

***Interactive comment on* “Time-resolved characterization of primary and secondary particle emissions of a modern gasoline passenger car” by P. Karjalainen et al.**

Anonymous Referee #3

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This manuscript characterises the primary and secondary particle emissions of a modern gasoline passenger car using a state-of-the-art set of instruments. The concept of the study is very good and attempts to provide a complete picture of the total particle matter produced from a modern gasoline car. However, the manuscript suffers from a number of serious limitations related, mostly, to the methodology of determining secondary particle formation and should not be accepted for publication in its current state.

Main comments: 1. What are implications for the findings of this study of the difference between exposing a given amount of VOCs to very high levels of oxidants in a very

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short space of time (10s of seconds) to that of exposing the same amount of VOCs to lower, atmospherically realistic levels of oxidants for a longer period of time (~a few days)? In other words, could the results of this study under conditions of fast and high exposure oxidant conditions be used to inform our understanding of what actually happens in the atmosphere? How does this affect the chemistry of the system?, what are the implications for SOA formation and its relevance to the atmosphere given the higher supersaturation in the PAM reactor and its effect on nucleation potential?. The manuscript should include a wider discussion of the effect of OH levels vs OH exposure on the results of this study.

2. The light source (185 and 254 nm) used in the PAM reactor is a very strong UV source, which is not representative of tropospheric solar radiation (mostly >300nm). Given the complex mixture of VOCs generated from combustion sources and the wide range of their chemical structure and that of the early generations of their oxidation products, what are the potential implications of the high energy, sub 300 nm UV radiation on the chemistry of this complex system?. Potential differences caused by using this UV radiation both on the absolute mass as well as the chemical composition of the formed SOA needs to be acknowledged and discussed. Would the reported SOA mass produced under these conditions be relevant to SOA formed from combustion sources in the troposphere?

3. The manuscript does not contain any discussion of the effect of losses of VOCs and particles to the walls of the PAM reactor and the potential influence of this effect on the reported results. According to Lamb et al., (2011), the elemental ratios and SOA formation potential were strongly affected by reactor design and operating conditions, with wall interactions seemingly having the strongest influence on SOA yield. This is clearly an important factor that should be discussed and clarified in the manuscript given that this it reports absolute mass concentrations of chemical species as well as their emission factors.

Other comments:

1. The exhaust sampling conditions need to be explicitly stated in the materials and methods section. For example, what was the dilution ratio of the exhaust during the reported experiments? What was the temperature of the dilution setup?
2. The conditions used in the PAM reactor should be explicitly stated. This should include specifying the PAM type used in this study (i.e. the 185/254nm or the 254nm only), the actual OH levels and the cumulative OH-exposure for these experiments should be mentioned or at least indicated. It is not sufficient to only state that the voltage of the two UV lamps was set at the maximum value of 190V (page 33259). In addition, the variability in OH levels or OH exposure during different stages of the experiment should be discussed given potential changes in PAM conditions as well as changes in the reactivity of the VOC mixture under different engine conditions.
3. The actual O₃ levels in the PAM reactor should be mentioned and their effect on suppressing reaction between Nitric Oxide (NO) and organic peroxy radicals (RO₂) resulting from the OH oxidation of VOCs and the potential influence of this suppression on SOA formation and composition should be discussed.
4. Have the reported PAM results been corrected for corrected for size-dependent particle transmission efficiency as shown by Lamb et al., (2011)? This should be clarified.
5. SOA produced in this study was reported to be higher or similar to that produced in two previous studies (Suarez-Bertoa et al., 2015; Platt et al., 2013). The authors did not provide sufficient discussion with regards to the conditions under which those two other studies were conducted; in particular, their light sources and oxidant levels assuming they also used reasonably similar gasoline passenger cars.
6. Does the version of the PIKA code used for the analysis of the HR-AMS data use the old Aiken et al., (2008) calibration method or the more recent updated calibrations by Canagaratna et al., (2015)? This has a direct effect on the reported O:C values and should be stated. Also, on a related note, what AMS collection efficiency value has been used for reporting the AMS mass? How was the corrections for gas phase CO₂

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applied to the AMS data to ensure that only particulate contribution to this m/z channel is reported.

7. The sulphate profile in Fig 5 appears to anti-correlate with the organic loading. I wonder if this is a real effect or an artefact with the AMS measurement given the known interferences between organics and sulphate at a number of m/z channels. I realise that this measurement was taken using an HR-AMS, where such effect could be avoided more easily compared to a unit resolution AMS, but I found the temporal trend intriguing!

8. The discussion regarding growth of nanoparticles during deceleration and their contribution to secondary aerosol formation (page 33269 form line 12) is not clear and needs re-writing in order to clarify the point of the authors. Where is the evidence referred to in this discussion about the real atmosphere?

Editorial changes:

Page 33255, line 25: change “on” to “to”

Page 33260, line 12: should be 600 oC

Page 33264, line 10: shouldn't this be Fig 4 instead of 3?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 33253, 2015.

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