

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

Anonymous Referee #2

Received and published: 22 July 2019

In this work, the authors characterise emissions from a modern GDI vehicle running at a constant load and investigate their SOA formation potential and their effect on SOA formation from α -pinene (used here as a model for biogenic emissions). The study concluded that the precursors measured by PTR-ToF-MS could only account for a fraction of the total SOA formed and concluded that lower volatility VOCs, not measured in this work, was likely to be a major contributor to SOA formation. It also reported a suppression of the α -pinene SOA mass yield when mixed with the anthropogenic emissions from the GDI engine and attempted to explain the main effects causing this suppression as “NO_x” and “anthropogenic” effects. The NO_x effect is clearly demonstrated through the set of experiments conducted and presented and it is consistent with what is known and reported in the literature. However, the “anthropogenic effect” reported by the au-

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thors is not sufficiently supported by the data presented in the current manuscript. The evidence for this interpretation is weak and not convincing given the limited number of mixed experiments and the lack of consistent results in Figure 4. The further reduction in α -pinene SOA mass yield is only shown for one of the two mixed experiments. The effect is not observed for the second mixed experiment compared to the pure α -pinene high NO_x results. Although the authors attempted to attribute this to the effect of the initial surface area of particles, the surface area influence does not appear to be evident in the pure α -pinene NO_x free experiments and in two of the three pure α -pinene high NO_x experiments. Additionally, the effect of competition for oxidant in the mixed experiments has not been discussed as a potential reason for the changes observed in these work. As the “anthropogenic effect” is presented as one of the key “dual” effects of mixing anthropogenic and biogenic precursors, the current manuscript should not be accepted for publication in ACP in its current state and major revisions should be made to re-interpret the main findings before it could be considered for publication.

Specific comments:

Page 2, 13: most of our knowledge, to date, on the detrimental effects of aerosols on human health is related to PM_{2.5} or PM₁₀ based on epidemiological studies. The effect of individual chemical components or classes is very plausible and often speculated on but it has not been yet fully established. Mixing the effect of SOA with the effect of total aerosols is a common practice but should be corrected until further evidence is established.

Page 2, 20: comment on the fuel sulfur content used in this study. This is also mentioned again on page 10 and should be qualified there too.

Page 5, 28: Specify the light characteristics during this work. The total actinic flux and photolysis rates of NO₂ and O₁D should be stated.

Page 6, line 32: elaborate on what is meant by “atmospherically relevant VOC/NO_x ratios” reported in this study, Are the numbers in Table 2 based on the amount of VOCs

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measured by the PTR for a specific number of compounds?. As discussed in the manuscript, these are only a subset of the total VOC present. This should be clarified in the manuscript.

Page 7, line 4: justify the choice of adding 5ppb of α -pinene in relation to the amount of AVOCs available from the emissions in terms of their potential to compete for the oxidants available. A quick calculation based on numbers in Table 2, indicate that the total VOC available in the experiments ranged from around 180 to 560ppb.

Page 7, 25: The Hao et al., method used for particle wall loss corrections assumed that particle wall loss rate constant is independent of size. The effect of size-resolved loss correction on total mass and SOA yield should be evaluated and reported.

Page 7, section 3.2.2: This approach adopted in this section is very simplistic and assumes that the SOA formation is an additive process and it ignores any potential non-linear interactions such as competition for oxidant or effect on product yields as recently demonstrated in McFiggans et al., 2019. Although some of these effects are later referred to in the text, stronger emphasis should be made earlier in the paragraph on these potential effects and the purpose of this analysis should be stated more clearly.

Page 11: section 3.1 appears to attempt to comment on the composition of the gas and condensed phase of the GDI exhaust. However, the supporting figures do not really support the overall message of the paragraph. The section needs more discussion including wider engagement with the relevant literature. The section lacks clear quantitative observations. For example, the statement made on line 15 of page 1 is not really supported by the data in the Figure or in table 2. I suggest that initial values for BC and organic matter should be included in Table 2.

Page 11, 17: Table 2 does not reflect the NO_x emissions from the engine as it appears to report the values after the addition of ozone and NO₂ top up as stated in the text. Therefore, the statement about “significant” amounts of NO_x from the GDI engine cannot be made based on this data.

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Page 11, 19: quantify what you mean by atmospherically relevant NO₂/NO and VOC/NO_x ratio and link it to a specific type of environment.

Page 11, 29: elaborate more on what you mean conditions were similar to Barcelona or Rome!. This statement appears “out-of-the-blue” and is not supported.

Page 12, 7: The statements made about SOA and POA in pure vehicle exhaust experiments need to be supported by data. These should be presented in a table or in a summary plot.

Page 12, 12: the classification of “high NO_x” experiments should be placed within the context of what has been discussed in the literature of high/low NO_x conditions. This should not be based only on the absolute amount of NO_x as it should take into consideration the VOC/NO_x ratio. As it stands, the definition used in the manuscript can be confusing or misleading when thought about in the wider context of the literature on high/low NO_x experiments.

Page 12, 14: This statement is not really supported by the data shown in the figure 3. The formation of O₃ and titration of NO appeared to happen almost immediately after lights on and SOA build up didn't take very long at all to begin.

Page 18, 11: what is the source of ammonium nitrate in these experiments?

Page 18, 14: Ratio between 1.5 up to 3 for NO₊/NO₂⁺ is quite typical of ammonium nitrate depending on which AMS instrument is being used. The ratio for organic nitrate is typically larger than 5. The presented data show a very limited evidence for the formation of organic nitrate.

Editorial comments:

Page 3, 4: change “that” to “the”

Page 3, 9: change “affects greatly” to “greatly affects”

Page 3, 19: delete “an”

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Page 3, 21: change “in” to “on”

Page 7, line 4: Express the 3 ul of butanol in ppb similar to what has been done for a-pinene

Page 8, 19: add model and manufacturer for the PTR

Page 9, 13: specify the instrument’s resolution

Page 9, 30: delete “in the campaign”

Page 9, 30: change “switched” to “switching”

Figures 2 and 3 should be improved. They are currently of poor visual quality.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-330>, 2019.

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