

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 authors 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 Fig. 5. 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.

The effect of seed surface concentration on SOA yield has been thoroughly discussed and shown in previous studies e.g. in Zhang et al., where this was demonstrated both by experimental data and theoretical approach. Also in our previous paper (Kari et al., 2017) we have shown by measurements a clear influence of seed surface area on α -pinene SOA yield in the same chamber used in this study. Two out of the three data sets in Figure 5., shows an increasing trend in SOA yield with increasing seed surface area. The clarity of this effect is somewhat blurred due to variations in experimental conditions (which are contributing to our the fairly large error bars). E.g. in “pure α -pin high NO_x” (blue points in Fig. 5) experiments there was some variability in VOC-to-NO_x ratios resulting in less clear trend. The reason why “Pure α -pin NO_x-free” (black points in Fig 5) doesn't show an increasing trend in yield with increasing aerosol surface area is unclear, but we refer to the general experimental uncertainties related to the measurements. Taking into account both 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 concerned 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.

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.

The oxidant levels used in this study were high enough to ensure that we were not oxidant limited in the experiments.

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.

As indicated above, we have modified the title and rephrased the manuscript based on the criticism.

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.

Thank you for pointing this out. We have corrected this accordingly.

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.

We have reported the concentrations of SO₂ in each experiment in Table 2 of the original manuscript (now moved to new Table 3 in the revised manuscript).

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

The light characteristics were as follows: actinic flux was $9.5963 \cdot 10^{15}$ photons cm⁻² s⁻¹; NO₂ photolysis rate was 0.0035 s⁻¹; O₁D photolysis rate was $2.2130 \cdot 10^{-5}$ s⁻¹. We have added the information also to the revised manuscript.

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 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.

Atmospherically relevant VOC-to-NO_x ratio means the ratio observed in the real atmosphere that enables all radical branching channels to occur in smog chamber experiments similarly with the real atmosphere under certain conditions. The range for this ratio was taken from the review of Hoyle et al. (2011, ACP). VOCs were measured by FID to determine VOC-to-NO_x ratio prior to photochemistry period. We have specified this in Table 1.

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.

First 180 ppb to 560 ppb reviewer is referring to are actually ppb(C) values measured by FID (as shown in Table 2). Hence, these values are not directly related to VOC concentrations (for example 5 ppb of α-pinene corresponds to 50 ppb(C) as α-pinene contains 10 carbon atoms). 5 ppb of α-pinene was chosen based on the first pure vehicle experiments. We found out that the GDI vehicle emission introduced in to the chamber was comprised of approximately 2 ppb of PTR-ToF-MS detectable aromatics (the main SOA precursors from VOCs detected in this study) when the feeding time of the exhaust was comparable between Pure vehicle and Mixed experiments. Obviously vehicle exhaust contained other VOCs as well that did not contribute to SOA formation but were present inside the chamber and underwent photo-oxidation. Hence, 5 ppb of α-pinene was chosen to have biogenic model compound in a comparable level with the aromatics (SOA forming anthropogenic VOCs).

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.

The Hao et al. method was used to correct the mass loss of particles to chamber walls, which is widely used method (e.g. Hao et al. 2011 ACP, Presto and Donahue 2006 Environ. Sci. Technol., Pathak et al. 2007 J. Geophys. Res-Atmos.). In this method, we assume that the aerosol mass wall loss is first order and that the loss rate constant is independent of particle size. The loss rate was estimated using the last 2 hours of data of the measurements to make sure that SOA formation had stopped inside the chamber and therefore would not interfere the wall loss correction. As shown in the figure below, the fit of ln(V) vs time is excellent (R²=0.97), giving us confidence that the model assumptions of diameter-independent mass loss is valid for our data set. We have clarified this in the manuscript on page 7. Consequently, we think that we don't need to use an alternative method to correct particle wall losses suggested by the reviewer.

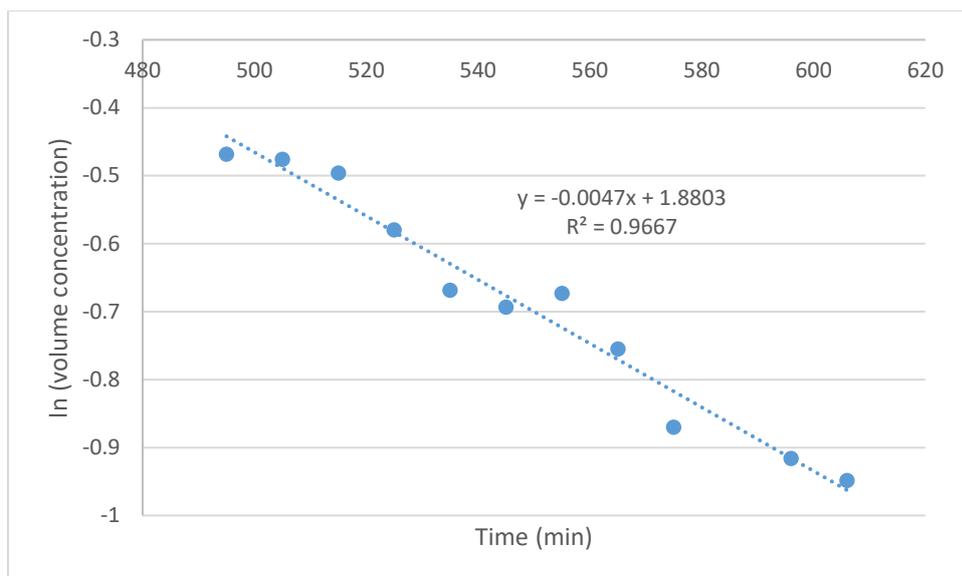


Fig. 1 Example how wall loss rate was determined. Example plot is taken from Mixed 2 experiment.

