtained in this study. The precipitation and temperature behavior also contribute to the modulation of the CO seasonal cycle.

Concerning the temperature, the months of June/July in the Megacity of São Paulo present generally lower values, when the concentrations of pollutants are higher (except for ozone). In this situation, the atmosphere becomes more favorable for conditions of stability. Critical episodes of air pollution occur during the dry period (except for ozone episodes), under the influence of the subtropical atlantic anticyclone (a high-pressure system) which prevents the cold fronts from reaching the MRSP, limiting their influence to south of the state of Sao Paulo. These synoptic circumstances influence the meteorological conditions in this region, causing a decrease in wind speed (which are usually less than 1,5 m s^{-1}) and many hours of calm winds (wind speed on surface less than 0.5 m s^{-1}), as seen in Figure 3. Clear sky conditions prevail, together with great atmospheric stability and the formation of thermal inversion layers very close to the surface (below 200 m). These conditions are unfavorable for the dispersion of the pollutants emitted in the Megacity of São Paulo. Normally, this situation of atmospheric stagnation is disturbed by the arrival of a new air mass in the region associated with a frontal system, increasing ventilation, instability and, in many cases, causing precipitation. Another peculiarity is that the relative humidity in the dry period reaches values of 15%. During the studied period, August and September presented days of low relative humidity, below 30%, which also presented calm, weak winds and thermal inversion layers at low levels, mainly in winter. This causes great respiratory discomfort to the population [2]. This stability inhibits the dispersion of CO, and consequently increases its concentration.

Emission ratios are higher in summer (especially for hydrocarbons) due to evaporation, and higher in winter (especially CO and HC) due to the incomplete burning of fossil fuels and biofuels from vehicle exhaust. The emission of thermal NOx decreases in lower ambient temperature. All these facts show the influence of meteorological conditions on emissions, and, therefore, the necessity of greater attention from public managers and policymakers to these issues during the winter months.

Figure 2c shows the average diurnal cycle of CO concentration for the three studied sites. The values represent the average for each hour (except at 05 local time) of every day during the studied period. There are two peaks of concentration for Osasco and Congonhas: the first at 8 and 9 hours and the second at 19 and 20 hours for Osasco (2.76 and 2.36 ppm) and Congonhas (1.79 and 2.46 ppm). It is associated to the rush hour when people commute (see Figure 2c). Other studies, such as

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[29], [30] found these same patterns for the CO daily cycle, as did [31] for downtown Sao Paulo. In Ibirapuera Park station, the peaks occur at 9 and 24 hours (0.91 and 1.00 ppm). This station presents the lowest values of concentration and lowest variability. Because the station is inside a park, there is no direct influence from vehicular emission. The CO measured in this station is probably associated to the advection of emission from roads in adjacent regions (see Figure 1).

