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## Ambient concentrations and insights on organic and elemental carbon dynamics in São Paulo, Brazil



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### HIGHLIGHTS

- Carbonaceous particles dominate PM<sub>2.5</sub> concentrations in São Paulo.
- Campaign averaged OC:EC ratio for the sampling sites ranged from 0.56 to 1.89.
- Contribution of secondary OC was estimated around 30–40% for all sites.
- The OC3 and OC4 fractions depict a more regional behavior across sampling sites.
- The OC1 fraction is identified to be more dependent of local sources.

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### ABSTRACT

The São Paulo Metropolitan Area (SPMA) is a megacity with about 20 million people and about 8 million vehicles, most of which are fueled with a significant fraction of ethanol - making it a unique case world-wide. This study presents organic and elemental carbon measurements using thermal-optical analysis from quartz filters collected in four sampling sites within the SPMA. Overall Organic Carbon (OC) concentration was comparable at all sites, where Street Canyon had the highest concentration ( $3.37 \mu\text{g m}^{-3}$ ) and Park site the lowest ( $2.65 \mu\text{g m}^{-3}$ ). Elemental Carbon (EC), emitted as result of incomplete combustion, has been significantly higher at the Street Canyon site ( $6.11 \mu\text{g m}^{-3}$ ) in contrast to all other three sites, ranging from  $2.25 \mu\text{g m}^{-3}$  (Downtown) to  $1.50 \mu\text{g m}^{-3}$  (Park). For all sampling sites, the average OC:EC ratio are found on the lower bound ( $<2$ ) of what is usually observed for other megacities, highlighting the significant contribution of EC in Sao Paulo. At the Street Canyon site, average OC:EC ratio was 0.56, to our knowledge the lowest value ever observed for any urban site. An approach for apportionment between primary and secondary organic carbon based on primary OC:EC ratio was evaluated. The secondary OC was estimated to be 30–40% of total OC concentrations throughout the various sampling sites.

The organic carbon dynamics has been further studied using each of the thermally-derived organic carbon fractions. Each of these has been studied regarding their correlation with EC and the correlation between different sites. The analyses have identified that the OC3 and OC4, i.e., the carbon fraction which evolves from the filter at temperatures above  $450^\circ\text{C}$ , presents a regional behavior, with high correlation among all sites. Conversely, OC1, the first fraction to evolve, has depicted a more local characteristic. Furthermore, the fraction of OC which becomes char during the temperature increase under inert atmosphere (the Pyrolytic Carbon-PC) has been the only fraction not to present a significant correlation with EC. Since that EC is assumed to be a primary emission marker, it indicates that PC is not significant in traffic emissions. This study provided innovative insights of the organic aerosol content associated with air pollution dynamics in a megacity impacted by a unique vehicular fleet. It also shows the need of implementation of EURO VI technology and to improve mass transport systems such a metro and more bus corridors to allow better transport for 19 million people in the SPMA.

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## 1. Introduction

Air pollution in megacities threatens human health and significantly contribute to global greenhouse gases emissions (Beirle et al., 2011; Gurjar et al., 2008; Zhu et al., 2012). The São Paulo Metropolitan Area (SPMA) is a megacity located in the southeast of Brazil, with a population of about 19 million inhabitants and a fleet of more than 7 million vehicles (CETESB, 2015). A particularity of SPMA vehicle fleet is the significant amount of ethanol fueling light-duty vehicles, making SPMA a unique case of large-scale biofuel usage worldwide (Brito et al., 2015; Salvo and Geiger, 2014).

The large use of biofuel in Brazil is a direct result of governmental policies. Ethanol was first introduced by the implementation of the National Pro-Alcohol Program (Proalcool) in the early 1980s as an alternative to imported fossil fuel. Over the last 15 years, ethanol use has strongly increased due to the introduction of flex fuel vehicles (FFV), capable of using any proportion of ethanol/gasoline mixtures from 20% ethanol (mixed with gasoline, named gasohol or E20) to pure hydrous ethanol (E100). In 2013, the year of our study, the consumption of ethanol in São Paulo state was higher in volume than gasoline (9100 million m<sup>3</sup> of ethanol and 8000 million m<sup>3</sup> of gasoline). In 2004, a national program was implemented in order to stimulate the production and the use of biofuels, similar to Proalcool, as an alternative to decrease the dependence on imported diesel. Currently, heavy-duty vehicles in Brazil are fueled with 5% biodiesel content, while gasohol contains 23% ethanol mixed in the gasoline. Pure ethanol is also used as fuel, and its share varies with prices of gasoline versus ethanol (Salvo and Geiger, 2014).

