Vehicular emissions of organic particulate matter in Sao Paulo, Brazil

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The authors would like to thank the anonymous reviewer for the helpful comments and suggestions. All comments are addressed below. For clarity, the referee's comments are copied in italic, the author's replies in normal font, and the content added to the manuscript is highlighted in yellow.

Responses to anonymous Referee # 1

Major comments 1: *Background subtraction is a major issue with the results described here and I am not convinced that EF values are well calculated, to state the least. Prior acceptance of the manuscript, the authors must provide convincing arguments that EF values calculated using ambient measurements at one site as background values for tunnels – which apparently are not nearby (not clear also!) – is accurate. One suggestion to make it in the least justifiable is to compare, if existing, concentration of parameters such as OC, EC, PM2.5, O3, CO, SO2, NO, NO2, NOx, NOy and so forth from the tunnel entrance and the ambient sampling site. Please also expand thoroughly explanation on how was it implemented, as only very broad and unclear explanation was provided in the manuscript from P.33761 L.20 to P.33762 L.16.*

Reply:

We thank the reviewer for this suggestion. The background correction used previously considered the results from samples collected during an ambient campaign located 5 km away from TJQ and 15 km from TRA. This method raised questions related to its representativeness and also how much the meteorological conditions would affect the EF calculation. Although we think that the background subtraction is defendable by the means suggested by the reviewer, we decided to use a more robust method, as presented below. Both methods yield similar results, however, the new method (based on correlation with CO) allowed also to distinguish between aerosol from engine exhaust and aerosol from other vehicle operation (braking, tire wear etc.). The new method for background correction considers only information collected during the experimental tunnel campaigns, inside and outside the tunnels:

The following part regarding the background correction will be added in the revised manuscript:

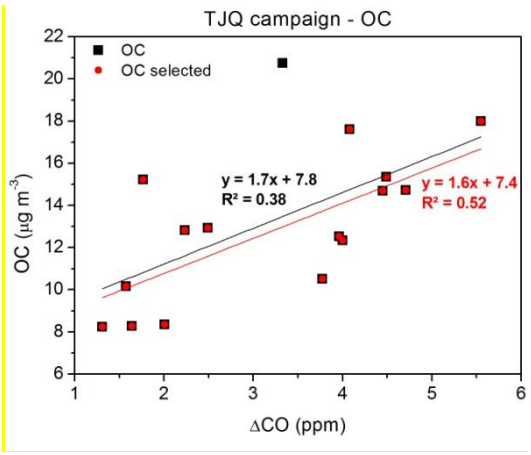
"The ventilation system in the tunnels brings the air from the outside to the interior by ventilation fans on the roof of the tunnels operating according to the CO level in order to provide fresh air inside. This air already contains some urban background aerosol and hence a subtraction of this background is necessary to remove any contribution not originating from the traffic inside the tunnel itself. Considering that the difference of CO between inside and outside (ΔCO) is directly related to the vehicular emission (for Sao Paulo, more than 90% of CO

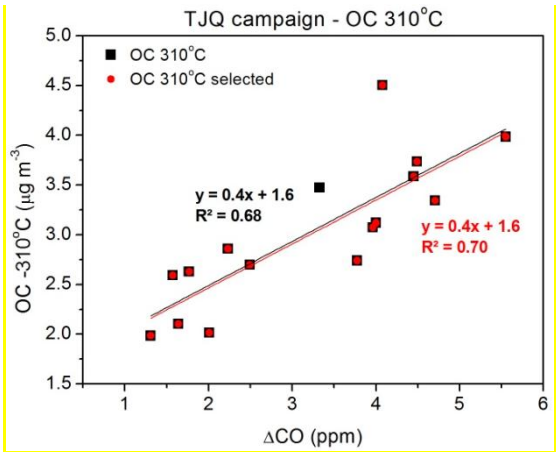
comes from vehicular emissions), a linear relation between ΔCO and the pollutant from the same source is expected. Therefore, the intercept of this fit was considered the background concentration. This relation between ΔCO and OA (and OC) was mainly observed for the TJQ campaign. For the TRA campaign, this linear relation was not as evident as for the TJQ campaign. This is mainly ΔCO did not vary strongly in the TRA tunnel, which made a linear fit unreliable. We considered the background air near the tunnels was the same for both tunnels, and consequently subtracted the background estimates obtained for TJQ. Due to the high concentrations in the TRA tunnel, any type background subtraction will have not a strong effect on the final results. More details about the background correction can be found in the supplement."

