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.

Anonymous Referee # 2

Major comments:

Treatment of ambient data and background subtraction:

Overall the data appears to have high potential for yielding useful information, but the approach taken has serious issues. The greatest issue in this reviewer's view is the background subtraction method. First the authors discuss in a relatively vague way that previous studies have demonstrated that year-to-year variability of aerosol concentrations are consistent and that spatial variability is also low. They use this to justify subtracting an averaged value from their filter results. However, later in the manuscript they talk about potential issues related to the background subtraction such as in the final paragraph before section 3 and when discussing Figure 5, starting on line 13 of page 13. Furthermore, there are two types of backgrounds discussed which further confuses their arguments: the background for defining true EF values and that found during off-line analysis. This reviewer suggests that the authors discuss in more detail all the potential issues related to this background subtraction method including: 1) discussing variability of the 31 ambient air filters taken including total concentrations and chemistry and how these compare to the tunnel measurements, and 2) how the different meteorological conditions could affect PM concentrations and composition, especially since the ambient samples were taken during a different time of year as the tunnel samples. Some of these details could be provided in the supplementary information. The reviewer acknowledges that the authors only use the filters with the highest concentrations for LDV EF calculation in order to reduce background PM influences, however, this issue is brought up later in the manuscript which makes the overall discussion on background treatment seem scattered.

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).