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.

We assume that the reviewer is talking about section 2.3.2. Reviewer is right that this approach is a simplified approach, but still the approach enables us to estimate within some uncertainty levels the formed amount of SOA from the identified SOA precursors. In addition, this kind of approach has been used in several previous publication (e.g. Du et al. 2018 ACP, Peng et al. 2017 ACP, Platt et al. 2013 ACP). Anthropogenic VOC mixtures and the potential non-linear interactions have not been systematically studied, and there is an obvious need for this kind of studies. We have now clarified the purpose of the analysis, and mentioned possible non-linear interaction, in the section 2.3.2.

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.

We have included the initial BC and organic matter values in new Table 3.

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.

We have added the NO_x concentration emitted by GDI vehicle to new Table 3.

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.

The ratios of 3-8 for VOC/NO_x ratios and 3-6 for NO₂/NO were applied in our experiments, referring to a typical suburban atmospheric environment (Seinfeld, 1991). We have added this to the revised manuscript.

- Seinfeld J.H., National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press.
<https://doi.org/10.17226/1889>.

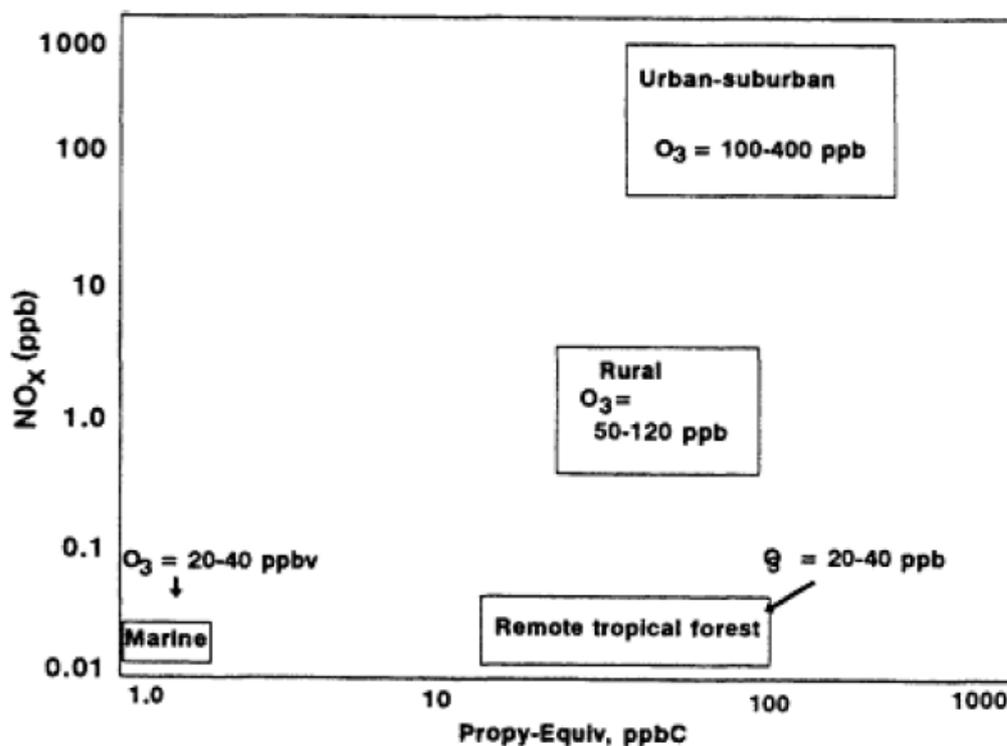


Figure 8-13
VOC, NO_x and ozone concentrations in the atmospheric boundary layer at four locations. VOC is shown as Propyl-Equiv concentrations in units of ppbcarbon.

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.

The purpose of this statement was to highlight that our experimental conditions were representative to conditions found from the real atmosphere. References after this statement include information about the conditions in Rome and Barcelona that support the statement. Even though it's a bit unclear to us what the referee pointing with this comment, we clarified the sentence.

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.

We have added this information to new Table 3 to the revised manuscript.

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.

We agree with the reviewer that the term “high NO_x” conditions should always take into consideration the VOC-to-NO_x ratio. We have discussed about this already in the original version of the manuscript

that different groups have defined high or low NO_x conditions differently and this affects predicted SOA reported in different studies (page 14). We have made the corrections to the manuscript as reviewer suggested (page 12 of the revised manuscript).

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.

It's not clear to us what the referee means by this comment, we state in the manuscript that "This additional reaction pathway causes the delay in the start of SOA formation as Figure 3 shows— SOA formation did not start until the most of NO had reacted." And this is clearly shown in Figure 3.

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

Ammonium nitrate was formed through the reaction of background ammonia (NH₃) in the chamber with nitric acid (HNO₃), which is produced in the photooxidation of NO_x.

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.

As stated in the manuscript, the NO⁺/NO₂⁺ ratio of ammonium nitrate is 1.46±0.02. After UV lights were switched on, the ratio monotonically rise to 2 in the α-pinene NO_x-free experiments and to 3 in the α-pinene high-NO_x experiments. The rising values of NO⁺/NO₂⁺ ratios in these experiments can't be interpreted by other reasons except for the formation of organic nitrates. We agree with referee that the ratio for organic nitrate is typically larger than 5. Hence, the values of 3 and 2 are measured as an outcome of mixed ammonium nitrate (lower NO⁺/NO₂⁺ ratio) and organic nitrate (higher NO⁺/NO₂⁺ ratio).

Editorial comments:

Corrected

Page 3, 4: change "that" to "the" Page 3, 9: change "affects greatly" to "greatly affects"

Page 3, 19: delete "an"

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 α-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.