Among the most important constituents of urban pollution, particulate matter smaller than 2.5 μm (PM<sub>2.5</sub>) has been associated to both health issues (Pope and Dockery, 2006) and to significantly impact Earth's climate (Forster et al., 2007; Boucher et al., 2013). A significant fraction of the fine aerosol mass has been identified to be composed of carbonaceous material - around 80% in São Paulo during a recent springtime campaign (Almeida et al., 2014). Particulate carbon may be broadly treated as composed by organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC), which is mostly present as carbonate carbon (Karanasiou et al., 2015).

Tunnel measurements within the SPMA (Brito et al., 2013) have identified that the PM<sub>2.5</sub> emissions due to light duty vehicles and heavy duty vehicles are mostly composed of organic matter (42% and 39%) and elemental carbon (17% and 52%), corresponding to a significant fraction of carbonaceous material directly emitted by vehicles. Furthermore, during the past decade several studies around the globe have identified a high importance of secondary organic aerosols to total OC (Hu et al., 2015; Jimenez et al., 2009; Xu et al., 2015). Also, a recent numerical study estimated that about 30% of PM<sub>2.5</sub> in the SPMA is secondarily formed in the atmosphere from gaseous precursors from vehicular origin (Vara-Vela et al., 2015). Despite substantial improvements in the understanding of SOA formation mechanisms, models often do not correctly predict the ambient concentrations of organic aerosol, usually underestimating it (Heald et al., 2005; Spracklen et al., 2011).

To quantitatively determine the concentration of carbonaceous aerosol in ambient air, thermal optical analysis is widely used and is currently considered a reference method (Karanasiou et al., 2015). A well-established thermal optical analysis, the EUSAAR2 protocol (Cavalli et al., 2010), was used to evaluate OC and EC concentrations. Such protocol provides a separation and quantification of OC and EC fractions according to their volatility profile. But it is important to mention that other commonly used protocols such as NIOSH and IMPROVE provides different values for EC and OC and its components (Karanasiou et al., 2015).

The transport system in São Paulo is basically done through buses and automobiles, since the metro extent is very limited. There are approximately 18,000 buses in the SPMA. It is important to emphasize that buses in São Paulo have very basic emission controls. Most of the buses are old Euro III emission standards. This and other studies shows the importance of implementing EURO-6 standard in the large bus fleet, as well as a larger use of hybrids and electrical buses.

The goal of this work is describe the OC and EC levels at the atmosphere of SPMA, as well as individual fractions of OC separated by the EUSAAR2 analytical protocol. Moreover, the sources and processing of organic carbon, including its individual fractions, are studied taking in account its relative changes to EC, and their correlation between different sampling sites.

## 2. Experimental

The sampling campaign took place in São Paulo, Brazil, from September to November 2013, i.e. the austral spring. Average temperature during the campaign was 20.6 ± 3.3 °C with total precipitation of about 360 mm. Aerosols were sampled with 24 h-time resolution on four different sites, identified as Street Canyon, Downtown, Park and University site, shown in Fig. 1 and described in section 3.1.

### 2.1. Sampling sites

The Street Canyon site (23° 36' 58.94" S, 46° 39' 48.33" W, 760 m ASL) is located at the crossing of two heavy traffic avenues (Bandeirantes and 23 de Maio avenues), within the air quality monitoring sampling site Congonhas, from the São Paulo State Environmental Agency (CETESB). The majority of the traffic is composed of light duty vehicles, with a significant contribution of heavy trucks and buses. As the name implies, the sampling site is located in a street canyon, with rather reduced pollutant dispersion.

The Downtown site (23° 33' 12.38" S, 46° 40' 21.74" W, 817 m ASL) is also subject to strong traffic emissions, however with different fleet profile and pollutant dispersion than the Street Canyon site. Vehicular emissions at the site is mostly dominated by cars, as well as some contribution of metropolitan buses (Brito et al., 2015). Sampling was carried out at the rooftop of Public Health Faculty of the University of São Paulo at about 20 m AGL.

The Park site is located in the Ibirapuera park (23° 35' 30.66" S, 46° 39' 38.31" W, 750 m ASL), a green area of over 1.5 km<sup>2</sup> surrounded by a densely urbanized area. Sampling was carried out within the Ibirapuera CETESB air quality monitoring sampling station. Most of the traffic surrounding the park consists of cars. Furthermore, given the large emissions of biogenic volatile organic compounds, the park is one of the areas of the city that most often exceeds ozone standards (CETESB, 2015).

The University site (23° 33' 38.41" S, 46° 44' 4.85" W, 750 m ASL) is located roughly 10 km from the city center, at the campus of the University of São Paulo. The university campus is a vast green area of 5.5 km<sup>2</sup> with low impact of direct vehicular emissions (Almeida et al., 2014; Backman et al., 2012). The aerosol sampler was deployed at the rooftop of an 8-floor building, sampling at 34 AGL in a well-ventilated area, collecting well-mixed aged air masses from the city.

