Response to Reviewer #1

General comment

The authors present an interesting piece of work, regarding the partitioning of HOM (highly oxygenated organic molecules) and formation and fate of HOM in the particulate phase. With their setup they tried to compare the loss of HOM from the gas phase (what they somewhat unfortunately call condensed phase) with those they could detect in the particulate phase. For both phase they utilized NO_3-CIMS, equipped with a new VIA inlet for measurement of the particulate phase (Vocus Inlet for Aerosols), though. The VIA inlet essentially uses thermal evaporation to make the SOA components available to the mass spectrometer. Within their Teflon flow chamber the authors addressed a range of different chemical regimes with the purpose to achieve a range of products distributions and to verify particulate observations in response to the change of the actual chemical regime. Unfortunately, it is not clear (yet) how far the observations in particulate late phase are methodologically biased. Here the authors suffer from the usual problems of thermos evaporation and the quantitative transfer in into the mass spectrometer (and other instruments). Insofar it is not quite clear to me in how far we look at interesting and new results in SOA formation or at interesting artefacts of baking and loss of SOA components. I find also the modelling efforts a bit simple, but ok, they are not in center of the manuscript.

Nevertheless, I find that the results of the study are very interesting, and what is more important: the courageous approach is inspiring. I see to initiate discussions and new approaches also as part of good science. Of course, the authors did efforts to characterize the limits of their methods and very positively they discuss the limits quite openly and self-critical. They speculate but never do improper claims. Moreover, the paper is well written and well structured. The material is presented clearly and in a suited manor. The figures are dense however after some looking at them keep the important information together in one place.

Having all limitations in mind, I would still say this is a quite excellent piece of work. Therefore, I suggest to publishing the manuscript as it is in ACP.

The authors may consider my suggestions for slight improvements.

We thank the reviewer for the positive and insightful comments, and we answer the specific comments point-by-point below. The reviewer’s comments are in **blue**, and our answers are in **black**.

Specific comments

Comment #1:

I have questions regarding the shift from RO_2 regime to HO_2 regime:

Line 391/397: If you shift from RO_2 to HO_2 regime, wouldn't you expect that the different set of termination products in the gas-phase – more hydroperoxides - should affect also the particulate chemistry?

Response:

Yes. If the Baeyer-Villiger reaction played an important role in the particle phase to form dimers, then enhanced gas-phase formation of hydroperoxides, as the key precursors of the Baeyer-Villiger reaction, would result in enhanced formation of dimers in SOA. This hypothesis is supported by the experiment with CO addition— although dimers decreased largely in the gas phase, we still observed quite high dimer signals in the particle phase.

However, the changes in the chemical composition of the particle-phase HOM were not as significant as we expected (at least not as the changes in concentration mentioned above). One possible explanation might be that there was already a large amount of hydroperoxides condensed in the RO_2 regime. Converting more RO_2 to hydroperoxide monomers instead of forming ROOR dimers in the gas phase, would lead to enhanced condensation of hydroperoxides. These monomers have similar structures (and chemical properties) as the products from pure α-pinene ozonolysis. Thus, a higher concentration of hydroperoxides might mainly increase the formation rate of dimers and through similar pathways. Consequently, they end up as comparable dimer products.

Comment #2:

Line 400: The shift to more $C_{10}H_{16}$ compounds alone does not mean that autoxidation is hold by HO_2. Were the $C_{10}H_{16}$ compounds on average less oxidized than the $C_{10}H_{14}$ compounds they replaced?

Response:

The reviewer is correct that “the shift to more $C_{10}H_{16}$ compounds alone does not mean that autoxidation is hold by HO_2”. Instead of the argument we made— “the RO_2 autoxidation in some cases being outcompeted by HO_2”, it would be more appropriate to mention that “the RO_2 autoxidation and RO_2 cross-/self- reaction were shifted towards RO_2 and HO_2 termination reaction”.

The decreased RO_2 autoxidation is supported by the results in Figure S5 and Figure R1, showing that $C_{10}H_{14}O_{>7}$ compounds are in general less oxidized with CO addition. The decreased RO_2 cross-/self-reaction is supported by the results in Figure S5 and Figure 5, showing that the gas-phase dimers were largely decreased with CO addition.