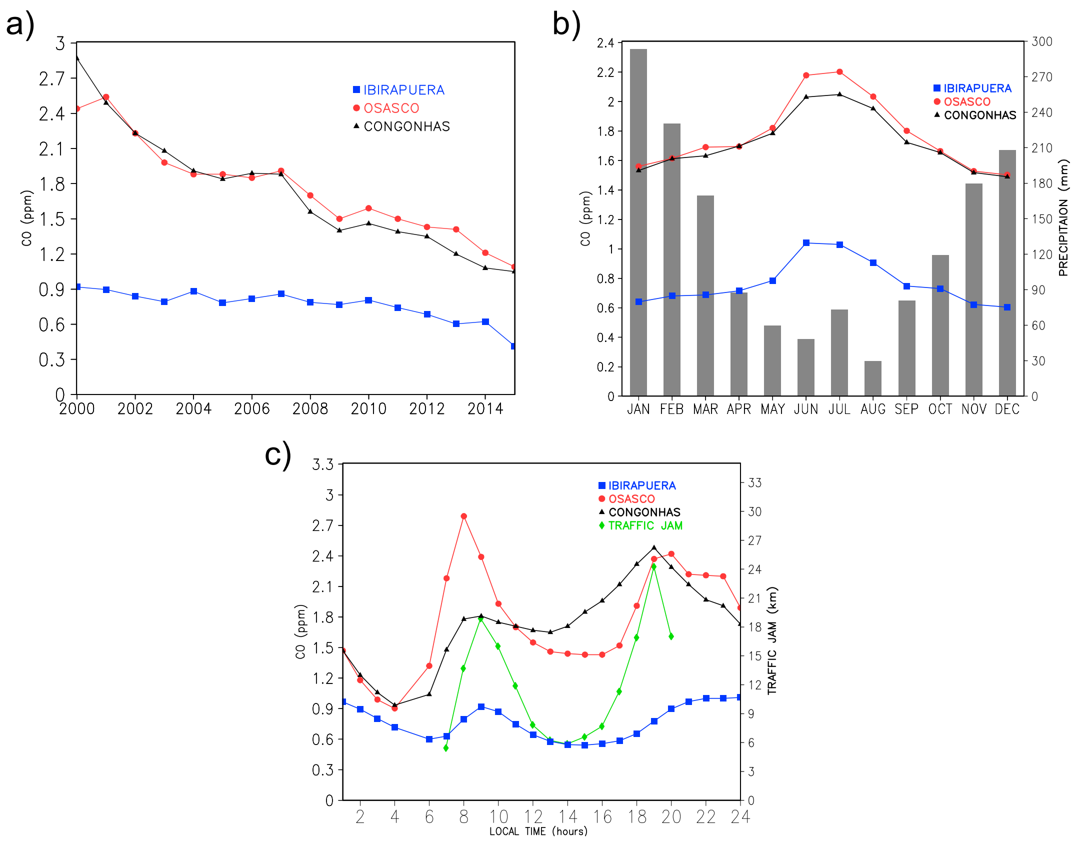

Figure 2. (a) CO concentration time series for annual mean (ppm), (b) monthly CO and cumulative precipitation average and (c) hourly CO averages for monitoring stations Osasco, Congonhas and Ibirapuera Park, and traffic length (km) in São Paulo city measured by the local Traffic Engineering Company - CET (km), for the same period of the CO measurements (2000 to 2015).

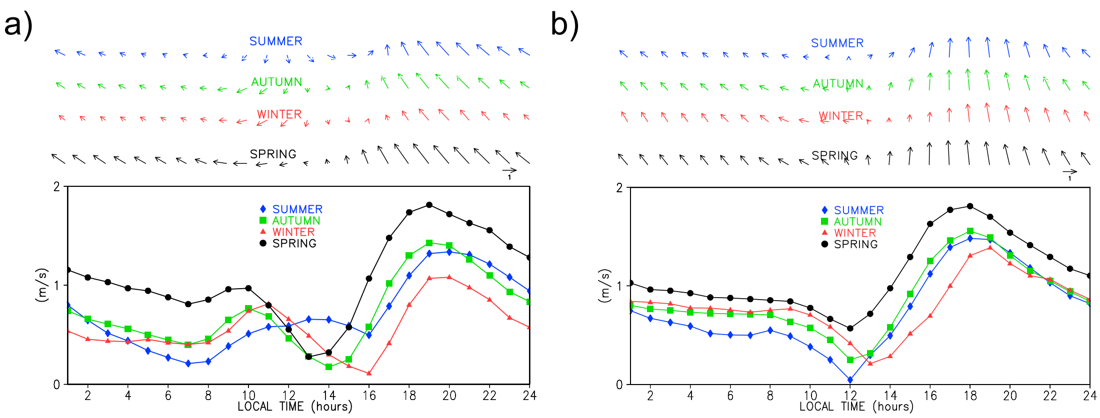

Figure 3. Wind speed (m s^{-1}) at air quality monitoring station (a) Osasco and (b) Ibirapuera CETESB station, from 2000 to 2015 (where the monitoring sites of CO are located).