The following part, regarding the background correction, will be added in the supplement:

"Background correction for emission factor calculation

The background correction for TJQ campaign was based on the linear fit between OA (and OC) and ΔCO. These linear relations are presented in Figure S1, for TJQ campaign. For PTR-MS analyses, the OA concentrations were calculated from the sum of all temperature step contributions. Figure S1 presents the best linear fit, obtained by excluding outliers (based on standard boxplot analyses). After excluding the outliers, the background correction was performed for each compound (PTR-MS) and fraction (TOT), per temperature step. For OC and OA analyses, 1 (TJQ06) and 5 (TJQ01F, TJQ06F, TJQ08F, TJQ09F and TJQ17F) samples were excluded, respectively. It is important to highlight that the exclusion of outliers did not have significant impact on the slope and intercept, and improved mainly the correlation (R^2).





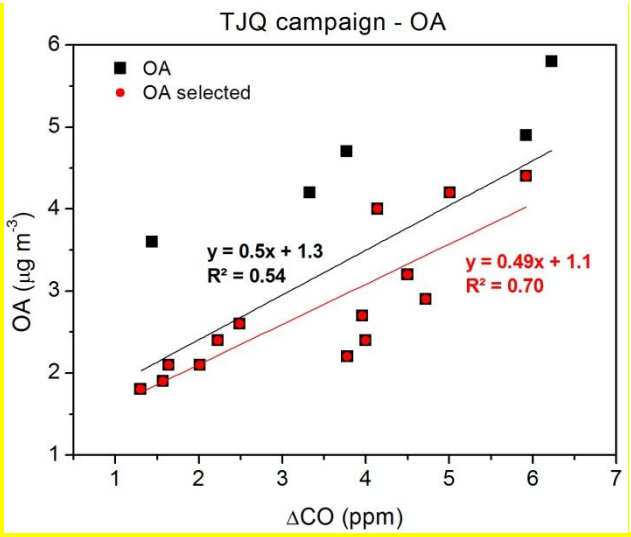


Figure S1 Comparison between ΔCO and OC. OC measured at 310°C and from 310 to 870°C, and OA for TJQ campaign. Black squares represent the whole data set used for the linear fit (in black letters), and red circles represent the data set excluding the outlier used for the linear fit (in red letters)

We used the same background correction for TRA like for TJQ, mainly due to the fact that the concentrations measured in TRA. A symmetrical variation of the background correction (± 50%) implied in a range of the result below than ±5%, see in Table S1.

Table S1: EF of OA and OC averages emission factors and SD (in brackets) for HDV (estimated from TRA tunnel campaign), in mg kg^{-1} of burned fuel.

	PTR			TOT	
Correction	**AO**	**Oxygenated**	**Up to 300°C**	**OC**	**OC up to 310°C**
0.5*bg	84.6 (13.0)	54.6 (8.3)	78.4 (12.5)	458.3 (86.3)	94.1 (10.3)
1* bg	80.8 (13.0)	52.2 (8.4)	74.9 (12.4)	423.7 (89.2)	87.0 (10.2)
2*bg	73.4 (12.9)	46.8 (8.3)	68.1 (12.3)	354.4 (95.5)	72.8 (10.3)

The background correction was performed based on the linear fit between the compound and ΔCO: slope > 0, (i) the intercept > 0 and lower than the measured concentration then, the correction was the subtraction of the intercept from the measured concentration, (ii) if the intercept was negative, but R^2 > 0.45 (related to vehicular emission), then no subtraction was performed. A small number of compounds (16 in total) were present in the tunnels at significantly higher than ambient concentrations, but did not show a significant correlation with ΔCO. An example is mass 149.024, that was present in the TJQ Tunnel at 354.6 ng m^{-3} on average versus 108.5 ng m^{-3} in ambient air during a winter campaign performed in the city of Sao Paulo, 5 km away from TJQ and 15 km from TRA (yet unpublished results). For this mass we could not estimate a background using the correlation with ΔCO.

Therefore we subtracted the ambient concentration instead. However, due to the high concentrations in the tunnel, the emission factors for this compound were not very sensitive to the subtracted background, e.g. at 150°C the ambient concentration of m/z 149.024 was 53.9 ng m^{-3}, and the average concentrations of the filters collected in the tunnels were 203.1 and 182.5 ng m^{-3} for TJQ and TRA, respectively."

