Answer to reviewer comments on “Vehicular emissions of organic particulate matter in Sao Paulo, Brazil” by Oyama et al.

We thank two anonymous referees for valuable comments and suggestions. We improved the language as requested by referee 1, and corrected all minor editing/typing issues that have been pointed out by both referees. Also we decided to slightly change the title to “Vehicular emissions and chemical characterization of organic particulate matter in Sao Paulo, Brazil”, which we find more appropriate. The remaining issues are addressed point by point below. The referee comments are repeated in *blue italic* letters.

Specific replies to Referee #1:

If one is to thrust the measurement and data treatment, which is sound, explaining outstanding results is a major scientific goal of this work. However, the discussion on nitrogen-containing groups on section 3 is somewhat loose (especially after being revised) and needs to be better constrained. As for the first hypothesis in L. 391-398, the large contribution of N-compounds can really be attributed to biodiesel use, even at that small percentage in diesel? How much higher was NO_x EFs compared to elsewhere? 2) Then, the authors claim that nitrate chemistry could produce SOA within the tunnel. As discussed elsewhere in the text OA in the TRA did not correlate well with CO. Did individual fractions (e.g. CH) present a good correlation with CO? Simple analysis in this line can shed a light into this important result and must be further explored to strengthen the manuscript.

Since the fraction of biodiesel is rather low, our dataset is not appropriate to fully explore the effect of biodiesel on the emission of nitrogen compounds. Therefore, we shortened and focused the discussion on nitrogen compounds:

“The nitrogen-containing groups contributed around 20% to the measured OA. Such a high percentage in the aerosol may be due to NO_x chemistry during the combustion process (thermal effect). Another production pathway for CHON compounds is facilitated by the absence of sunlight in the tunnels, which mimics nighttime chemistry. Several studies have shown that most nighttime secondary OA is due to NO_3 radicals formed by anthropogenic NO_x emissions (e.g. Rollins et al., 2011)). It is an open question to what extent the production of CHON compounds can be attributed to the use of bio-diesel, however, it is worthwhile to note that Hoekman and Robbins (2012) associated bio-diesel use with higher NO_x emissions."

As for correlations between CO and sub-sections of OA in the TRA tunnel, we wish to point out that they were all poor. Most likely this is due to the fact that most aerosols were emitted by diesel engines, which emit limited amounts of CO, whereas enhanced levels of CO in the tunnel were to the larger part associated with the gasoline driven vehicles in the tunnel (which contributed only minor fraction to the aerosol burden).

1. Abstract, L.26: "fine particles" is misleading towards number concentration, which is not the measured parameter. Please rephrase it to make it clear that it indicated mass concentration.

We replaced 'fine particles' by $PM_{2.5}$.

2. Introduction, L. 69 and L. 88: Salvo and Geiger showed an INCREASE of O3 by replacing gasoline with ethanol, please correct the article citation accordingly.

Corrected. Thanks for spotting this mistake!

3. Section 2.4: Not all LDVs are fueled with E25, as your fig.1 clearly shows. This means that assuming all LDVs are fueled with E25 introduces a bias. Please adjust your calculation using equation 5 and henceforth accordingly.

More than two thirds of the LDV run on E25, which can be estimated by the amount of fuel sold in Sao Paulo city in 2011 (National Agency of Petroleum, GNV and Biofuels, see http://www.anp.gov.br/?pg=79093&m=&t1=&t2=&t3=&t4=&ar=&ps=&1473870726611). We checked for sensitivities and found that a 35% fraction of E100 would result in ~10% lower and 3% higher emission factors for LDV and HDV, respectively (based on kg burned fuel). Both values are much smaller than the 20-30% uncertainty given in Table 3. For this reason, and because the real use of LDV fuel during the time of sampling is hard to estimate, we decided not to change the calculations.

4. Section 2.4 & supplement material: Please include the plots of OA x dCO for TRA in the supplement material as well, although linear fit is eventually not used.

Since the linear fits are not useful we prefer not to include them in the supplemental information. However, we are happy to share these plots in our answer to the reviewer's request:

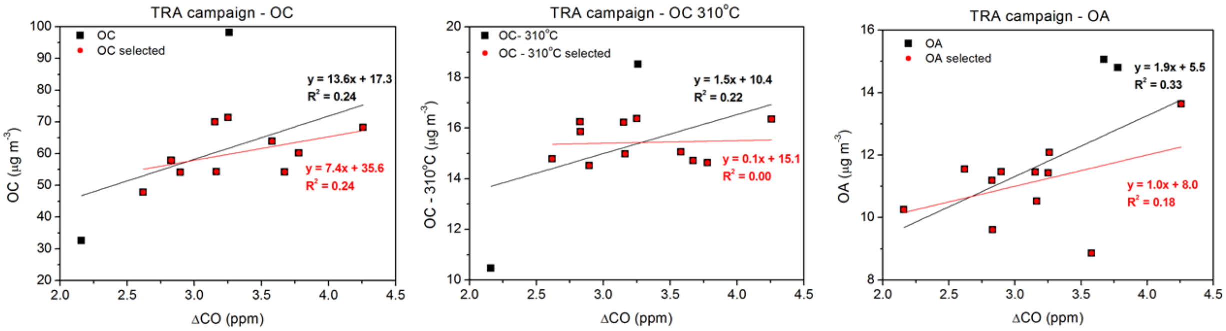

Figure S2: Comparison between ΔCO and OC. OC measured at 310°C and from 310 to 870°C, and OA for the TRA campaign. Black squares represent the whole data set, and red circles represent the data set excluding the outliers.

