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 NOx and without NOx, 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 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 NOx 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.

We thank the reviewer for his/ her comprehensive and helpful comments. Below we answer point by point the questions and criticism raised by the reviewer.


* from table 2 it seems that the NOx 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 NOx is directly dependent on the NOx concentration, I think it should be explored whether the suppression could be caused by this difference.

Indeed, there was a difference in NOx concentration between different experiments, as our main target was to try to adjust VOC-to-NOx concentrations as well as possible. As the referee points out, there's no clear evidence showing that NOx concentration itself would affect the yield if the VOC-to-NOx ratios are equal. According to earlier studied comparable VOC-to-NOx ratios between the experiments is a critical factor in SOA formation (see e.g. Presto et al., 2005, Hoyle et al., 2011). We would like to point out that actually in the Pure α-pinene- High NOx experiments we had slightly lower VOC-to-NO$_x$ ratios than in Mixed experiments as shown in Table 2 (Pure apinene experiments: 4.6 - 4.8 - 7.5; Mixed 5.6 – 6.3). This should lead to slightly decreased α-pinene SOA mass yields in Pure α-pinene- High NOx experiments compared to Mixed experiments (Presto et al., 2005). The difference in VOC-to-NOx ratios are actually larger, than in NOx concentrations, hence we believe that the VOC-to-NOx ratio difference should dominate over NOx concentration difference and this should result in lower yield in Pure α-pinene- High NOx compared to Mixed experiments.

* The difference between the high-NOX 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 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?

There was a nucleation in the case of less initial particle surface. We did re- plot the Figure 5. using the surface area in the beginning of the SOA formation (see the Figure below). But as the steepness of the curves in Figure 6 are quite different between different experiments, it turned out to be challenging, to define the point that would physically correspond each other in different experiments. This resulted in large uncertainties of the initial surface area as can be seen in the figure below.

Figure also shows, that the similar trend can be seen in the replotted Figure as in the original Figure 5., so we decided to keep the original Fig, 5 in the manuscript.
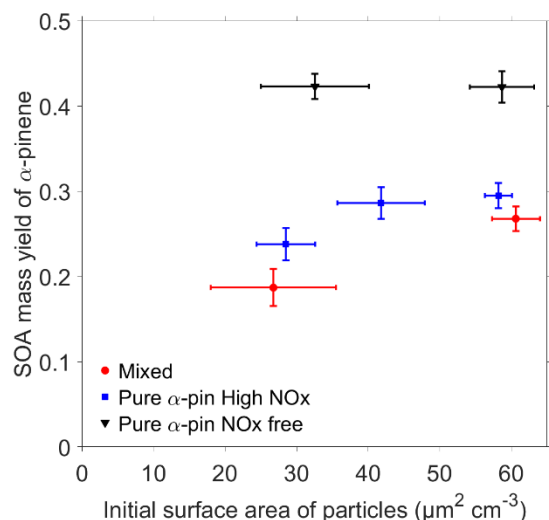
* In figure 6, the second mixed experiment (which has a higher surface area) starts off slower but then reaches a higher yield than the other mixed experiment and even higher than alpha-pinene experiments (although the latter has a higher surface area). Is there an explanation for this anomalous behaviour (the other lines do not cross each other)?

Yes, this is interesting point, and we tried to find an answer to this question already when analyzing the data. Unfortunately, we don't have a clear explanation to this behavior.

* 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 dilution effect should not affect the results, since we measured the α-pinene concentration inside the chamber by the PTR-MS. Hence the potential differences in the dilution reflects to measured α-pinene concentrations. α-pinene vapor pressure is so high (on the order of 10^4 µg/m3), that wall losses are negligible as shown e.g. in Kokkola et al., 2014. We would like to highlight that the chamber used in this study has larger volume-to-surface ratio than the one used in Kokkola et al. study, hence the wall losses are even smaller than those modelled and measured in Kokkola et al.

* 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?*

We did not detect Sulphur compounds in our experiments most likely due to the low concentration of SO_2 introduced into the chamber by the vehicle exhaust (see Table 2). However, we cannot rule out the possibility of Sulphur compounds contributing to the additional suppression of α-pinene SOA yields, but our data indicates that the main reason for this suppression (in addition to NOx) would have been anthropogenic VOCs. We are well aware that there might be other possible explanations for this additional suppression, and we are pointing out in the manuscript (for example page 18, line 32) that we cannot rule out other possible suppression mechanisms, given the limitations of the instrumentation used (and data obtained) in this study. We have now added a mention of SO_2 to the text. (page 20).

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 i much more clear how it adds more evidence.

Indeed, our point was to show that the mixed experiments lie in the lower edge of the line. We do agree with the reviewer that the figure is more confusing than informative. Hence we have removed the Figure S5.

Based on these above points, I think that the claim of a 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 NOx levels 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.

Taking into account our dataset and the underlying experimental uncertainties, we do agree that our presented results are only indicative, and hence we have reworded the parts of the manuscript that discuss about the dual effect of the vehicle exhaust on α-pinene SOA mass yields. We hope that these modifications make it more clear to the reader that the conclusions involve a certain degree of speculation and that more experiments are required in future studies to verify the suggested "anthropogenic" effect. We have also modified the title accordingly.

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.

