Reply to reviewer #2

We thank the reviewer #2 for the helpful comments. We addressed all points raised.

Comments of Referee #2

The goal of this work is to explore the observed and documented suppression of SOA formation in the presence of NOx from previous studies. The authors hypothesized the observed decrease in SOA mass could be due to HOM termination reactions, in particular the reactions that form gas-phase accretion products or HOM organic nitrates. To test their hypothesis, they performed a series of chamber experiments at the Jülich Plant Atmosphere Chamber, a well characterized environment. They primarily used a Chemical Ionization Mass Spectrometer with NO3- ionization which has been repeatedly shown to be useful in measuring HOM, and studied the photooxidation of _and _-pinene. They found that HOM accretion products were much more heavily suppressed than non-nitrate monomer products in the presence of NOx. They determine this loss of accretion products is a possible and even likely reason for SOA mass suppression in the presence of NOx.

Section 4.4 discusses the suppression of accretion products but notably lacking is the possibility of precursor decomposition as a result of RO2 + NO (R7, page 3 line 24) forming an alkoxy which can rapidly decompose, resulting in smaller RO2 building blocks for accretion chemistry. This is brought up briefly on page 11 line 23, but is not worked into the discussion in section 4.4. It is however noted in the last sentence of the manuscript, only to say that it will be discussed in a further manuscript. This seems warranted to be discussed within this manuscript, and as-is I find it to be a major deficit of this work that should be discussed somewhere, potentially section 4.4.

Reply:

The referee is of course correct, reaction RO_2 + NO leads to alkoxy radicals RO. However, fragmentation is not the only reaction path of RO.

Alkoxy radicals can react with O_2 and under H-abstraction and formation of carbonyl compounds. If the alkoxy radical is a HOM-RO then the product will still contribute to SOA. However, reaction with O_2 is the major path for small peroxy radicals, although Finlayson Pitt and Pitts in their textbook listed substantial branching ratios for this path, p. 190)

RO radicals fragment often by α-scission. In ring systems, like the pinenes, this can lead to ring opening keeping the back bone intact. If the alkoxy radical that breaks apart is a HOM alkoxy and the larger fragment has 7, 8, or 9 C atoms, they could still contribute to SOA formation.

In addition, RO can rearrange very fast by H-abstraction forming an OH group and a radical, which can continue the radical chain. If the H is abstracted from a C atom, O_2 can add to the carbon centered radical and the resulting peroxy radical can continue autoxidation.

If H is abstracted from a hydroperoxide group, then the new peroxy radical will be formed in a unimolecular step. Both rearrangement pathways will contribute to SOA formation.

And autoxidation - maybe in combination with the alkoxy pathway - is fast, as can be seen by the high degree of oxidation of the detected HOM-ON.

The referee is correct that fragmentation of alkoxy radicals could lower the SOA yield, however, although fragmentation occurs this does not affect the condensable mass. This can now be seen in the modified Figure 3. We separated the total HOM into monomers and

accretion products and specified for the monomers the contribution of C_{10} compounds and $C_{<10}$ compounds as f[NOX]$_{SS}$. Figure 3 is limited to a mass range where compounds will condense according to our analysis (section 4.2, Figure 6). We assume that $C_{<10}$ compounds arise mainly from alkoxy radical decomposition. The importance of $C_{<10}$ compounds increases with NO_X, but they must carry more oxygen to get molecular masses larger than 230 Da, i.e.one O atom more per C atom lost. Therefore the $C_{<10}$ compounds will still contribute to the SOA mass. As a consequence, the major reduction of HOM mass at high [NOX]$_{SS}$ is due to the suppression of HOM-ACC, as can be seen in new Figure 3.
Our reference to a next paper dealing with alkoxy radicals in the conclusion section referred to the mechanistic aspects of HOM formation.

Action: We provided an extended Figure 3, and modified and extended the text in section 3.3 accordingly (p.12, line 26 –p.13, line12 in the revised manuscript). We further added text passages to section 4.4 (p.20, line 32 – p.21, line 6, in the revised manuscript) where we discuss the role of fragmentation via alkoxy radicals on HOM and SOA yield. We added one sentence to the conclusion section (p.23, line 23-25, in the revised manuscript).

Additionally, the grammatical errors throughout impede understanding of the manuscript and need significant improvement before publication.

Reply:
We apologize for that many mistakes and typos. We thank the reviewer for the careful reading of the manuscript and for the corrections. We went through the manuscript in order to improve language and grammar.

All in all, this work is novel and of interest to the readers of ACP, so after addressing these major concerns and the other minor technical edits detailed below this manuscript should be suitable for publication.

Page 1, line 33-35: This could also be due to the higher vapor pressure of HOMON relative to similar non-nitrates as you reference on page 17 line 26-27. Consider rewording to make clear you're basing this statement off the results in this paper.

Thanks for that hint. We clarified, that we are referring to our results of effective uptake of HOM-ON (p.1, line 33-35, in the revised manuscript).

Page 2, line 28: "the absence of particles in the presence of NOx": consider rewording. The presence of NOx doesn't mean there's no particles around.

Sentence modified (p.3, line 1-2, in the revised manuscript).

Page 5 line 28 – Page 6 line 7: It would be helpful to include the average or typical concentration of OH more clearly. It is state on Page 6 line 3 but it feels a bit buried and is a single value as opposed to the range stated for O3 and shown for OH in Fig.1. Furthermore, the range of O3 stated on page 5 line 13 does not match that on page 6 line 2. I would suggest adding the O3 and OH concentrations to Table 1.

Table 1 extended as requested.

Page 8, line 10: please justify ignoring wall loss by providing a reference for particle- wall loss rates on similar chambers, or a loss rate estimate from your measurements.