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During the Olympic Games in Atlanta, USA, series of measurements were implemented in order to reduce urban pollution. During the three weeks of the games, traffic decreased by around 22%. There was a reduction in the daily peak levels of O_3 (28%), NO_2 (7%), CO (19%) and MP_{10} (16%) compared to the three weeks before and after the games. In that period, there was a 40% reduction in asthma consultations in children and a decline of 11-19% in asthma care at all ages in emergency services in the city [32]. At the Beijing Olympics, there was a decrease in $MP_{2.5}$ from 78.8 μg m^{-3} to 46.7 μg m^{-3}, and in O_3 concentrations, from 65.8 ppb to 61 ppb and a decrease of 41.6% in asthma treatment in emergency services [33].

In Munich, Germany, 2,860 children were monitored from their birth up to 4 years of age, and another 3,061, up to 6 years of age, to study the pollution influence on their health. The authors categorized the distance of children's houses to major traffic routes in: less than 50 m, 50-250 m, 250-1,000 m, and > 1,000 m. The study showed significant inverse associations between the distance from the house to the traffic routes. Among those who lived less than 50 m from high traffic routes, the highest ORs for asthma (OR = 1.6, 95% CI: 1.03 2.37), hay fever (OR = 1.6; (95% CI: 1.1-2.3), and allergic sensitization to pollen (OR = 1.4; 95% CI: 1.2-1.6) were found [34].

A Swedish study between 1991 and 2002, in which 2,725 nonsmokers aged 18-60 years were evaluated, showed that those who lived in more polluted areas had a greater risk of developing asthma (about 30% for each increase of 1 μg m^{-3} in MP_{10} concentration emitted by the traffic) [35]. As observed in Figure 2, Ibirapuera station, 500 and 750 meters far from the vehicular traffic routes, has average CO concentrations 56% lower than the Osasco stations, approximately 20 and 45 meters far from main routes, 53% lower than Congonhas, that is located approximately 6 meters from Avenida dos Bandeirantes and 400 meters from Congonhas National Airport. This data emphasizes the importance of monitoring air quality in large urban centers as São Paulo, for decision-making in terms of housing construction and exposure profile of the population in their workplaces and regions where they live. It is important to point out that, in the Megacity of São Paulo studied stations with higher concentrations of pollutants (CO, NOx, SO_2, $PM_{2.5}$), ozone concentrations are lower, and the reverse occurs for stations with higher concentrations of O_3 [2,36]. Considering all 20 air quality monitoring stations in the MRSP, Ibirapuera station has the second highest ozone concentration. As O_3 is a secondary pollutant, the highest ozone concentrations are observed downwind from its precursors (VOC, CO and NO_x) emission sources, sometimes many miles downwind. The most important ozone precursors source in the MRSP are vehicles [37]. In urban and suburban areas, anthropogenic VOC emissions prevail and, in conjunction with anthropogenic NO_x emissions, lead to peak concentrations of ozone observed in urban areas and regions downwind of major cities [3,5,37,38]. Considering the 15 stations that measure CO in the MRSP, Osasco and Congonhas have the fifth and sixth largest CO concentrations, respectively, and the Ibirapuera station, the ninth.

In a prospective study in 12 communities in California with different ozone levels, 3,535 schoolchildren with no previous history of asthma were monitored for 5 years. During the monitoring, 265 children developed asthma. In communities with high ozone concentrations, children who played three or more sports had 3.3 times more risk to develop asthma (95% CI: 1.9-5.8) compared to whose did not play sports. In areas with low concentrations of O_3, the amount of sports practiced did not prove to be a risk factor for the development of asthma. The same behavior was observed for the exposure time in the external environment, which was shown to be a risk factor directly associated with the development of asthma in areas with higher concentration of O_3 [39].