### 2.2. Instrumental setup

Aerosol were sampled on 47 mm quartz membrane fiber (Pall Life Science) using a low-volume sampler with a flow rate of 16.6 Lpm equipped with 2.5 μm Sierra Andersen inlet. Measurements of

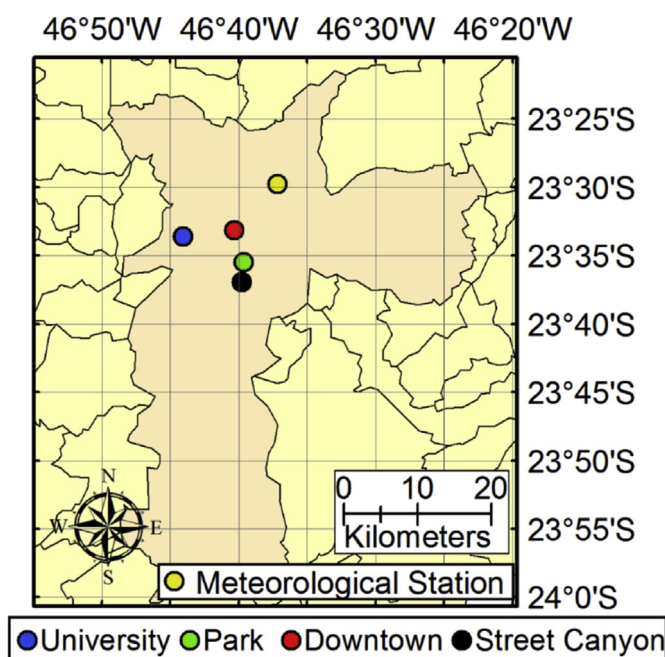


Fig. 1. Map of the SPMA region showing the location of the 4 sampling sites used in this study and the location of Brazilian Meteorological Institute INMET (that provided meteorological parameters). The stations cover the region directly impacted by vehicular emissions as well as aged aerosol relatively far from direct sources.

OC and EC were performed using thermal–optical transmittance analysis (TOT) (Sunset Laboratory Inc. (USA) (Birch and Carya, 1996). In this analysis, the carbonaceous material contained in aerosol particles collected on quartz-fiber filters evolves thermally under different temperature steps according to a prescribed temperature protocol, first in a completely oxygen-free helium atmosphere and then in an oxidizing atmosphere containing a 2% oxygen/helium mixture. Ideally, organic compounds are vaporized in the inert atmosphere stage and oxidized to carbon dioxide in an oxidizer oven with  $MnO_2$  catalyst. However, during the first phase there are usually some organic compounds that are converted to elemental carbon. This pyrolytic conversion is continuously monitored by measuring the transmission of a laser through the filter and automatically corrected. Many steps were taken to ensure an accurate determination of the EC and OC concentrations, such as regular split point determination for the pyrolytic carbon determination, and regular analysis of blank filters. We have not used stacked quartz filters for OC artifact correction.

The TOT analysis was performed using the optimized thermal evolution protocol EUSAAR\_2 (Cavalli et al., 2010). In the first stage (He), the conditions of temperature and time steps are: 200 °C for 120s, 300 °C for 150s, 450 °C for 180s and 650 °C for 180s. In the second stage (He- $O_2$ ), the four steps are 500 °C for 120s, 550 °C for 120s, 700 °C for 70s and 850 °C for 80s. Therefore, nine temperature-resolved carbon fractions were provided: four organic carbons ( $OC_{1-4}$ ), four elemental carbons ( $EC_{1-4}$ ) and the organic pyrolyzed carbon fraction (OP). Total OC is operationally defined as  $OC_1 + OC_2 + OC_3 + OC_4 + PC$ , total EC is defined as  $EC_1 + EC_2 + EC_3 + EC_4 - PC$  and the total carbon concentration (TC) is the sum of OC and EC.

Hourly data from  $PM_{10}$ ,  $PM_{2.5}$  and trace gases ( $CO$ ,  $O_3$ ,  $NO_x$  and  $SO_2$ ) were provided by São Paulo State Environmental Protection Agency (CETESB) monitoring stations nearest to the samplers. For Street Canyon and Park sampling sites, the samplers are collocated with instrumentation from CETESB. The Downtown site is located

about 30 m from CETESB station Cerqueira Cesar and the University site is some 200 m from IPEN-USP station. Meteorological parameters are provided by the Brazilian Meteorological Institute INMET, and the station is located at 23° 29' 46" S, 46° 37' 11" W, 792 m ASL.

