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# ***Interactive comment on “Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber”***

**by S. M. Platt et al.**

**Anonymous Referee #2**

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## General Comments

This paper describes the characterization of a mobile smog chamber and its application to simulation studies of the atmospheric processing of emissions from a gasoline-powered motor vehicle. Typical characteristics of the chamber are described such as leak rate, particle losses and photolysis parameters. Two test experiments were performed at a dedicated vehicle emissions laboratory. The main finding from these experiments is that emissions from gasoline-powered vehicles produce significantly more secondary organic aerosol (SOA) than those fuelled by diesel.

Overall, this is a well written paper which describes a useful new facility for studying the

atmospheric processing of vehicle emissions. The characteristics of the chamber are reported adequately, although not in as much detail as for other reaction chambers (e.g. Wang et al., 2011 and Glowacki et al., 2007). The results from the test experiments are of high quality and are well presented and interpreted. However, the amount of new information reported here is less than that of a regular research article. It is also remarkable that no data were presented from the SMPS or PTR-ToF-MS instruments and only limited use of the HR-ToF-MS has been made. For example it would be very interesting to follow the evolution of the organic mass spectra in both the gas and particle phase as the primary emissions were being processed.

Ultimately this paper falls between two typical types; a regular research article and chamber characterization paper (e.g. Wang et al., 2011 and Glowacki et al., 2007), which might be more appropriate for a journal like Atmospheric Measurement Techniques. In my opinion, major revision - such as the inclusion and interpretation of data from SMPS, PTR-ToF-MS and HR-ToF-MS - is required to make this article suitable for publication in ACP.

There is also one point of major concern that needs to be addressed, as well as some major and minor comments.

#### Major Concern

Page 28353, lines 4-18: Here the authors outline the reasons why they added ozone and propene to the chamber containing the primary emissions. However, I am not fully convinced by their explanation and since the addition of these species clearly influences the reaction conditions and hence the amount of SOA formation, further clarification is required. Firstly, the addition of ozone in the dark will result in the conversion of NO to NO<sub>2</sub>, with the total amount of NO<sub>x</sub> remaining largely unchanged. Unfortunately, the amount of ozone injected into the chamber is not provided and it is therefore unknown if any NO is remaining at the start of the photolysis. The ozone mixing ratio shown in Figure 4 also does not help since it has missing data from this

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part of the experiment. However, soon after photolysis is initiated, the ozone mixing ratio begins to rise quickly, suggesting that the initial NO concentration is low. From 30 min onwards the amount of ozone is sufficiently high to indicate that the NO mixing ratio is negligible and that SOA formation is occurring under low-NOx conditions which are largely unrepresentative of urban environments. Moreover, evidence from smog chamber studies show that SOA formation yields are considerably higher under low-NOx conditions (than in the presence of NOx) and there is a serious concern that the amount of SOA formed in these test experiments, as well as the derived emission factors, are considerably higher than would be expected in ambient urban atmospheres.

There are also a number of other possible reactions that may occur following addition of ozone to the primary emissions in the dark; (i) reaction of ozone with alkenes, (ii) reaction of ozone with NO<sub>2</sub> to yield NO<sub>3</sub> radicals which in turn may also react with VOCs or with NO<sub>2</sub> to yield N<sub>2</sub>O<sub>5</sub>. Is there any evidence to suggest that these reactions are occurring?

Finally, the reason for adding propene is not clearly explained. Although it will increase the VOC/NOx ratio, it will also scavenge a large portion of the OH produced in the chamber, which implies that less OH is available to react with the other VOCs in the chamber. This is expected to result in lower SOA formation yields (Song et al, 2007).

Ultimately, the authors need to demonstrate that the reaction conditions employed in the test experiments are relevant for the derivation of organic aerosol emission factors

#### Major Comments

1. The procedure outlined for derivation of J(NO<sub>2</sub>) appears to be oversimplified. It relies on the assumption that a photostationary state is achieved. However, there are other possible processes that may need to be taken into account including the formation of NO<sub>3</sub> and its subsequent reactions, as well as wall loss of NO<sub>2</sub> and O<sub>3</sub> (Wang et al., 2011). Is a photostationary state really observed? i.e. do the measured mixing ratios of NO, NO and O<sub>3</sub> remain unchanged for a sufficient amount of time?