We added a reference to an earlier study: Mentel et al. 2009, lifetime of particles ≈ residence time of air in the chamber.

Page 8, line 25: what is meant by “molecules with finite vapor pressures”? Isn’t the vapor pressure finite with a given structure at a given temperature and pressure?

reformulated at both instances

Page 10, line 7-9: is Sp the surface area of the particles? Sentence starting with “Varying Lp(HOM)” is confusing, isn’t that relationship linear by definition? Consider rewording to replace the verb “led”, similar to the sentence on page 13, lines 11-12.

now: surface area added

We reformulated the passage according the suggestions (p.10, line 25-29, in the revised manuscript)

Page 11 line 16-17: the comment about the endo versus exocyclic bonds should either be explained and/or cited here, or be moved to the discussion section. Fig 2: Should note what these were normalized to as in Figure 4 caption.

Since we are referring to well-known properties of compounds with exocyclic and endocyclic double bonds, we will not move that to discussions. We reformulated the text passage.
The caption of Figure 2 was changed accordingly (p.12, line 7-17, in the revised manuscript)

Page 13 line 11-13: is this based on assumptions or was new particle formation observed? Consider rewording for clarity. Does loss to particles include loss to NPF in the correction?

The formation of new particle does not matter much for the uptake experiments themselves as long as the particle surface area is determined correctly. However, one needs particle free conditions to measure directly the reference c^0(HOM) at the same HOM production rate. The wall loss coefficient L_W can be determined at lower concentrations. Too low c^0(HOM) because of NPF will cause negative intercept in L_P vs. S_P plots like Figure 5. We modified the manuscript and explained more precisely what was done to determine c^0(HOM) despite of NPF during the non-seeded part of the experiment (p.10, line 31 – p.11, line 2, and p.14, line17-22, in the revised manuscript).

Fig 6: why does the C10H16O7-10 vary so much from the C10H14O7-10 & C10H16OxNO2 homologues in that oxygen range? Is it possible that the peaks are mis-assigned or contain multiple compounds? On page 13 line 22 it is stated that: “the potential to condense on particles was about the same for HOM-PP and HOM-ON”, however this is not entirely consistent with C10H16O7-10 in Figure 6?

We checked and the peaks are not miss-assigned. And yes, more than one compound can contribute to a given molecular formula. For example, a compound with molecular structure that causes very low vapor pressure could dominate the signal. We added a short discussion of that issue to the manuscript (p.19, line 4-5, in the revised manuscript).

Page 16 paragraph starting line 15: Where does the factor of 1/5 come from? Also, I find the distinction, or lack thereof, of OrgNO3 and ON confusing throughout the manuscript but particularly in this paragraph. Please clearly define the difference somewhere or use the same acronym throughout.

The factor 1/5 is the mass fraction of nitrate (NO_3-, 62 Da) in ON with an average molecular mass of 300 Da. We clarified that.
The referee is correct, there are places where $OrgNO_3$ and ON were mixed. Otherwise $OrgNO_3$ is a terminus technicus used by the AMS community and we would like to stick to it. We defined $OrgNO_3$ clearly in the AMS section, and underlined its importance as diagnostic quantity for linking particulate phase observations and gas-phase observations.
We went through manuscript and tried to clearer distinguish ON and $OrgNO_3$.We added a note to section 2.3 (p.8, line 16-17, in the revised manuscript), reformulated section 4.1. in large parts (p.18 line 2-15, in the revised manuscript) and modified the first paragraph of section 4.2 (p.18, line 22-23, in the revised manuscript).

Page 17 line 4-5 & 7-8: would be helpful to define HOM with respect to # of Oxygens or to define “few O-atoms” with a number. This could be defined on page 3, lines 13-14 or lines 33-34.

We specified the number of Oxygen numbers as requested
We added the definition of HOM in the introduction section (p.4, line 12-13, in the revised manuscript).

Page 18, line 9-10: do you see this higher SOA mass for NOx experiments relative to no-NOx? Has it been reported elsewhere?

This effect will be very difficult to determine. At SOA yields of 10-20% with 50% pON it would be a 1 % effect. It might be overlapped by effects of varying [OH] and the HOM-ACC suppression. It has thus not been reported elsewhere. More importantly, hydrolysis of ON in the particulate phase will probably mask the effect. That is what we tried to address.
We reformulated this part of the manuscript to indicate that the effect would be small (p.19, line 29-31, in the revised manuscript).

Page 18, 1st paragraph section 4.3: can you describe better what Zhao did and do a more complete comparison? As-is, it seems like you’re in perfect agreement that 10-11% of the OrgNO3 is in the particle phase, but then lines 18-19 says you’re not in agreement?

We added more information of the Zhao experiments (p.20, line 3-7, in the revised manuscript).
Zhao et al. find agreement between expected $OrgNO_3$ from HOM and observation in the particulate phase, whereas in our study we only realized 20-30% of the expected $OrgNO_3$

from HOM in the particulate phase. We expressed clear wherein the studies do agree and do not agree (p.20, line 8-10, in the revised manuscript).

Section 4.4: language could be formalized more throughout this section. “Mass loss” is a somewhat misleading phrase to mean converting potentially condensing species to non-condensable, not a direct loss of SOA mass due to, for example, evaporation. Please rework to be clearer and more streamlined.

Paragraph was reformulated in large parts. The notation mass loss was omitted, where possible. (p.21, line 5 – p. 22, line 8, in the revised manuscript)

page 21 line 12-13: please provide citations

references provided

References

Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y., and Wahner, A.: Photochemical production of aerosols from real plant emissions, Atmospheric Chemistry and Physics, 9, 4387-4406, 2009