### 3. Results and discussion

#### 3.1. Sampling sites characterization

Average concentrations of PM and other pollutants ( $CO$ ,  $O_3$ ,  $NO_x$  and  $SO_2$ ) provided by CETESB monitoring stations are shown in Table 1. The Street Canyon site has presented the highest  $CO$  levels, compatible to poor local dispersion and intense local traffic. Overall, the average  $NO_x:CO$  ratio for the sampling sites are compatible to light-duty vehicles emissions derived from tunnel measurements ( $0.049 \pm 0.05$ , Brito et al., 2013), namely  $0.06 \pm 0.03$ ,  $0.04 \pm 0.03$  and  $0.04 \pm 0.03$  for Downtown, Park and University sites, respectively. These numbers contrast strongly to  $NO_x:CO$  ratio associated to heavy-duty vehicles emission ( $2.4 \pm 1.6$ ) (Pérez-Martínez et al., 2014). Also notice the importance of coarse mode particles, especially at the Street Canyon and Downtown sites, heavily impacted by local traffic.

#### 3.2. Concentrations of OC and EC

Time series of OC and EC concentrations are shown in Fig. 2, while averages and standard deviations (including the different fractions of OC and EC; OC:EC and EC:TC ratio) are given in Table 2. Both OC and EC concentrations are lower in the Park and University sites compared to the Street Canyon and the Downtown site. The average concentration of EC is 2.7 times higher at the Street Canyon site than in the Downtown site and almost 4 times higher than in the Park and University sites. Average OC:EC ratio at Downtown, University, Park and Street Canyon sites were  $1.57 \pm 0.69$ ,  $1.88 \pm 0.68$ ,  $1.89 \pm 0.56$  and  $0.56 \pm 0.13$ , respectively. The significantly lower OC:EC ratio observed at the Street Canyon site is a clear indication of the strong impact of heavy-duty vehicle emissions on elemental carbon. Previous tunnel studies in the SPMA reported values of OC:EC ratio of 1.5 for light duty vehicles and close to 0.5 for heavy duty vehicles (Brito et al., 2013). Despite the strong contribution of EC at this site, similar to heavy duty tunnel measurements, impact of atmospheric dilution can play a significant role on other species. The OC:EC ratios observed at Downtown, Park and University sites ranging from 1.6 to 1.9 can be attributed to comparable carbonaceous aerosol sources, with important impacts from light-duty vehicles (although they differ in absolute concentration), combined to some extent to secondary organic aerosol formation, a topic discussed in a later section.

Table 2 also shows the average concentrations of each carbon fractions for the four sites. Interestingly, the concentration of the EC1 fraction was comparable among all sites, ranging from  $0.41 \mu g m^{-3}$  (University) to  $0.51 \mu g m^{-3}$  (Downtown). The

Table 1

Averages and standard deviations for particulate matter mass concentrations in  $\mu g m^{-3}$  and gas mixing ratios in ppb. Average values calculated during the measurement campaign.

Pollutant	Street canyon	Downtown	Park	University
$PM_{2.5}$	$19 \pm 10$	$12 \pm 10$	$10 \pm 3$	$11 \pm 10$
$PM_{10}$	$34 \pm 17$	$35 \pm 21$	$27 \pm 21$	$22 \pm 8$
$NO_x$	–	$45.0 \pm 37.3$	$22.0 \pm 20.0$	$14.6 \pm 21.9$
$SO_2$	$2.0 \pm 1.3$	$1.3 \pm 1.2$	–	–
$CO$	$1107 \pm 487$	$708 \pm 380$	$504 \pm 316$	$369 \pm 354$
mid-day $O_3$	–	–	$32.3 \pm 15.0$	$33.7 \pm 14.5$

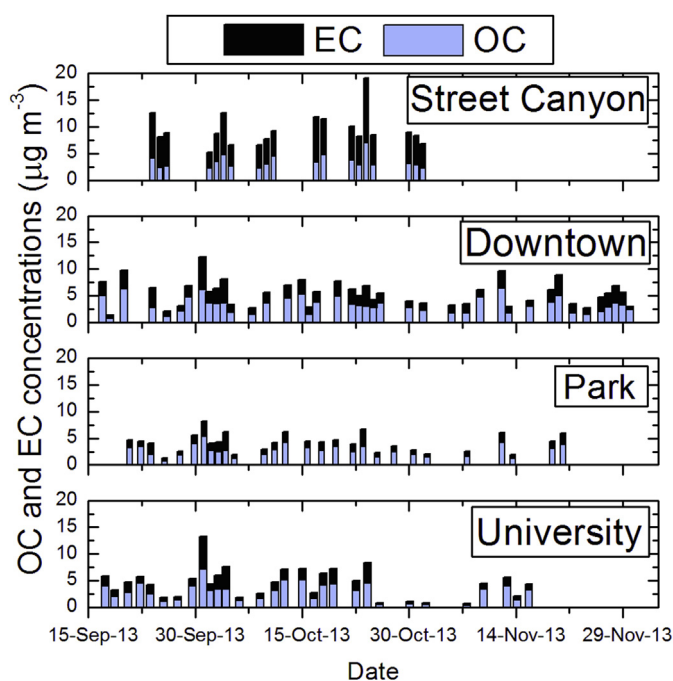


Fig. 2. Time series of OC and EC concentrations at Street Canyon, Downtown, Park and University sites.