Major comments 2: *The motivation of the work is somewhat lost along the manuscript. The abstract and introduction mention ethanol being used by LDV, but no deeper discussion is provided on expected changes in tailpipe emissions resulting from the fuel itself, whereas there is already abundant literature in the topic: Karavalakis et al., 2014; Matti Maricq, 2012; Myung et al., 2009 just to name a few.*

Reply:

We thank the reviewer for the suggestion and we included more discussions related to the specific characteristics of Sao Paulo fleet to the introduction:

"The usage of ethanol blends on flex-fuel vehicles has been widely discussed. Some advantages on increasing the ethanol blend in gasoline by flex-fuels vehicles were discussed by Karavalakis et al. (2014). They showed a significant reduction in the emission of particulate matter (PM) mass including soot, and particle number, but, a sharp increase of acetaldehyde. Besides, they also discussed that the way the gasoline injection is performed in the vehicle has a significant impact on soot emissions, e.g. gasoline direct injection vehicles emitted more soot than port fuel injection. In an investigation of the size distribution of soot formed from ethanol/gasoline blend diffusion flames, Matti Maricq (2012) found only little effect on the size distribution with the addition of small amount of ethanol. Furthermore, they found that high amounts of ethanol in the fuel (85%) lead to significant reduction of semi volatile organic formation.

In a comparison between ethanol fuel contents (E85 and E75, 85 and 75% of ethanol in gasoline respectively), in two different studies, Suarez-Bertoa et al. (2015a) and Suarez-Bertoa et al. (2015) concluded that a higher amount of ethanol resulted in a reduction on nitrogen oxides ($NO+NO_2=NO_x$) emitted, however, it increased acetaldehyde and ethanol emissions, which leads to a significant increase of ozone formation potential (OFP). This finding was in line with the work by Salvo and Geiger (2014). Based on observation of road traffic levels, meteorological conditions and pollutant concentrations associated to a consumer demand

model (for ethanol and gasoline), they concluded that ozone ambient levels reduce with decreased ethanol amounts in fuel.

The emissions due to the use of diesel and bio-diesel have many important differences that affect the formation of secondary organic aerosol and the formation of fine particles. The use of biodiesel is associated to an increase in NO_x emission (Hoekman and Robbins, 2012), carbonyl compounds (Machado Corrêa and Arbilla, 2008) and also some poly aromatic hydrocarbons (PAH's) (Karavalakis et al., 2011). The number and size distribution of particles are also affected by the use of biodiesel. The ambient air in Sao Paulo city is highly affected by the implementation of different fuels and this has to be better evaluated as the ozone and fine particle concentrations are presenting frequent violations of air quality standards (Cetesb, 2014)."

Major comments 3: *As a general issue of the manuscript, hardly the results presented were put in context by comparing with known literature, and when performed, very poorly. The clearest example is the V-K diagram (P.33770 L:7-12 and figure 5) which were frequently studied from the AMS community but very lightly compared in the manuscript, in particular for ambient measurements. Would be interesting a comparison of different chemical groups and their volatility with results elsewhere.*

Reply:

We thank the reviewer for the suggestion. In the revised version we extended the discussion concerning Table 3, Figure 5, and Figure 6.

Table 3:

"Table 3: OA (TD-PTR-MS), OC (TOT) and $PM_{2.5}$ averages emission factors (mg kg^{-1} of burned fuel) and standard deviation of the filters, for LDV and HDV. (Values in brackets correspond to the EF in mg km^{-1})

	PTR-MS			TOT		Gravimetry[b]
	up to 300°C	Total[a]		at 310°C	310 - 870°C	$PM_{2.5}$
		All compounds	Compounds with O			
LDV	27.2 ± 7.5 (1.7 ± 0.5)	30.3 ± 8.5 (1.9 ± 0.5)	21.5 ± 6.5 (1.3 ± 0.4)	23.3 ± 8.4 (1.5 ± 0.5)	84.3 ± 66.3 (5.2 ± 4.2)	300 ± 100 (20 ± 8)
HDV	74.9 ± 12.4 (18.9 ± 3.1)	80.8 ± 13.0 (20.4 ± 3.3)	52.2 ± 8.4 (13.2 ± 2.1)	89.2 ± 10.2 (22.5 ± 2.6)	423.7 ± 87.0 (107.0 ± 22.0)	700 ± 300 (277 ± 108)

