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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Comparison of primary and secondary particle formation from natural gas engine exhaust and of their volatility characteristics” *by* Jenni Alanen et al.

Anonymous Referee #2

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Alanen et al. studied the secondary particle formation potential from natural gas engine exhaust using a potential aerosol mass (or an oxidation flow) reactor and concluded that the secondary particle formation was (i) substantially higher than the primary aerosol emissions, (ii) dominated by organic compounds but had significant contributions from inorganic compounds, (iii) dependent on the catalyst type and temperature, and (iv) lower than the secondary particle formation observed for gasoline and diesel vehicles.

The manuscript provides strong motivation for the study and the instrument- and analysis-related methods employed for this study are adequate. My concern with the methods is the operation and use of the oxidation flow reactor (see major comment (1)

below). The manuscript, for the most part, is well written and the results are robust. However, I am hesitant on accepting the manuscript for publication in its current form. I would like the authors to consider the following major and minor comments:

Major comments:

1. Operation and use of the oxidation flow reactor (OFR): I have two concerns surrounding the use of the PAM or the OFR. One, the authors have not examined the formation of secondary particles as a continuous function of the photochemical age, in contrast to previous studies. This is a problem because, as has been shown previously, secondary particle formation increases with photochemical age at low ages but eventually decreases (presumably from gas-phase fragmentation reactions and heterogeneous chemistry) at higher ages. Since the current study does not simulate this continuous evolution, it is unclear if the authors would have seen a pattern similar to that observed with other OFR studies. Do the authors have that data? Can the study be repeated at least for one of the engine load-catalyst conditions? More importantly, this creates the problem of comparing the data obtained in this study with other chamber and OFR studies (that have quantified secondary particle formation on at least a semi-continuous basis for photochemical age) and presents challenges in making conclusions about the natural gas engine (see next major comment below). Second, the authors have not considered known artifacts of using an OFR related to the loss of vapors to the OFR walls and accelerated chemistry (Palm et al., 2016) and the short residence times and small condensation sinks (Jathar et al., 2017) in an OFR that might not allow the oxidation products to condense as secondary particles (since the natural gas engine produced very few primary particles, I think this might be an important factor). All of these contribute to underestimating the secondary particle formation in OFRs, again affecting the comparison with chamber studies. A discussion of these effects and an attempt to correct for these effects will tell the authors if and how these artifacts could affect the results and conclusions. I would refer the authors to Palm et al. (2016) for methods to correct for these artifacts. In addition, a brief discussion of the

pitfalls in using the OFR (e.g., accelerated chemistry leading to multiple reaction steps in the gas-phase) and particularly its comparison to chamber data would be helpful.

2. Comparison with earlier studies: Based on the above comment, I have a few questions that center around the conclusions of this study: (i) can the results of this study at high photochemical ages (several days) be compared to chamber studies of gasoline and diesel vehicles performed over several hours of photochemistry (in my opinion, probably not)? (ii) how would the OFR artifact corrections change the comparison described in Table 2 (the Table could also add recent measurements made by Jathar et al., 2017 for diesel engines)? (iii) how confident are the authors in claiming that the secondary particle production from natural gas engines is quite small compared to gasoline and diesel engines, especially in urban areas where photochemical ages are low (0.5-1.5 days). (ii) how relevant are the high photochemical age results in this study to the atmosphere given that the there are other processes (e.g., transport, deposition) that are relevant at the same time scale? The operation of the OFR and the artifacts linked to the OFR do not allow for definitive answers to any of the above questions. This fact needs to be considered for the summary/conclusions from this work.

3. Style and phrasing: The writing, while detailed, needs to be paid more attention and the style and phrasing need to be improved throughout the manuscript. Here are just a few examples: (i) Page 11, line 30: ‘Although’ instead of ‘However, although’, (ii) Page 11, line 8: ‘remained similar at all catalyst temperatures’ instead of ‘remained similar in all catalyst temperatures’, (iii) Page 10, line 29: ‘waited’ instead of ‘was waited’, (iv) Page 7, line 6: ‘condense’ instead of ‘condensate’.

Minor comments:

1. Page 2, line 27: Is there a reference for the comment on diesel vehicles? Also, can this comment be made for other combustion/energy sources?

2. Page 2, line 30: May be use the word ‘oxidative catalyst’ to refer to the aftertreatment device?

3. Page 3, line 4: Is there a newer reference instead of Weitkamp for the last sentence? Examples: Gordon et al., 2014 or Jathar et al., 2017.

4. Page 4, lines 9-14: It would help if there was a brief mention of the size, horsepower, typical application, on- or off-road characteristics for the natural gas engine used.

5. Page 4, lines 15-24: What is the rationale for using two different aftertreatment configurations and the different temperatures? Is it based on the drive cycle expected for these engines? It is likely this fact is hidden in some of the earlier literature by the group but it would be beneficial to mention it here.

6. Page 5, lines 9-29: This is a novel application of the MCM to determine photochemical exposure given that exhaust reactivity can significantly suppress OH exposure. Peng et al. (2015) and Li et al. (2015) have developed empirical relationships to calculate OH exposure based on the mixture reactivity, residence time, and humidity in OFRs. Can the authors comment on why the method of Peng+Li was not used to calculate OH exposure? Or in other words, is there reason to believe that the MCM offers better predictions? Has the MCM output been evaluated against OH exposure measurements for an OFR application?

7. Page 5, lines 30-34: I am not sure I understand how the RH in the PAM chamber was as high as 80% when the clean dilution air (which was dry or 30%) accounted for 24 parts by volume to the exhaust. The mass balance on the water vapor does not seem to work out. The only way to explain the result is that water vapor is being generated in the PAM?

8. Page 6, lines 27-31: Subtraction of primary particle mass needs to be done when presenting the secondary particle production factors. For instance, SOA emission factors in Table 2. Do the authors know of the recent work of Link et al. (2017) where they examined photochemical production of inorganic compounds from light-duty vehicle exhaust? That might be another study to incorporate within the inorganic particle production discussion.

9. Page 7, lines 17-21: Long sentences beginning with ‘It is possible’ and ending with ‘into the atmosphere’. Consider breaking into multiple sentences.

10. Page 8, lines 14-18: Why isn’t the standard calculation of EF based on the CO2 concentrations and carbon intensity of the fuel, employed in this work?

11. Page 9, line 21: While I understand what the authors mean, ‘oxidated alpha-pinene particles’ is not correct.

12. Figure 2: The pie charts are too small. Please consider increasing them in size. Will the plots a, c, and d benefit from being in emission factor units?

13. Figures 5 and 6: Do the EEPS and HRLPI size distributions compare well with the AMS size distributions? Can the EEPS, HRLPI, and the AMS data be combined to provide a more complete picture of the size- and composition-resolved emission/production of particles?

14. Can the authors speculate on the species in the exhaust and photochemical mechanisms that can explain the secondary organic particle production?

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