Table 2

Average concentrations and standard deviations for OC, EC and their fractions. Also show are the values of OC:EC and EC:TC ratios. <sup>a</sup> Concentrations are reported in  $\mu\text{g m}^{-3}$ . N samples is the number of collected samples at each site.

N samples	Street canyon site	Downtown site	Park site	University site
	19	41	28	30
OC <sup>a</sup>	3.37 ± 1.17	3.24 ± 1.44	2.65 ± 1.07	2.91 ± 1.62
EC <sup>a</sup>	6.11 ± 2.01	2.25 ± 1.12	1.50 ± 0.73	1.70 ± 1.26
OC1 <sup>a</sup>	0.47 ± 0.19	0.24 ± 0.17	0.13 ± 0.14	0.21 ± 0.16
OC2 <sup>a</sup>	1.41 ± 0.49	1.08 ± 0.42	0.81 ± 0.36	0.93 ± 0.49
OC3 <sup>a</sup>	0.59 ± 0.35	0.54 ± 0.32	0.41 ± 0.28	0.54 ± 0.38
OC4 <sup>a</sup>	0.63 ± 0.22	0.61 ± 0.27	0.40 ± 0.17	0.55 ± 0.29
PC <sup>a</sup>	0.27 ± 0.30	0.75 ± 0.51	0.81 ± 0.45	0.69 ± 0.46
EC1 <sup>a</sup>	0.48 ± 0.19	0.51 ± 0.31	0.43 ± 0.26	0.41 ± 0.29
EC2 <sup>a</sup>	0.96 ± 0.41	0.76 ± 0.42	0.61 ± 0.32	0.56 ± 0.38
EC3 <sup>a</sup>	2.84 ± 1.24	1.30 ± 0.67	0.92 ± 0.46	0.99 ± 0.71
EC4 <sup>a</sup>	2.08 ± 1.20	0.55 ± 0.35	0.29 ± 0.25	0.44 ± 0.43
EC:TC	0.64 ± 0.05	0.41 ± 0.09	0.36 ± 0.08	0.37 ± 0.08
OC:EC	0.56 ± 0.13	1.57 ± 0.69	1.89 ± 0.56	1.88 ± 0.68

concentration of EC2, however, has depicted a more significant variability between sites, with values of 0.96, 0.76, 0.61 and  $0.56 \mu\text{g m}^{-3}$ , for Street Canyon, Downtown, Park and University, respectively. EC3 was the dominant elemental carbon fraction at all sites in present study. The average values of EC3 were higher at the direct vehicular impacted sites, Downtown ( $1.30 \mu\text{g m}^{-3}$ ) and Street Canyon ( $2.84 \mu\text{g m}^{-3}$ ), than Park ( $0.92 \mu\text{g m}^{-3}$ ) and University ( $0.99 \mu\text{g m}^{-3}$ ). This result is an indication that the EC3 fraction might be more strongly associated with heavy vehicles emission. Consistently, previous studies (Cao et al., 2006; Watson et al., 1994) has shown that EC fraction which evolved nearly  $750^\circ\text{C}$  is the most abundant in the exhaust of diesel-fueled vehicles. Moreover, results of source apportionment of carbonaceous fractions inside tunnel (Zhu et al., 2010) has identified a diesel factor with significantly higher concentrations of EC fraction that evolves at  $740^\circ\text{C}$  than that in gasoline. Finally, EC4 fraction showed quite different behavior at each site. In Downtown and University sites, the levels of EC4 were

comparable to the EC1 fraction. At the Street Canyon site, EC4 was the second most abundant elemental carbon fraction, with average concentration of  $2.08 \mu\text{g m}^{-3}$ . In contrast, the Park site average concentration of EC4 was  $0.3 \mu\text{g m}^{-3}$ , representing the smallest fraction of EC at this site.

The highest contribution of the OC fractions was from the OC2 for all sites (Fig. 3) representing from 30 to 40% of total OC concentrations. The Street Canyon site presents higher levels of OC1 and OC2 fractions, while OC3 and OC4 depicted comparable concentrations at all sites (with average values ranging from  $0.40$  to  $0.60 \mu\text{g m}^{-3}$ ). Consistently, Zhu et al. (2014) has attributed high levels of OC1 to fresh vehicle exhaust and poor dilution conditions, while Cao et al. (2006) found that OC2 were mainly derived from diesel exhaust. Similar levels of PC fraction were found at Park, University and Downtown sites, depicting an average value ranging from  $0.69$  to  $0.81 \mu\text{g m}^{-3}$ . The PC fraction contributed 20–30% of total OC at Downtown, Park and University sites, while at Street Canyon it represents less than 10% of OC. Similarly, previous source apportionment results (Zhu et al., 2010) obtained lower abundance of PC fractions in diesel emissions than those in gasoline factor.