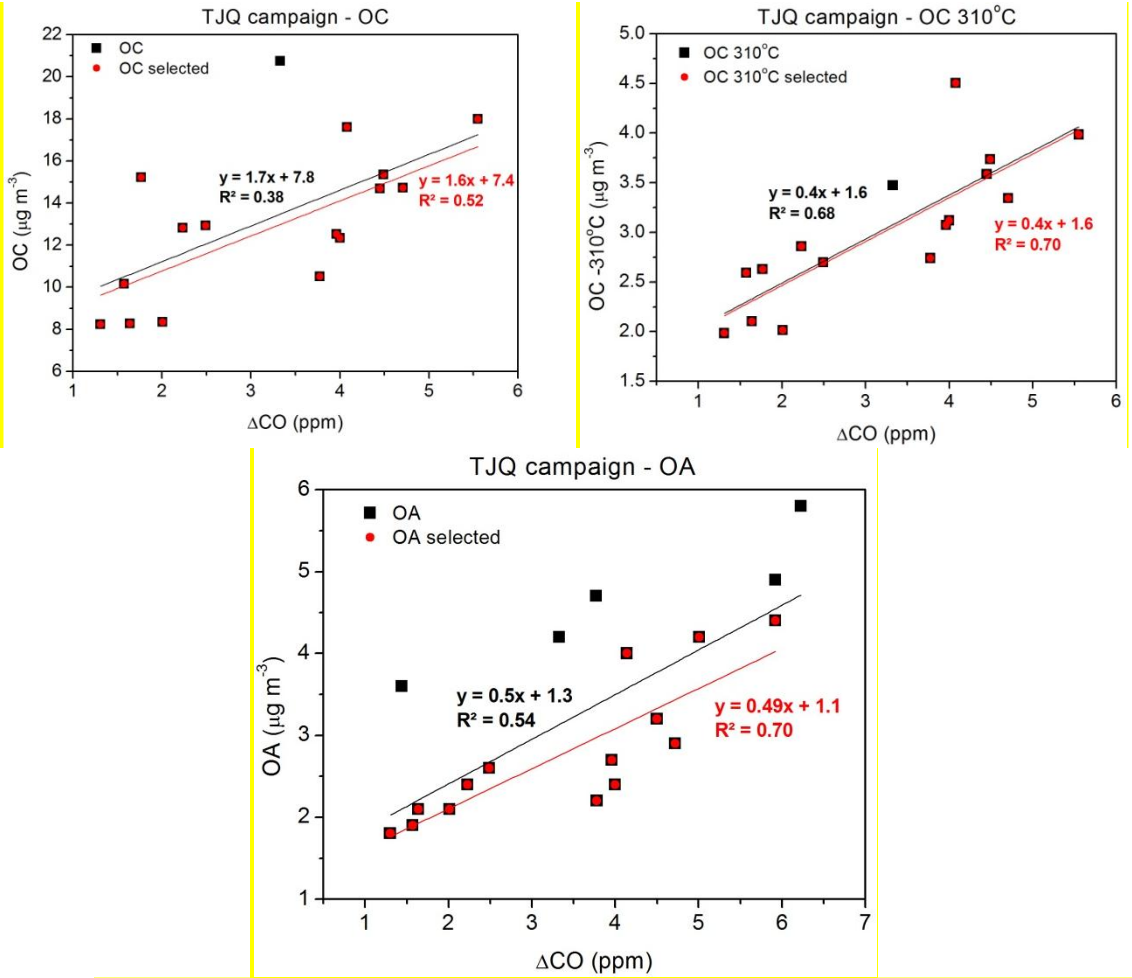

Figure S1 Comparison between ΔCO and OC. OC measured at 310°C and from 310 to 870°C, and OA for TJQ campaign. Black squares represent the whole data set used for the linear fit (in black letters), and red circles represent the data set excluding the outlier used for the linear fit (in red letters)

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	**OA**	**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."

Technical details of tunnel measurements:

One minor issue but which has implications on the EF discussion as well as the background subtraction discussion is the description of the measurement within the tunnel and the ventilation of the tunnel using outside air. It wasn't clear to this reviewer whether the ventilation brought in fresh air before or after the measurement location. A diagram in the supplementary would be very helpful for describing the method. As written the description was vague. Further details in related articles could not be found.

Reply:

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 continuously to provide fresh air to inside, therefore also during the sampling time. Furthermore, the vehicles running inside also contribute to the ventilation, the normal flows inside the tunnels were 4.9 (TJQ) and 6.1 m s^{-1}(TRA), and during congestion, these values decreased to 1.0 m s^{-1}, for both tunnels. In conclusion, even during the congestion periods, the fresh air from outside was still coming inside the tunnels, and consequently the background correction for emission factors calculation was still necessary.

EF of individual ions and PTR-MS:

Another major issue is the discussion of EF of individual ions. The analytical method used, TD-PTR-MS, could introduce some issues that are not discussed explicitly in this paper. Compound dependent ionization efficiencies would affect the quantification of the compounds identified. The authors would have to identify the original parent molecules that produce the principal ions presented in tables 4 and 5 and using standards identify their respective ionization efficiencies. This would facilitate a proper quantification for the purpose of EF calculation. That entails significantly more analysis and lab work. Alternately, the authors can discuss these issues openly and even quote some literature values for previously determined ionization efficiencies (using the same or similar technique and/or instrument) of important compounds identified here. Furthermore, the tracer identified for LDV (m/z 149.131 C11H16H+; pentyl benzene) is collocated with an ion discussed possible positive artifact (m/z 149.024 C8H4O3H+; phthalic anhydride). How well are these ions separated? What is the resolution of this instrument and what limitations exist in quantifying and identifying ions using this method? A close-up of the ions identified at m/z 149 would be helpful.

Reply:

As specified in the manuscript all concentrations were calculated according to the method outlined in Holzinger et al. 2010. We assumed a reaction rate constant of 3 x 10^{-9} cm^3s^{-1}, which implies the same sensitivity for all compounds. . This is a standard method for PTR-MS when complex mixtures of unknown composition are measured. Typical errors in the order of ~40% apply for individual species as discussed in Holzinger et al. (2010) and Timkovsky et al. (2015). The mass resolving power of the TOF was in the range of 3000-4000 (FWHM) for all measurements and the peak shape was near Gaussian. So, the peaks detected at 149.024

and 149.131 were well separated by more than 5 sigma of the normal distribution. We included this relevant information to the revised version of the manuscript.

PM Composition:

In Figure 4 the authors provide the fractional contribution of major ion types based on their elemental composition. One major result is that 20% of the composition is comprised of nitrogen containing ions. This is a huge value. A quick literature search showed that nitrogen containing molecules typically make up much smaller percentages of vehicle emissions. Although the authors provide one possible explanation, this reviewer feels that they do not go far enough in explaining this striking result. This could be an issue of improper background subtraction, effect of after-treatment devices, or it may indeed be something to do with biodiesel emissions. Because this result is so striking, the authors should provide proof that their identification of nitrogen containing ions is indeed sound. In the supplementary it would be useful to show the raw mass spectrum with ions fit showing that nitrogen containing ions unambiguously exist in their results. A discussion of information available in the literature on nitrogen containing components in vehicle emissions seems necessary. See for instance:

Inomata S, Fushimi A, Sato K, Fujitani Y, & Yamada H (2015) 4-Nitrophenol, 1-nitropyrene, and 9-nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas treatments. Atmospheric Environment 110:93-102.