The EF(OA) values presented here were lower than the ones found in other studies. Chirico et al.(2011) found 33.7 (HDV) 5.6 (LDV) mg km^{-1}, and another study in Zhujiang Tunnel, Guangzhou, China (He et al., 2008) found 76 (HDV) and 19 (LDV) mg km^{-1}. The observed differences are mostly due fact that in our study a large fraction of OA is missed due to the 350°C limit for thermal desorption. Additional effects could be due to the different fuel composition used in Brazil, since the Brazilian gasoline includes 25% of ethanol. It has been shown that an increased percentage of biofuel can lead to the reduction of the particulate matter emission (Karavalakis et al., 2014; Mamakos et al., 2013). This may explain the larger difference observed for LDV as compared to HDV.

Regarding the EF (OC), most of the references found did not distinguish between the contribution of LDV and HDV for EF calculations. In a studys conducted in China (Cheng et al., 2010) in Shing Mun Tunnel for diesel emission characterization found an emission factor of 67.9 mg km^{-1} for OC. Zhang et al. (2015) found 19.2 mg km^{-1} (12% HDV and 27% liquefied petroleum gas vehicles). Hung-Lung and Yao-Sheng (2009) and Handler et al. (2008) found 4.7 (~15% HDV) and 2.3 (~10% HDV) mg km^{-1}, respectively. These values, although comparable, were lower than EF (OC) considering only LDV. In conclusion, we can affirm that the vehicles in Sao Paulo city emit more OC/km^{-1} than in several other cities.

Figure 5:

Figure 5 shows the relation between the atomic ratios H/C and O/C (Van Krevelen Diagram) calculated from the mass concentration, without the background correction proposed by the EF calculation. Besides the ratios from the tunnels campaigns discussed here, Figure 5 also present the average ratios from an ambient campaign performed in the Sao Paulo city (5 km away from TJQ and 15 km from TRA) during the South Hemisphere winter on 2012 (yet unpublished results). The average ambient O/C was higher than measured in the tunnels. This can be associated to photochemical reactions in presence of sunlight producing oxygenated aerosol. The high H/C ratios found for the tunnels samples indicated that fresh aerosol were collected on the filters due to primary emission from vehicle exhaust.

The O/C and H/C ratios presented more variation for the samples collected during the TJQ campaign than for the samples collected in TRA; possibly due to the differences in the traffic and congestion (see Table 1). In general, the samples collected during the morning (for 6 h) and at night (for 12 h) were more oxidized than the others. This can be related to a smaller

177 number of cars and consequently to less POA emissions. In addition, the contribution of
178 external air was more significant during these times. The afternoon samples (sampled for 3 h)
179 were collected during the traffic congestion periods (between 5 and 8 pm, Brito et al., 2013)
180 suggesting that POA dominated the burden sampled on the filters. Samples collected during
181 the day (for 12 h) were mainly dominated by afternoon traffic congestion profile.
182 Consequently, we used the 12h-day samples and the afternoon samples from the TJQ tunnel
183 to calculate LDV emission factors.

184 The O/C ratios ranged between 0.16 and 0.21 (O/C), indicating a higher amount of
185 oxygen in POA for the OA desorbed up to 350^{o}C than reported in previous studies. The ratios
186 found here were significantly higher than the ratio found for gasoline and diesel (around 0.04)
187 measured on POA formed under controlled conditions (Aiken et al., 2008). In a different tunnel
188 study, Chirico et al. (2011) also found significant differences, the O/C ratios ranged between
189 0.073 (workday) and 0.199 (weekend). Collier et al. (2015) estimated O/C ratios around 0.19
190 for low particulate matter concentrations, measured in vehicles using a dynamometer. Given
191 the fact that O/C ratios measured with the TD-PTR-MS are usually biased low (Holzinger et al.,
192 2013), the values found here indicate a more oxidized aerosol originated from the fuels used in
193 Brazil, which may be related to the use of ethanol and bio-diesel.

194 Chirico et al. (2011) found H/C ratios ranging between 1.84 and 1.71, for working and
195 weekend days, respectively. These values were higher than 1.62, found by Aiken et al. (2008),
196 in ambient measurements performed in Mexico City. In both studies the H/C ratio was higher
197 than found here, ranging between 1.25 and 1.45. This is in agreement with the higher O/C
198 ratio found in this study, showing a higher oxygenation state of the particulate compounds
199 sampled in the tunnels comparing to results from Mexico City or Switzerland. It is important to
200 highlight here that the AMS operates at high vaporization temperatures (usually constantly at
201 600^{o}C), measuring smaller particles (PM1) than discussed here, and uses a different method of
202 ionization, namely electron impact ionization.