The reviewer is right that PTR-ToF-MS is not the most optimal instrument to measure lower volatility compounds. However, the main reason for this does appear to be instrumental and line losses. As long as lower volatility compounds have higher proton affinity than water the ionization would take place in the ionization chamber (if it were not for those proposed losses). The line and instrumental loss issue with the PTR-ToF-MS was also pointed out by Riva et al. (2019) "*As discussed earlier, the inlet of the PTR-TOF is not well enough designed to sample OVOCs with low volatility, which explained the lack of correlations for larger and more oxidized products between the PTR-TOF and the nitrate CI-APi-TOF.*" In the same study Riva et al. were in fact able to detect a large range of OVOCs (relatively low volatile compounds), by using Vocus-PTR that uses proton-transfer ionization mechanism but employs a different type of inlet design, which minimizes the inlet line and instrumental losses. In addition, Breitenlechner et al. (2017) state in their publication that "Existing PTR-TOF instruments are known do detect VOC and could in principle also detect highly oxidized organic compounds such as LVOC and ELVOC but PTR-TOF-MS inlets were not optimized to avoid wall losses of such low volatility compounds. In addition PTR-TOF-MS is not sensitive enough to quantify second order and even higher order oxidation products at atmospherically relevant concentrations." (2017, Analytical chemistry) To solve this problem, Breitenlechner et al. developed the PTR3 instrument that (like the Vocus-PTR) is capable to measure low volatile oxidation products using proton-transfer-reaction chemical ionization method. Therefore, it is likely that instrumental and

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.

We agree with the reviewer that the loss rate of vapors may play a role here. We have now mentioned this 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?

Below we are presenting formed amount of SOA from a-pinene photo-oxidation as a function of OH exposure as reviewer suggested. The figure shows quite a similar behavior compared to Figure 6 of the manuscript (Fig 6 showed also below for comparison purposes). For example, the similar delay in start of SOA formation is observed.
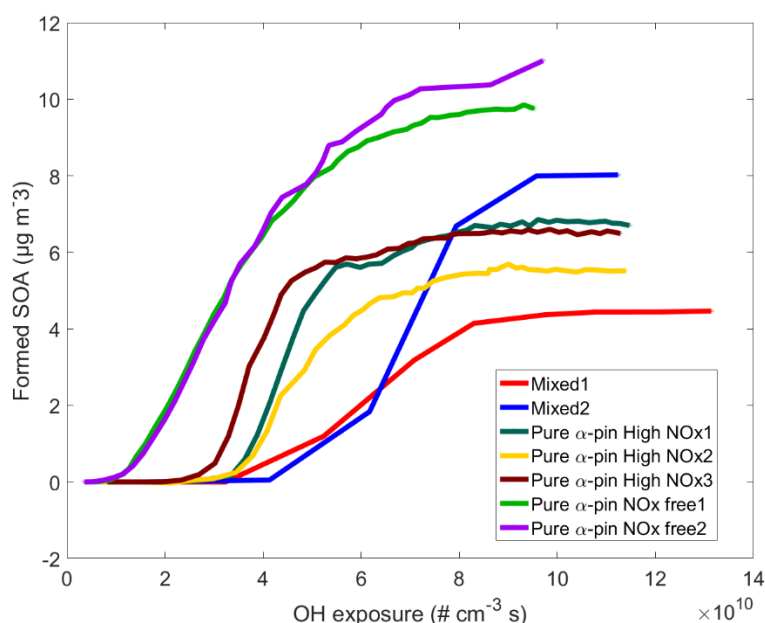
α-Pinene SOA as a function of OH exposure from all experiments
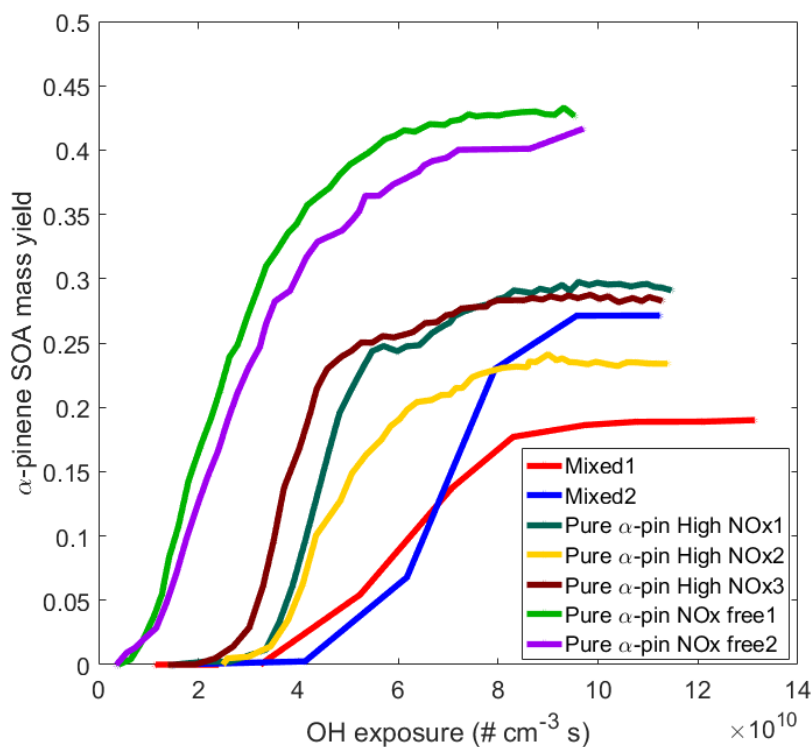
α-Pinene SOA mass yield as a function of OH exposure from all experiments (manuscript Figure 6).

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