### 3.3. Estimation of secondary organic carbon

The OC:EC ratio can be a rough indicator of sources as well as the processes undergone from emission to sampling, such as removal and condensation of species into preexisting aerosol particles. This ratio also depends on analytical protocols, artefact corrections, split point between OC and EC determination, the kind of optical correction (i.e. reflectance or transmittance) (Chow et al., 2004) and other factors. The formation of secondary organic aerosol (SOA) is an atmospheric process which leads to an increase in the OC:EC ratio. Castro et al. (1999) proposed that the minimum value of OC:EC ratio at a given sampling site would be representative of the least contribution of SOA, and thus enhancement from this value could be used to estimate Secondary OC (SOC). According to Pio et al. (2011), this method could be used as a tool to differentiate OC from primary and secondary sources, with two major exceptions: aerosols from biomass burning and plume of wild fires, sources that not presented high impact at sampling sites of present work (Castanho et al., 2001). Given that one cannot know the true OC:EC ratio from the sources at a given site to be used as reference, the SOC value calculated using this method are considered to be a lower bound estimate. Another important aspect of the methodology is the underlying assumption that the dominating primary aerosol source is fairly constant throughout the whole campaign (about three months here). The estimate of SOC is as follows:

$$\text{SOC} = \text{OC}_{\text{total}} - \text{ref}\left(\frac{\text{OC}}{\text{EC}}\right) \times \text{EC}_{\text{total}}$$

where  $\text{ref}(\text{OC:EC})$  was chosen here as the 5th percentile of the OC:EC ratio for each sampling site. This value is considered less prone to outliers which affect the minimum value, as has been used in other works. Possible changes in semi-volatile sampling efficiency, which can severely affect SOC estimates, are considered negligible here given a fairly constant temperature throughout the campaign (Section 2.1).

The values of  $\text{ref}(\text{OC:EC})$  obtained in this study were 0.39, 0.80, 0.89 and 1.03 at Street Canyon, Downtown, Park and University sites, respectively. Previous observations in Europe (Pio et al., 2011) reports minimum OC:EC ratio was in the range of 1.1–1.4 in background air and 0.3–0.4 near emission sources. Estimates of SOC and POC concentrations are shown in Fig. 4 indicating (a) absolute and (b) percentage assignments. These results represent an average contribution of 43, 46 and 38% of total OC attributable to SOC at

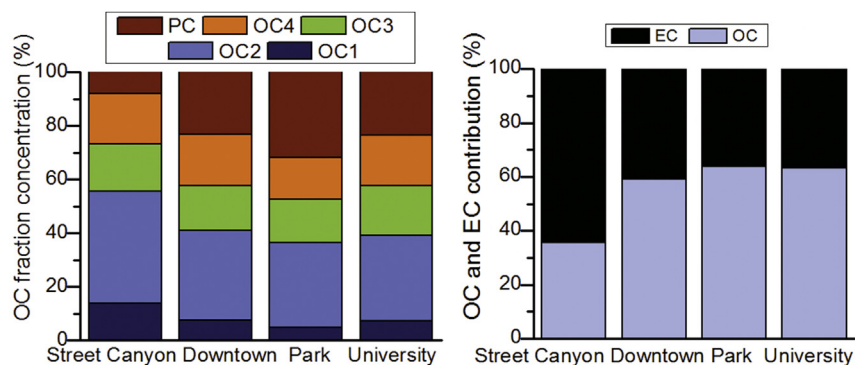


Fig. 3. Average percentage contribution of (a) OC fractions to the total OC concentrations, and (b) of OC and EC to TC at Street Canyon, Downtown, Park and University sites.

Downtown, Park and University sampling sites, respectively. On the other hand, Street Canyon shows a different profile with the SOC fraction represents only 27% of total OC. The lower secondary formation is consistent with the high impact of primary sources at this site. Studies using this method in other urban areas with comparable meteorological conditions have also estimated a contribution of secondary OC ranging from 30% to 65% (Mancilla et al., 2015; Na et al., 2004; Zhang et al., 2012) and somewhat lower contribution in winter (17–37%) (Castro et al., 1999).

### 3.4. Correlations of OC fractions and EC

As a product of incomplete combustion (Bond et al., 2013), temporal correlation of EC eventually could provide insights on the nature of the OC fractions. Since the EC is assumed to be essentially primary, this correlation analysis can indicate the relationship of EC with these OC fractions. Calculated Pearson correlation coefficients between each OC fraction and EC concentrations for all sampling sites are presented in Table 3.