5. Section 2.4 & supplement material: If there is no other reason to use only a subset of the data (other than improving R2 by a little) to retrieve the background values, please use all data points. Also include the uncertainties of the background values (as a result of the linear fit).

As specified in the supplemental information we used a standard boxplot method to remove outliers from the dataset. We acknowledge that there are different opinions whether this should be done or not. However, as we pointed out in the SI, removing the outliers had a very limited effect on the linear fit (on both slope and intercept). Therefore we prefer not to change our analysis.

We decided not to provide an error analysis based on the quality of the linear fit – one important reason for this was the ambiguity concerning the outliers. We provided a sensitivity analysis instead that showed that the emission factors changed less than 5% if the background value is varied by +/- 50%.

6. Section 2.4 & supplement material: Background values seem reasonable for OC and OA, how reasonable are they for each individual ions? Please include in table S2 retrieved background values with uncertainty for indication on how reliable are calculated emission factors.

After careful consideration we decided not to include background values in table S2. In the supplemental information we define clear rules how the background is subtracted and the bulk sensitivity check (see above) showed that the background correction does not influence the results critically. Therefore we decided to demonstrate the large variability (typically much higher than the 5% uncertainty induced by background subtraction, see table S2) by giving the average, median, standard deviation, and the range of calculated EFs. We feel that providing background values and the uncertainty in background values would rather be confusing because the focus would be shifted towards a minor source of error.

Specific replies to Referee #2:

Line 35-36 (abstract): The authors say that "chemical processing close to the engine/tailpipe region is an important control on primary organic aerosol emission." Usage of the term "control" is a bit ambiguous. I'm not sure what exactly the authors are trying to express. Please clarify the sentence.

Sentence changed: '…chemical processing close to the engine/tailpipe region is an important factor influencing primary organic aerosol emission.'

Line 69-70: With regards to findings of Salvo and Geiger, it's not clear to me what you're trying to say. Is it a lab study? Did they replace gasoline with ethanol? Or are you saying that they found an overall decrease in ozone and they speculate this was due to replacing gasoline with ethanol? Please clarify.

We clarified the sentence: , Salvo and Geiger (2014) attributed lower ozone levels to a shift in fuel use from ethanol to gasoline, while CO and NO_x exhibited an increasing trend.

Line 278: In line 122 you stated that Perez-Martinez found LDV emitted more CO than HDV. That contradicts what you have stated here. Is there a reason the study mentioned earlier has different findings than the studies you cited in lines 278-279?

We changed the first statement to make it consistent with the latter statements. Actually, it is more appropriate to state that Perez-Martinez found similar CO EFs for LDV and HDV (5.8+/-3.8 and 3.6 +/- 1.5 g/km, respectively).

Lines 371-374: Was this ion seen in PM10 filter results? I believe this whole study is only for PM2.5 but in your methods you state that PM10 particles were collected.

Yes, the ion detected at m/z=149.024 was also prominent in the coarse fraction, constituting between 3-8 % of the total measured burden in these samples – perfectly in agreement with the idea that this species is related to tire wear/break use rather than being a product of engine exhaust.

Line 389: again, the use of the word "control" is misleading. Maybe you mean that it's an important factor. But this begs the question of what you mean by "chemical processing close to the engine/tailpipe region". I'm not sure if you mean the actual combustion process or that somehow emissions are becoming oxidized at the tailpipe. This statement is extremely vague and should be clarified. Try to find an appropriate citation from another study that discusses the mechanism that converts fuel to a more oxidized emission.

Sentence changed: " …chemical processing close to the engine/tailpipe region is an important factor influencing primary organic aerosol emission."

We added following sentence to acknowledge that other groups measured moderately oxidized primary OA as well:

"Our findings are in line with Collier et al. (2015) who measured high O/C ratios in primary organic aerosol from gasoline and diesel engines."

Lines 419-429: Did you try recalculating H:C vs O:C after performing a background subtraction in a similar fashion as you did for total OC using the ΔCO method? I would still expect that this type of subtraction could be done in order to remove influence from background components and hence determine the chemistry of the vehicle emissions without external influences.

We implemented the suggested changes and revised Figure 5. The new Figure 5 looks very similar, but, as expected, the values shifted towards higher H/C and lower O/C ratios. Most samples of both TJQ and TRA are in the range1.37-1.45 and 0.15-0.18 for H/C and O/C, respectively. However, there are a few more oxidized samples and most of these were collected in the TJQ tunnel during night.