203

Figure 6:

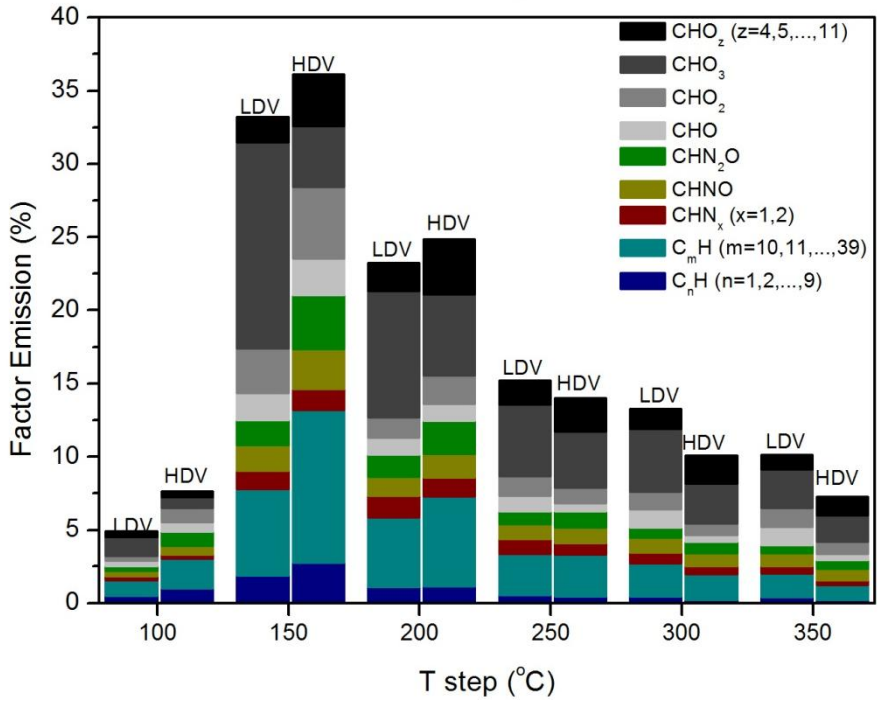


Figure 6: Fraction of total average emission (in %) divided into groups containing CH, CHO, CHON, and CHN, considering different numbers of carbon and oxygen atoms in the compounds, for LDV and HDV at each temperature step.

The distribution of the total emissions over the different desorption temperatures is presented in Figure 6. This analysis indicated that OA produced from HDV was slightly more volatile than OA from LDV. As expected, hydrocarbons (HC) represented the most volatile group. Their volatility was related to the number of carbons present in molecules: short-chain hydrocarbons (up to 9 carbon atoms) were more volatile than the long-chain ones (more than 9 carbon atoms). The short-chain HC contribution was very low at 250°C and higher temperatures, while the long-chain HC contribution was still significant at 350°C.

The oxygenated hydrocarbon compounds were the most significant group in the aerosol composition. The group containing up to 3 oxygen atoms was the predominantly due to m/z 149.024, mainly at 150 and 200°C, for LDV emission. The relative contribution from oxygenated compounds to the total OA increased during the last temperature steps.

In addition, the fraction of ions with at least one oxygen atom is higher than reported by Chirico et al. (2011) in a tunnel in Switzerland. Chirico et al. (2011)showed that CH-ions largely dominated the average OA mass spectra from online AMS measurements sampled during rush hours on working days. The difference to this study can be explained by both, the

different analytical techniques and the use of ethanol and biodiesel in Brazilian fuels, which have higher oxygen content than the fuels used in the Swiss."

Minor comments

Abstract. P.33756, L.1-2: This starting sentence provides the reader the (wrong) impression that there are these only four factors regulating the impact of vehicle emissions in urban pollution, and furthermore, that they are equally important, which obviously is not true. Please rephrase it.

Reply:

We agree that the statement could lead to confusion and hence we have changed the introduction s follows:

"Vehicular emissions contribute significantly to air pollution in big cities. Both, gas and particulate emissions, are highly variable and depend on factors such as the type of vehicle, type of fuel, cruising velocity or brake use."

Please use E25 throughout the manuscript as oppose to gasohol. Also, would be better for the reader E100 instead of hydrated ethanol.