Results show that most of the OC fractions present a statistically

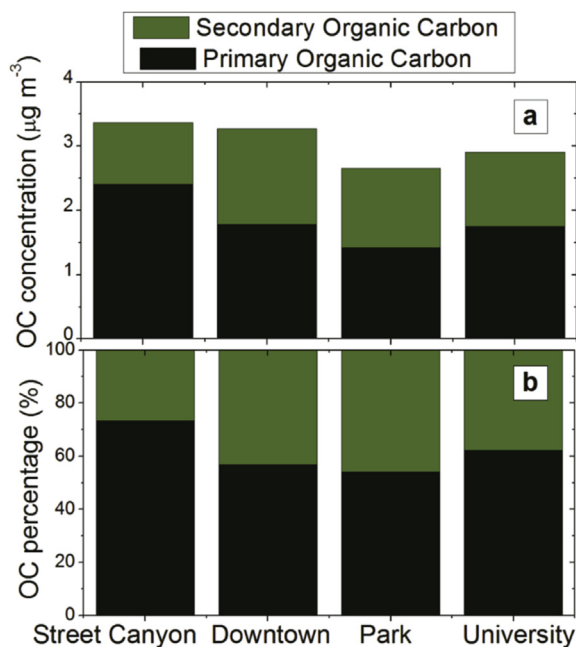


Fig. 4. Average concentration and percentage of total OC attributable to the estimated secondary and primary organic carbon at Street Canyon, Downtown, Park and University sites.

significant correlation with EC, excepting the PC fraction (ranging from  $-0.45$  at the Street Canyon site to  $0.40$  at the University site). Anti-correlation of PC with EC (especially at Street Canyon) could show that PC is not present in significant levels in traffic emissions (Kim et al., 2016; Sahu et al., 2011). The enhancement of PC levels in filters were previously attributed to water-soluble organic carbon (WSOC), which in turn is a proxy for secondary organic aerosol (SOA) (Tang et al., 2016; Yu et al., 2002). Interestingly, if one were to apportion PC to SOC described in the previous section, it would explain about 30%–60% of the secondary OC. It is important to take into account that the method described in Section 3.3 assumed to be a lower estimate of total SOC, not limiting the contribution of other OC fractions to SOC as well.

### 3.5. Correlations of OC fractions between sampling sites

The spatial variability of the OC fractions in the SPMA can be investigated by studying the temporal correlation between different sampling sites. Fig. 5 shows the correlation coefficient for OC1, OC2, OC3, OC4 and PC according to the distance between sites pairwise, which ranged from 3 to 10 km.

The OC3 and OC4 fractions depict high correlation for all sites, indicating a joint variability and homogenous distribution in the atmosphere of SPMA. Such regional behavior, coupled to high correlation with EC (Section 4.4), allows us to speculate that these fractions are linked to whether well-processed primary aerosols from vehicular sources, or secondarily formed from anthropogenic gaseous precursors. The assumption of homogeneous distribution of the OC3 and OC4 in the atmosphere is supported by similar average concentrations of these fractions at all sites (Table 2). Hourly resolved measurements of OC and EC conducted elsewhere have also identified that OC3 and OC4 contribution to OC tends to increase in the afternoon (Vodička et al., 2015), thus depicting a behavior similar to the widely observed low-volatility oxygenated organic aerosol (LV-OOA) factor from the Aerosol Mass Spectrometer community, linked to highly processed organic material

Table 3  
Pearson's correlation coefficients (R) between OC fractions and EC for Street Canyon, Downtown, Park and University sites. All the values for the first 4 variables were statistically significant within the 95 percent confidence interval. <sup>a</sup> Values out of the 95 percent confidence interval.

	Street canyon site	Downtown site	Park site	University site
OC1	0.85	0.74	0.56	0.73
OC2	0.95	0.79	0.77	0.85
OC3	0.86	0.76	0.75	0.83
OC4	0.80	0.81	0.78	0.86
PC	$-0.45^a$	$-0.04^a$	$0.19^a$	$0.40^a$

(Jimenez et al., 2009).

Conversely, OC2 and PC also depict good correlation among sampling sites, excepting the Street Canyon. The fact that the PC fraction depicts fairly good correlation among sampling sites, but does not correlate with EC suggests a secondary nature from potentially biogenic source. Such results certainly motivate further studies. At last, the correlation coefficient of OC1 depicts a decreasing tendency with increasing distance between sites, indicating a more local characteristic than the other components. Interestingly, this fraction had the smallest contribution to OC in most sites.

#### 4. Conclusions

Carbonaceous aerosols were collected in four sampling sites within the SPMA. The analysis of thermally-derived organic carbon fractions, namely OC1, OC2, OC3, OC4 and PC allowed further insights on the dynamics of OC. The OC concentrations were comparable at all sampling sites from  $2.65 \mu\text{g m}^{-3}$  (Park) to  $3.37 \mu\text{g m}^{-3}$  (Street Canyon). However, results shown significantly higher EC concentrations at the Street Canyon site ( $6.11 \mu\text{g m}^{-3}$ ) in contrast to all other three sites, ranging from  $2.25 \mu\text{g m}^{-3}$  (Downtown) to  $1.50 \mu\text{g m}^{-3}$  (Park).