Karavalakis G, Boutsika V, Stournas S, & Bakeas E (2011) Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAHand oxy-PAH emissions. Science of The Total Environment 409(4):738-747.

Suarez-Bertoa R, et al. (2015) Primary emissions and secondary organic aerosol formationfrom the exhaust of a flex-fuel (ethanol) vehicle. Atmospheric Environment 117:200-211.

Chirico R, P.F. DeCarlo, M.F. Heringa, T. Tritscher, R. Richter, A.S.H. Prevot, J. Dommen, E. Weingartner, G. Wehrle, M. Gysel, M. Laborde, and U. Baltensperger (2010) Impact of Aftertreatment Devices on Primary Emissions and Secondary Organic Aerosol Formation Potential from In-use Diesel Vehicles: Results from Smog Chamber Experiments. Atmospheric Chemistry and Physics 10(23):11545-11563.

Chirico R, et al. (2011) Aerosol and trace gas vehicle emission factors measured in a tunnel using an Aerosol Mass Spectrometer and other on-line instrumentation. Atmospheric Environment 45(13):2182-2192.

Reply:

Compounds with one N atom can typically be attributed without doubt – these compounds constitute about 50% of the mass of N-compounds. Compounds with two nitrogen atoms are more ambiguous and false attributions cannot be ruled out completely, because there is often an alternative CHO compound with a mass difference of only a few mDa. We wish to point out that despite the high relative fractions of N compounds the absolute emission factors are still high but not dramatically above other reported values. To account for the reviewer's concerns we added discussion showing that high levels of N-compounds can be understood:

" The high levels of NOx chemistry may be enhanced due to the use of bio-diesel in accordance with findings in other studies, such as Hoekman and Robbins (2012). They compared the emissions from conventional diesel to biodiesel and concluded that the reason for the high emission factor for NO_x in the biodiesel can be associated to the injection timing, ignition delay and other combustion process. The increase of NO_x emission when biodiesel is used is very variable according to the amount and type of biodiesel used. The use of exhaust gas treatment can decrease the nitrogen oxides emission but only a minor fraction of diesel vehicles uses exhaust gas treatments in Brazil, as the implementation of regulation for new heavy-duty diesel emissions is dated in 2013 (Euro 7).

Another important point of concern is that if the increase in the use of biodiesel can result in higher amounts of NO_x emissions the formation of secondary particles can also be increased. Rollins et al. (2011), in an original work, showed experimentally that nitrogen oxides affect the formation of organic aerosol production mainly at nighttime. Particulate organic nitrates formation increases at night with NO_x, and most nighttime secondary OA is due to NO_3 radicals, formed by anthropogenic NO_x emissions. Due to the absence of sunlight, the chemistry inside tunnels can be compared to nighttime chemistry. This may be another aspect explaining the high nitrogen content found in the tunnel samples as presented here."

Discussion of external influences on EF values:

The authors do not explicitly discuss effects of partitioning, meteorology or driving behavior on their results. In table 1, for instance, the column labeled OAb, which corresponds to *total OA as measured by the TD-PTR-MS, shows systematically higher values between May 4th and May 6th but there do not appear to be more cars overall and there does not appear to be more OC or higher concentrations of CO and CO2. This is interesting and yet is not addressed or discussed. It appears that external factors may be influencing their results. This would affect their EF calculations. If these issues have been addressed in other articles it would be useful to provide a brief description and provide a citation.*

Reply:

The sampling time between 04th to 06th May varied between 6 (morning), 3 (afternoon/evening) and 12 (night) hours. For the beginning of the campaign, the samples were collected during the peak of congestion (7-10 am, and 5-7pm, as presented by Brito et al., 2013) and then for 12 hours during the night. After 9th May, the sampling time was extended to 12 hours, including not only the two main peaks of congestion on the same sample, but also during periods with lower volume of vehicles. In consequence, the average concentrations are lower than when the sampling would have only been done during the congestion periods. In contrast, the amount of vehicles, shown in Table 1, represents the total vehicle number during the respective sampling period. Since the 12-hours-samples also include sample air during periods with no congestion, a correlation of vehicles to OA can potentially only be observed between samples with similar sampling times.