Figure 4 shows the average diurnal cycle for the three sites separated by season. In Osasco (Figure 4a), the highest concentrations were observed during winter at all hours of the diurnal cycle, and the lowest, in summer. During the night and early morning, the differences between the other seasons were more significant. The peak of CO concentration occurs in the morning (8 hours) during autumn, spring and summer, whereas in winter, its magnitude is similar to that of the nocturnal peak (20 hours) (both around 3.2 ppm). Congonhas (Figure 4b) shows higher concentrations in winter during almost the whole cycle, except for the hours between 12 and 17 local time. The differences are most significant during the night and early morning hours. It indicates two peak

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concentrations, the first occurring at 8 hours and the second (with higher values) at 19 hours. For Ibirapuera (Figure 4c) the concentrations referring to summer and spring present similar patterns, but with small differences in magnitude (about 7% during night/early morning and 4% during the day). The most relevant differences occurred in winter, when the concentration is higher during most hours of the day, except between 13 and 17 hours (period in which all seasons have similar values). In general, the highest concentrations occurred during winter, and the lowest in summer, with the most significant differences between the seasons occurring during the night and early morning.

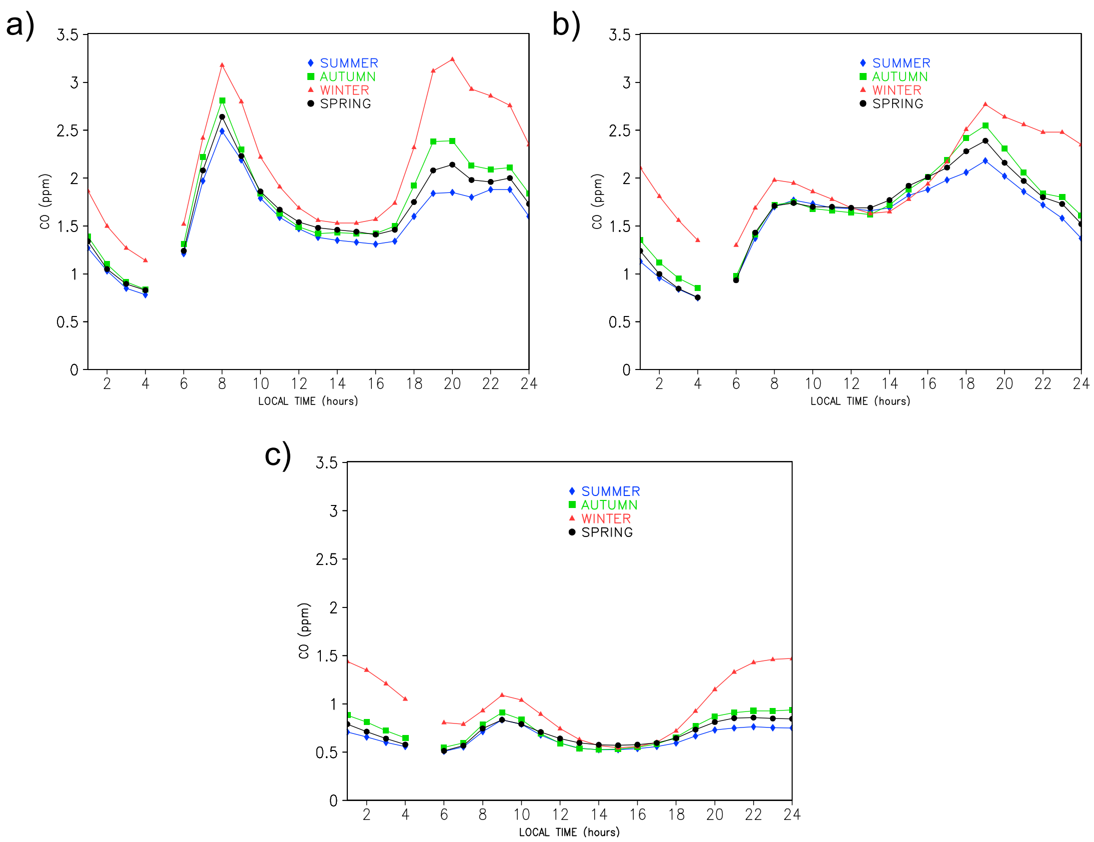

Figure 4. Average diurnal cycle for Osasco (a), Congonhas (b) and Ibirapuera Park (c), separated by seasons (summer, autumn, winter and spring).

