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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vehicular emissions of organic particulate matter in Sao Paulo, Brazil" *by* B. S. Oyama et al.

Anonymous Referee #2

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The authors present results from analysis of vehicle emissions filter measurements with the objective of determining emission factor values for both light duty vehicles (LDV) and heavy duty vehicles (HDV) in the city of Sao Paulo, Brazil. The interesting aspect of this data set is that the on-road fleet profile is composed of vehicles using ethanol-gasoline blends as well as diesel with 5% biodiesel, making it a potentially unique emissions profile. Furthermore, previous studies in the city claim vehicle emissions have a very high impact on fine particulate matter. The method consists of sampling air inside two different tunnels, one of which is impacted mainly by LDV and an arterial tunnel that has approximately 30% HDV. At least two other publications have used results from this same field campaign but in this paper the authors focus on results from the chemical analysis of the quartz fiber filters. They use Thermal

Optical Transmittance (TOT) as well as Thermal Desorption Proton Transfer Reaction Mass Spectrometry (TD-PTR-MS) for their analysis. Some of their main findings include defining PM2.5 organic aerosol and organic carbon emission factors for LDV and HDV, identification of potentially unique chemical markers for LDV and HDV, and identification of the chemical properties of LDV and HDV. The authors conclude that HDV EF tends to be higher and contains more organic carbon by percentage. Furthermore, HDV emissions tend to be more volatile in the lower temperature ranges as demonstrated by the TD-PTR-MS data. Authors speculate that these results are important for providing needed tracers for better source apportionment of the two vehicle types, which may help local government agencies enact effective policies for air quality improvement.

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.

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.

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 as a 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.

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-PAH and oxy-PAH emissions. Science of The Total Environment 409(4):738-747.

Suarez-Bertoa R, et al. (2015) Primary emissions and secondary organic aerosol formation from 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.

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.

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.

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 33755, 2015.