Changes made as suggested

The acronym for tunnel identification can be improved, maybe JQ and RMC?

Reply:

In the interest of consistency with other published work (including in ACP) from the same study, we decided to use the same identification (Pérez-Martínez et al.(2014) and Brito et al.(2013))

Abstract. P.33756, L.26-27: Please rephrase.

Reply:

In the revised manuscript we changed the respective part to:

"Additionally, 70% and 65% of the emitted mass (OA) originates from oxygenated compounds for LDV and HDV, respectively. This may be a consequence of the high oxygen content of the fuel. On the other hand additional oxygenation may occur during fuel combustion."

P.33758,L.10-12: It is not clear in the sentence the role of ethanol in gasoline and ozone by this sentence alone, please make it clearer.

Reply:

We changed the respective part in the revised manuscript as follows:

"Despite an increase in the number of vehicles, the program resulted in an improved air quality with lower concentrations of carbon monoxide (CO), sulfur dioxide (SO_2) and coarse particles (with diameters between 2.5 and 10 µm), as shown by Carvalho et al. (2015). Regarding the emission of fine particles ($PM_{2.5}$) and ozone (O_3), Pérez-Martínez et al. (2014) did not observe a decreasing trend. On the other hand, for ozone levels, Salvo and Geiger (2014) demonstrated a decrease by replacing gasoline with ethanol."

P.33758,L.23: This paragraph is disconnected from the rest of the text, please remove it or distribute it along the text where it would belong.

Reply:

We moved the discussion to P.33759, L13.

P.33758,L.28: Replace density by dense

Change made as suggested

P.33758,L.29: Remove "in"

Change made as suggested

P.33758,L.28 – P.33759,L.22: Please cut down these two paragraphs to the central question: What is the current knowledge of chemical-physical characteristics of vehicular emitted organic aerosols in Sao Paolo, and their role on urban pollution?

Reply:

We agree that this part should be cut down as suggested. In order to keep also the motivation for this study clear, we changed this part in the revised manuscript as follows:

"Due to its dense population, political and economic importance, the MASP has been in the focus of several studies that investigated the impact of vehicular emissions on the concentration and composition of particulate matter (Albuquerque et al., 2012; Andrade et al., 2012; Miranda and Andrade, 2005; Miranda et al., 2002), although only few publications focused on the organic part of the aerosols. In a study performed in 2008, Souza et al. (2014) estimated from OC measurements that around 26% of the $PM_{2.5}$ was composed of particulate organic matter. Recently, Brito et al. (2013) discussed the aerosol composition including OC and PAH in a tunnel study. They performed a chemical characterization of PM2.5 by separating the total mass into organic carbon, elemental carbon, and contributions from other trace elements. They concluded that the organic aerosol fraction estimated from OC measurements represented around 40% of $PM_{2.5}$ emitted by both light duty vehicles (LDV) and heavy duty vehicles (HDV).

Since the vehicular emission in Sao Paulo city is the main source for $PM_{2.5}$, it is of importance to distinguish the contributions from LDV and HDV. Different methods can be used in order to estimate the emissions from the vehicular fleet. Emission factors (EF) for gaseous and total $PM_{2.5}$ have been calculated based on tunnel measurements by Pérez-Martínez et al. (2014), showing that LDV emitted more CO than HDV, but much lower amounts of NO_x and PM2.5 ($EF_{PM2.5}$ of 20 and 277 mg km^{-1} for LDV and HDV, respectively). Nevertheless, no publication so far discussed the organic composition of aerosols formed from vehicular emissions.

We believe the main contribution of this work is to analyze the composition of organic compounds found in fine particles emitted by the transport sector in Sao Paulo, which has the unique characteristic of using bio-fuels on a large scale. Here, we discuss the composition of OA and EF of condensed organics from LDV and HDV, obtained from aerosol filter samples ($PM_{2.5}$) collected in traffic tunnels. For the first time, the TD-PTR-MS was applied to filter samples from Sao Paulo, where hundreds of organic compounds were identified to contribute to OA."

P.33760,L.11: It is missing a period between LT and TJQ.

Reply:

There was a typo, therefore the right sentence is now:

"The direction of the traffic in this tunnel alternated twice a day at 6 AM and 9 AM."

P.33760,L.18: it is missing the word "wind"

Change made as suggested

P.33771,L.12: Please combine this paragraph to the previous one.

Change made as suggested

New References

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