Concerning the weekly cycle, Osasco station (Figure 6a) also presented the highest CO concentrations among the analyzed stations. All stations presented similar CO concentrations for weekdays between 6 and 19 hours, except on Friday, due to the greater number of vehicles in the MRSP, which promoted higher concentrations at some hours of the day (see Figure 5). After 20 hours, Friday had higher concentrations comparing to the rest of the week (on average, 20% higher compared to other days of the week between 20 and 24 hours). On Saturdays, there is a decrease in the morning peak, and a displacement of the maximum nocturnal peak. Moreover, between 12 and 15 hours, the concentrations are highest than all other days, associated to an increase in traffic (Figure 5). On Sundays, the highest concentrations occur in the first hours of the day (between 1 and 4 hours), when they are higher than on weekdays, but at other times the concentrations are lower.

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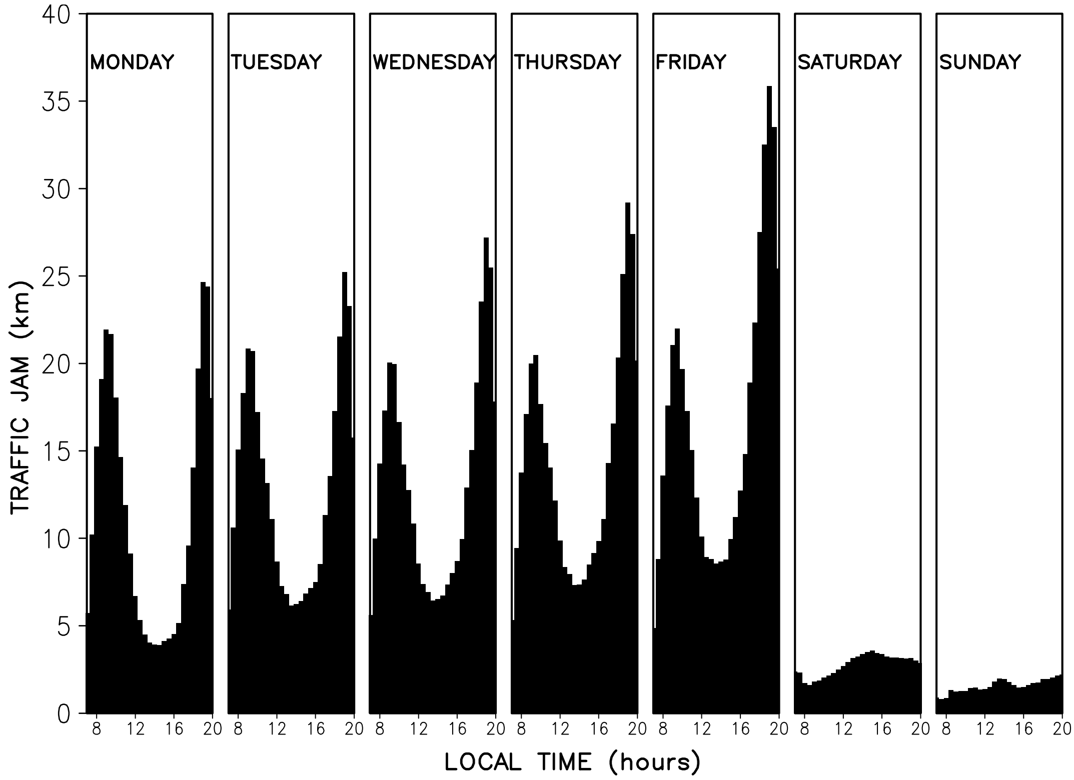

Figure 5. Average hourly traffic jam distribution (km) in São Paulo city measured by CET during weekdays and weekends for the CO sampled regions.