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2. The section describing the photolysis of HCHO (page 28360, lines 1-10) and its subsequent use in the validation of predicted photolysis rate constants is difficult to understand. It seems that the terms rate constant and loss rate (and their units) are mixed up and the numbers shown in Figure S3 do not appear to match those in the text. This section needs to be revisited.

#### Minor Comments

1. Page 28344, line 3: Should this be “emission” or “emissions”? This also appears at numerous points throughout the manuscript.
2. Page 28344, line 8: Change to “-7 to 25°C”. This also appears at numerous points throughout the manuscript.
3. Page 28344, line 9: The units for J(NO<sub>2</sub>) are incorrect and should simply be s-1
4. Pages 28344-28345: The Introduction section is a little repetitive and could be improved.
5. Page 28345, line 13: Change to “...or directly emitted, primary organic aerosol (POA)...”
6. Page 28345, line 26: Change to “...of 3.4 and 0.16 g kg<sup>-1</sup> were observed...”
7. Page 28346, line 3: Change to “...of 25.61 and 0.25 mg km<sup>-1</sup> were observed...”
8. Page 28346, line 4: As far as I can tell, Chirico et al. did not use EURO 4 fuels
9. Page 28346, line 5: Chirico et al. was published in 2010 and not 2012.
10. Page 28347, line 13: Should be “chamber”
11. Page 28349, line 26: What is meant by “...emissions’ hydrocarbons and aerosols”?
12. Page 28350, line 14 and 15: Was the NO gas 1000 ppmv in nitrogen?
13. Page 28350, line 16 and 17: How much ozone was injected?

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14. Page 28352, line 2: Insert space between number and units, e.g. 780 s
15. Page 28352, line 13: Toluene is not an alkane or alkene
16. Page 28352, line 27: Remove “as was”
17. Page 28354, line 4: Should be “sulfate”
18. Page 28354, line 29: Use full term “limits of detection”
19. Page 28358, line 9: The units for  $J(\text{NO}_2)$  are incorrect and should simply be s-1
20. Page 28359, line 13: Should it be “fig. 5b”?
21. Page 28362, line 9: Chirico et al. was published in 2010 and not 2012.
22. Page 28362, lines 14-18: This part is confusing and should be re-written
23. Page 28365, line 6: Overuse of “the”. Change to “Indicated in fig. 4 is the O:C ratio of POA and SOA determined. . .”
24. Page 28365, line 8: change “oxidisation” to “oxidation”
25. Page 28356, line 26-27: The first sentence of the conclusions section is an over-statement and needs to be changed.
26. Page 28369, line 13: “Krasenbrink”
27. Page 28369, line 28: “Journal of Medicine”
28. Page 28374: Abbreviation should be PTR-ToF-MS
29. Page 28377: The units for  $J$  are incorrect and should simply be s-1
30. Page 28377: Replace “>” with arrows
31. Page 28378: First line of the figure caption should be re-written, e.g. in a similar way to that in Fig. S1

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## References

Wang, J., Doussin, J. F., Perrier, S., Perraudin, E., Katrib, Y., Pangui, E., and Picquet-Varrault, B.: Design of a new multi-phase experimental simulation chamber for atmospheric photosmog, aerosol and cloud chemistry research, *Atmos. Meas. Tech.*, 4, 2465–2494, doi:10.5194/amt-4-2465-2011, 2011.

Glowacki, D. R., Goddard, A., Hemavibool, K., Malkin, T. L., Commane, R., Anderson, F., Bloss, W. J., Heard, D. E., Ingham, T., Pilling, M. J., and Seakins, P.W.: Design of and initial results from a Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), *Atmos. Chem. Phys.*, 7, 5371–5390, doi:10.5194/acp-7-5371-2007, 2007.

Song, C., Na, K., Warren, B., Malloy, Q., and Cocker, D. R.: Impact of propene on secondary organic aerosol formation from m-xylene, *Environ. Sci. Technol.*, 41, 6990–6995, 2007.

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