

Interactive comment on “Dual effect of anthropogenic emissions on the formation of biogenic SOA” by E. Kari et al.

Anonymous Referee #1

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The authors present a description of experiments in which a gasoline vehicle was run at constant speed and the exhaust was led into a chamber to perform photo-oxidation experiments. In addition, reference experiments, in which a biogenic model compound (alpha-pinene) was led into the same chamber together with NO_x and without NO_x, are presented. Finally, also experiments in which alpha-pinene and gasoline vehicle exhaust are led into the chamber together are presented.

Based on the experiments, the authors present results on the secondary aerosol formation process from both the vehicle exhaust and the biogenic aerosol precursors. Firstly, they present characterisations of the gasoline exhaust-produced SOA, and show that only a minority of the produced aerosol can be explained by precursors identified in the measurements, while the majority is produced from unidentified sources. Secondly, the

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authors show data with the purpose of showing two different mechanisms causing the secondary organic aerosol production from biogenic precursors to be lower when gasoline car exhaust is present. The first mechanism is the effect of NO_x on the emissions, which is expected as it has been seen earlier. The second effect is more novel, as the authors state that the anthropogenic VOCs change the reaction pathways, leading to lower yields.

I think that the experiments are very interesting and have been performed carefully, and the results are certainly of interest to aerosol scientists. However, I think that in the current form, the manuscript somewhat overestimates the magnitude of the second SOA suppression effect, and it is also lacking a more comprehensive discussion of possible other explanations that might cause the observed phenomena. There are several questions in relation to the evidence of the anthropogenic VOC effect that I think should be addressed before publication in ACP.

* from table 2 it seems that the NO_x values were clearly (70.2 vs 64.8 for the low-surface area and 72.1 vs 63.9 for more surface area) higher in the mixed cases than in the alpha-pinene cases, by a factor of 10% in the higher surface area case. In the latter case, the difference seems to be of the same order than the difference in the yields between the two cases. Although it is not certain whether the suppression of SOA formation caused by NO_x is directly dependent on the NO_x concentration, I think it should be explored whether the suppression could be caused by this difference.

* The difference between the high-NO_x alpha-pinene and the mixed case seems to be larger in the case of less initial particle surface. From the paper it was not directly evident whether there was formation of particles in the experiments (in addition to the existing seed particles). Is this the case? If yes, was there a difference between the different experiments in the number of particles formed? As this might change the dynamics of the gas-to-particle transfer, it would seem that the most relevant normalisation for the surface area (e.g. in Figure 5) would be the surface area at the time when the particles are being formed, i.e. during the time of the steepest increase in the yield

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in Figure 6. Would it be possible to produce such a figure, and is the result still similar (or even more clear) than when using the initial surface area?

* In figure 6, the second mixed experiment (which has a higher surface area) starts off slower but then reaches a higher yield than the other mixed experiment and even higher than alpha-pinene experiments (although the latter has a higher surface area). Is there an explanation for this anomalous behaviour (the other lines do not cross each other)?

* The different delay for the mixed experiments when compared to the alpha-pinene experiments seems a key issue to me. The authors state that wall losses of SOA-forming vapors are an issue that influences the SOA yield in the chamber. I would also think that some fraction of the injected alpha-pinene is lost to dilution in the chamber. Would it be possible to make an estimate of the magnitude of such loss processes of the precursors, and estimate if these could cause the differences in the yields?

* The authors call the new effect the anthropogenic VOC effect. There are also other compounds than VOCs in vehicle exhaust. Could it be possible that e.g. sulphur compounds or other such constituents could be the cause of the suppression?

* I am not convinced by the argument related to figure S5. For the mixed datapoint 5, I think it is evident that the mixed case produces less SOA than the combinations of vehicle and alpha-pinene measurements. However, for the data point 6, the authors choose a single comparison (points 6 and 21); however, one could as easily choose datapoints 20 and 6 and argue that actually the mixed experiment produced more SOA. I think that the purpose is to show that the mixed experiments lie on the lower edge of a 'line', but especially for the second experiment this does not fulfil the purpose, and I would either remove this figure or make it much more clear how it adds more evidence.

Based on these above points, I think that the claim of having found a dual effect of the anthropogenic emissions should be argued more convincingly. Especially the effect of the losses and potential sources for error, and also the effect of the different NO_x levels

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should be discussed. The presence of a compound in the mixed case that is not seen in the other cases is nice evidence of a changed chemistry, but the conclusions that can be drawn from the data points are still quite speculative and there is quite some doubt on the magnitude of the effect.

In total, the manuscript should possibly use a more careful wording, and maybe change the title to “Potential dual effect of...” Also, sentences that state that alpha-pinene oxidation pathways have changed in the presence of vehicle exhaust (e.g. in the abstract) should be reworded so that it is clear that this is speculation.

The following points should also be clarified:

p 13, line 7: “However, these SOA precursors were not detected by the PTR-ToF-MS, most likely due to sampling line and instrumental losses (Pagonis et al., 2017). “

It is my understanding that the PTR-MS is not really suitable to compounds that have lower volatilities in general, also partly due to the ionisation mechanism (see eg. Riva et al., 2019) This is not really reflected in this sentence; if it was mainly a loss issue, there could still be a signal that would in general be proportional to the concentration. This could be clarified.

p13, line 18; “Our results imply that the contribution of IVOCs and SVOCs to formed SOA is driving time dependent, at least when the modern gasoline vehicle is driven at constant load.”

To my understanding, there might also be other factors explaining the difference in a chamber experiment situation. SVOCs and IVOCs might be lost on the chamber walls at a different rate than VOCs; this is already implied in the section that my previous comment refers to. I think that the potential effects of wall losses should be discussed and maybe some reservation could be made in the text. Also, could a similar figure as Fig. 6 (with the amount of SOA as a function of the OH exposure) be shown to see if there is a difference in the ‘onset’ time of SOA formation?

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Reference: Riva et al., Atmos. Meas. Tech., 12, 2403–2421, 2019
<https://doi.org/10.5194/amt-12-2403-2019>

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