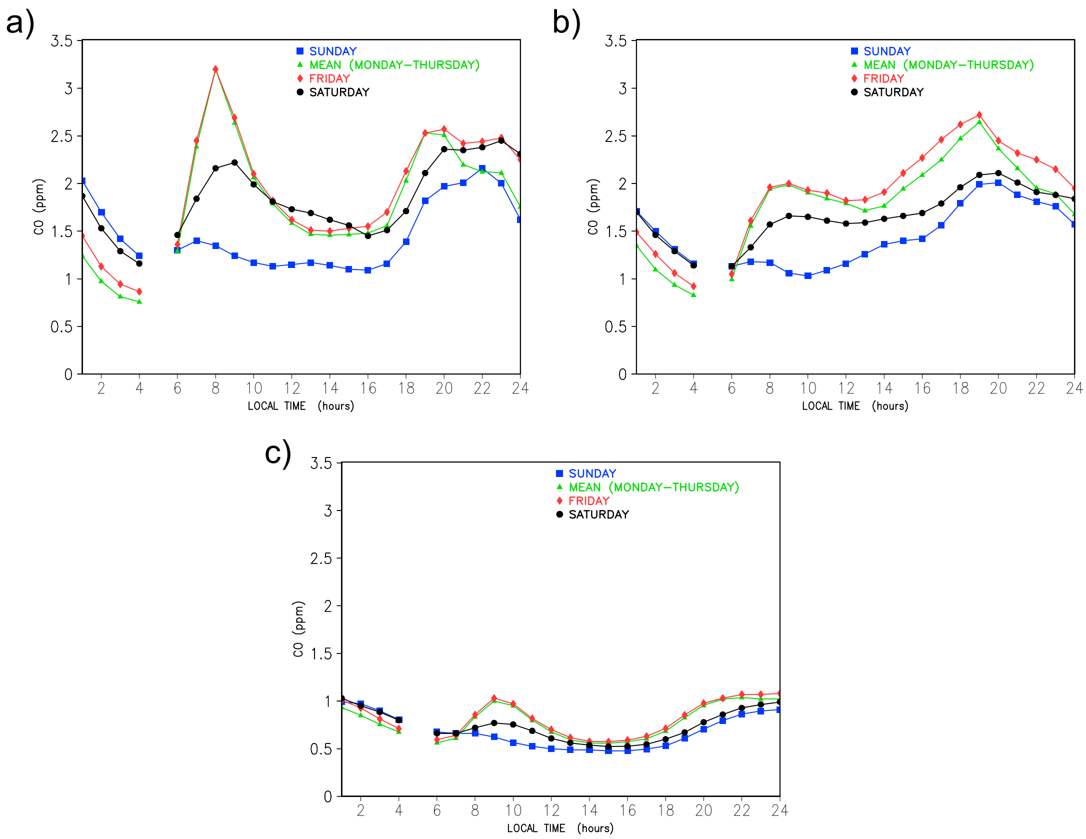

Figure 6. Average diurnal cycle for Osasco (a), Congonhas (b) and Ibirapuera Park (c), separated by day of the week.

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In Congonhas station (Figure 6b), a similar behavior occurs in the diurnal cycle during weekdays, with the peaks of maximum concentration occurring at 9 and 19 hours. Among the weekdays, especially after 12 hours, the lowest values of concentration were measured on Mondays, while the highest, on Friday. In the first six hours of the day, there are similar concentrations on Saturday and Sunday, and higher than the rest of the weekdays. After 7 AM, the behavior changes, i.e., CO concentrations are higher for weekdays and lower on weekends, with lower values attributed to Sundays due to the lesser number of vehicles circulating in the city.