Overall impact of results and conclusions:

Finally, in discussing their EF results, the authors do not compare their calculated values to other regions. It would be useful to determine how comparable these EF values are to cities with perhaps similar or different fleet compositions. This could further the discussion on how fuel/fleet types affect air quality, making this paper more relevant on a global scale. Given that this journal is widely read internationally, discussing their results and the significance of their work in order to appeal to an international audience would make it more relevant to other readers. ***(PART I)***

One of the conclusions of this paper is that OA emissions from LDV and HDV are complex and dynamic and that "emission patterns can be used to study processing of young aerosol in ambient air." This conclusion seems out of place given that the authors don't explicitly discuss aerosol processing. The authors do discuss the elemental composition as a function of time of day, such as in Figure 5, however their discussion is brief and serves to justify limiting EF calculation to afternoon filter samples. Overall, the focus mostly appears to *be on defining EF. This reviewer would suggest organizing the paper to make the arguments more cohesive.* ***(PART II)***

(PART I)

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

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

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

Figure 6:

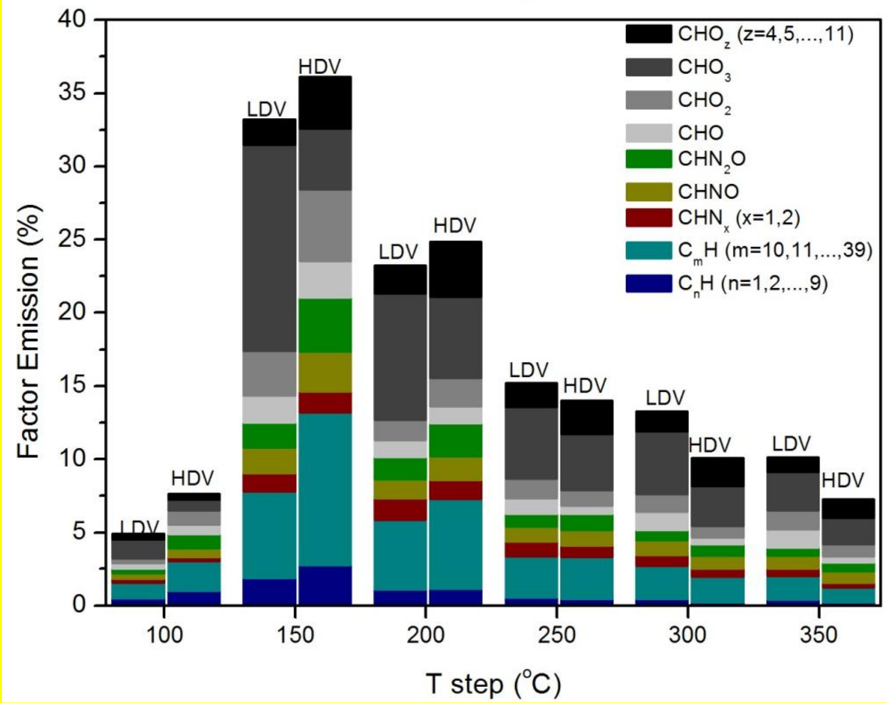

Figure 6: Fraction of total average emission (in %) divided into groups containing CH, CHO, CHON, and CHN, considering different numbers of carbon and oxygen atoms in the compounds, for LDV and HDV at each temperature step.

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."

<u>(PART II)</u>

We thank the reviewer for this suggestion and due to the restructuring of the manuscript; the mentioned part above was excluded from the content.

Technical issues:

There are a few technical issues such as improper method for including a citation within a sentence such as keeping the parenthesis while referring to the citation explicitly. For example line 9 of page 4 the citation should read "Carvalho et al. (2015)". There are a few issues with grammar that could be addressed but seems irrelevant compared to the larger issues discussed above.

We thank the reviewer for pointing some minor issues, and we changed them as suggested.

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