The average OC:EC ratio for samples collected in Downtown, Park and University site was  $1.57 \pm 0.69$ ,  $1.88 \pm 0.68$ ,  $1.89 \pm 0.56$ , respectively. The OC:EC ratios observed for these sites fall on the lower bound of values typical observed for other megacities under similar meteorology such as Los Angeles (3.6) (Hasheminassab et al., 2014), Beijing (2.5) (Zhang et al., 2013), Paris (2.1) (Bressi et al., 2013) indicating an important contribution of EC to

ambient aerosol. With an even lower OC:EC ratio, the samples from Street Canyon site had an average value of  $0.56 \pm 0.13$ , a value very close to diesel-fueled HDV results reported from tunnel measurements in the SPMA, presenting to our knowledge the lowest OC:EC ratio ever reported for any urban site.

The contribution of secondary organic carbon to the total OC concentrations was estimated using a method based on primary OC:EC ratio. Considering the 5th percentile of OC:EC ratio as the primary source for each location was estimated a participation of 43, 46 and 38% of total OC attributable to SOC at Downtown, Park and University sampling sites, respectively. At the Street Canyon site, the SOC fraction represents only 27% of total OC.

Results from correlation of each OC fraction with EC have identified significant correlations from EC with OC1, OC2, OC3 and OC4 for all sampling stations, interpreted as having a common source, vehicular emissions. On the other hand, no significant correlations were observed between EC to PC fraction, i.e., it does not scale with direct vehicular sources.

The correlation between different sites provided evidence of a well-mixed urban atmosphere. As expected, correlation coefficients from Street Canyon with other sampling sites are weaker, since this site is the most isolated and most impacted by very local traffic sources. Results have shown that OC3 and OC4 fractions correlate well among all sites, thus providing evidence that these organic fractions have a uniform distribution in the atmosphere of SPMA. The fractions OC2 and PC correlate well among different sites excepting the Street Canyon site, whereas OC1 depicts a more local behavior, decreasing correlation coefficient with distance.

Results showed the high impact of carbonaceous particles in São Paulo PM<sub>2.5</sub> aerosols. This study shows characteristics of carbonaceous aerosols at the metropolitan area of São Paulo with high population density and strong traffic using high emitting buses and a large fraction of ethanol in the fuel of cars. The different components of the carbonaceous aerosol carbon fractions were characterized according to local and urban behavior. The high diesel impacted sampling site shows different profiles than all other sites. These profiles of carbon fractions could be used to identify sources and atmospheric processes. This study shows clearly that is necessary to improve buses emissions rates in the SPMA, with the implementation of EURO VI technology. It is also important to improve mass transport systems such a metro and more bus corridors to allow better transport for 19 million people. The intensification of an automobile inspection system is also clearly necessary, since this essential service is not implemented anymore in the SPMA.

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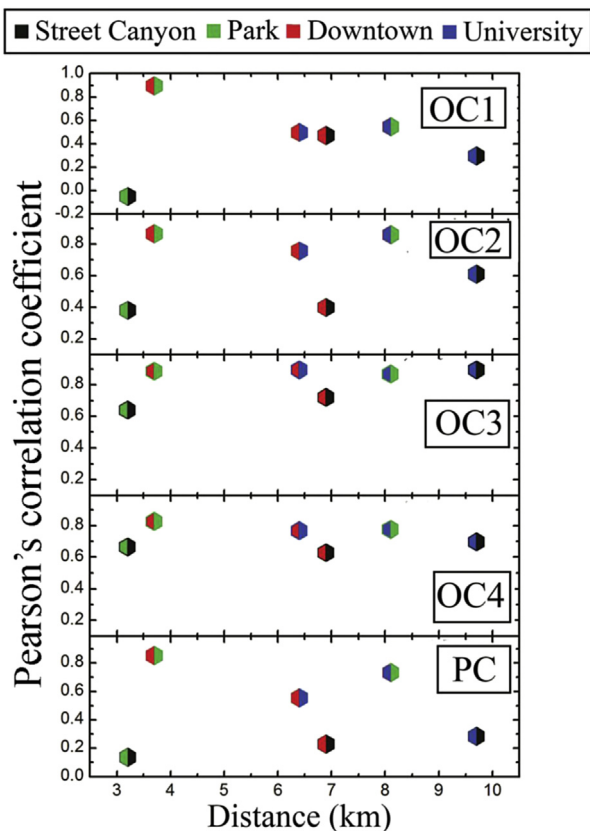


Fig. 5. Pearson's correlation coefficients (R) for the organic components OC1, OC2, OC3, OC4 and PC according to the pairwise distance between the different sampling sites.

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