For Ibirapuera Park (Figure 6c), the weekdays presented similar magnitude and behavior in the diurnal cycle. On weekends, there is a slight decrease in CO concentration, especially during rush hours, with the lowest concentrations on Sunday. In general, weekends present higher values of CO concentrations in the first four hours of the day (results similar to those of [30]. This fact is due to the high emissions at the end of the night of the previous days (Friday and Saturday). In the other hours of the cycle, the lowest concentrations are on Sundays, and the highest on Friday due to higher vehicular emission. On Saturday, except for Ibirapuera Park, there was an anomalous behavior between the hours of 12 and 14 hours. During these hours, there is usually a sharp decrease in concentrations (due to increased turbulence in the boundary layer during the afternoon); however, this decrease is not observed in Congonhas station, and in Osasco station, the decrease is less pronounced compared to weekdays. This is due to an increase in the vehicles traveling which is shown in Figure 5. In Congonhas station, this might be related to the busy airport located nearby this monitoring point, which increases local traffic due to the relatively constant flow of passengers over time.

4. Conclusions

The behavior of the annual, seasonal, weekly and daily variations of CO concentration in the Megacity of São Paulo were prospectively studied. Based on the results, we concluded that in terms of annual variations, CO concentrations decreased in all studied sites, in 0.114, 0.086 and 0.034 ppm per year^{-1} for Congonhas, Osasco and Ibirapuera, respectively. This trend in the reduction of CO over the years is attributed mainly to the decrease in vehicle emissions due to new technologies and the implementation of environmental laws which demand that the car manufacturers comply with the standards of emission enforced by public agencies, since the vehicle fleet has increased every year. Similar results were also observed in other studies for other locations [17,40,24]. Among the localities analyzed in this study, Osasco and Congonhas presented the highest levels of CO concentration, however, also indicated the greatest decreases. The high concentration of this pollutant for these two stations is due their location, close to avenues with intense vehicular traffic. Ibirapuera station, because it is located inside a park and more distant from the roads, presented the lowest values of concentrations when compared to the other stations (around 55% considering the average among 16 years).

In terms of seasonal variations, the maximum values of CO concentrations occurred in June and July (winter), while the lowest, in December and January (summer). This behavior is mainly due to meteorological and chemical factors. In terms of weather, the months of December and January (summer) are characterized by high temperature and precipitation ratios that provide unstable atmospheric conditions, promoting the dispersion or removal of CO. In this case, the dispersion is mainly due to the convective and turbulent processes in the boundary layer, while the removal, to the high rainfall ratio. In June and July (winter), higher atmospheric pressure and lower temperatures are associated to more stable atmospheric conditions and less rainfall. A lower planetary boundary layer reduces the convective and turbulent processes, and together with low rainfall rates, hinders CO dispersion. Considering the chemical factors, the reactions of CO oxidation by the hydroxyl radical (OH) play an important role. In the troposphere, the hydroxyl radical concentration (for the southern hemisphere) presents a reversed seasonal cycle when compared to the CO cycle [28] i.e., hydroxyl concentration maximums correspond to the CO concentration minimum [41]. This suggests that the chemical reactions between these compounds also contribute to the modulation of the CO seasonal variation.

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In general, the diurnal cycle of CO concentration presents two peaks, in the morning (between 8 and 9 hours) and in the early evening (between 19 and 20 hours). These maximum concentration values occur due to the heavy traffic of motor vehicles at these hours. Another important factor is the low efficiency (low turbulence) of the planetary boundary layer in dispersing the CO in these two periods of the day. The diurnal cycle analysis, analysed by each day of the week, clearly shows the impact of the vehicular traffic on the diurnal variation of CO concentration. On weekdays, a similar behavior is observed in the CO concentration levels, except after 20 hours. For these times, in most locations, Friday presents the highest CO concentrations. This feature is directly associated with highest traffic congestion according to the traffic engineering company. On Sundays, peaks occurred at night because of the return of vehicular traffic at the end of the weekend. For the first hours of the day (between 1 and 4 hours), weekends present higher values of CO concentration due to the contribution of the previous day's emissions and greater atmospheric stability during the nighttime. The diurnal cycle of CO concentration, analyzed for each season of the year, shows that the amount of CO in the atmosphere is higher during the winter months, followed by autumn and spring, with the lowest concentration observed during summer months

Supplementary Materials: Figure S1: Evolution of vehicle fleet in São Paulo city. Source: São Paulo State Traffic Department (Detran-SP).

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