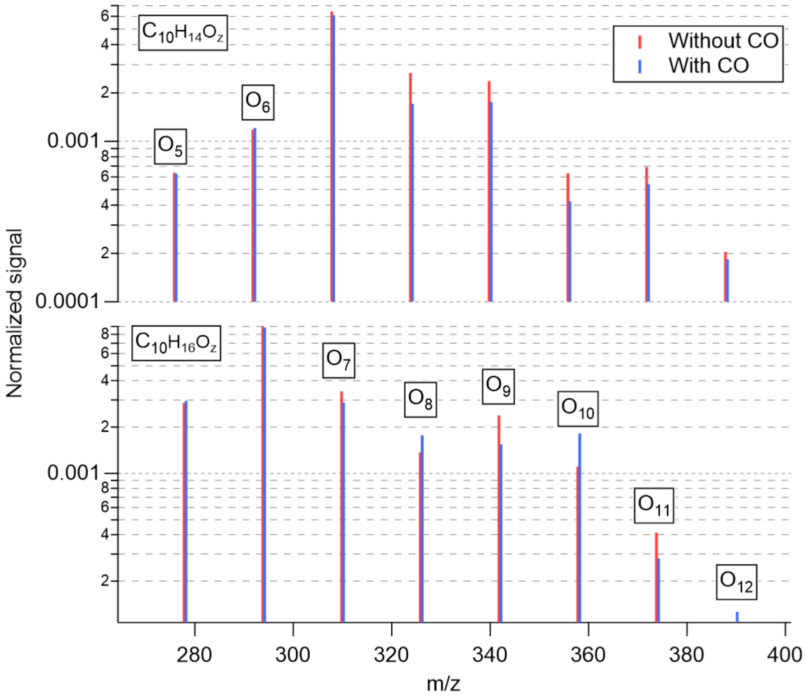


Figure R1. $C_{10}H_{14}O_z$ and $C_{10}H_{16}O_z$ compounds measured before and after CO addition in the gas phase.

However, if the “newly” formed $C_{10}H_{16}$ compounds are less oxidized than the “old” $C_{10}H_{14}$ compounds is complicated, since $C_{10}H_{16}$ compounds can be formed from both OH- and O_3-derived RO_2 through various uni-/bi-molecular pathways. 1) The increase of $C_{10}H_{16}O_{8,10,12}$ suggested that they might be formed through HO_2 and $C_{10}H_{15}O_{8,10,12}$, in particular the rapid increase of $C_{10}H_{16}O_{8,10}$ (Figure S5).

Otherwise, we would have observed decreases of $C_{10}H_{16}O_{8,10,12}$ if OH-derived $C_{10}H_{17}O_{7,9,11}$ dominated their formation. 2) $C_{10}H_{16}O_{7,9,11}$ decreased after CO addition, suggesting that either O_3 related RO_2-RO_2 pathway and/or OH related RO (carbonyl channel of two $C_{10}H_{17}O_{8,10}$ radicals) decreased. Thus, the average oxidation state of these $C_{10}H_{16}$ compounds with CO might be roughly comparable to the $C_{10}H_{16}$ compounds without CO and thus might be even more oxidized than $C_{10}H_{14}$ compounds (they are less oxidized). But there might be a point if we introduce an excess amount of HO_2, the entire RO_2 autoxidation could be really inhibited.

Overall, to make this point clear, we modified this argument to:

"Although $C_{10}H_{14}O_z$ and $C_{20}H_{30}O_z$ compounds were formed only through ozonolysis of α-pinene (Molteni et al., 2019), a general decrease was also observed, likely owing to the shift from RO_2 regime (i.e. RO_2 autoxidation and RO_2 cross-/self- reaction) to HO_2 regime (i.e. RO_2 and HO_2 termination reaction). The decreased RO_2 autoxidation is supported by the results in Figure S5, showing that $C_{10}H_{14}O_{>7}$ compounds are in general less oxidized with CO addition. The decreased RO_2 cross-/self-reaction is supported by the results in Figure S5 and Figure 5, showing that the gas-phase dimers were largely decreased with CO addition."

Typos etc.

Comment #3:

Line 43: I suggest to replacing "largest" by "most abundant" or so.

Response:

We changed "largest" to "most abundant" in the manuscript.

Comment #4:

Line 141ff: It is not clear if you use LTOF or HTOF MS. Are you connecting to an Eisele Inlet?

Response:

Yes, we used an Eisele Inlet and an LTOF MS. In order to make this clear to the readers, we added the following sentence in line 141: *"The NO_3-CIMS was equipped with an Eisele Inlet (Eisele and Tanner, 1993) and a long time-of-flight mass spectrometer, providing a mass resolution of ~8500 above 125 Th."*

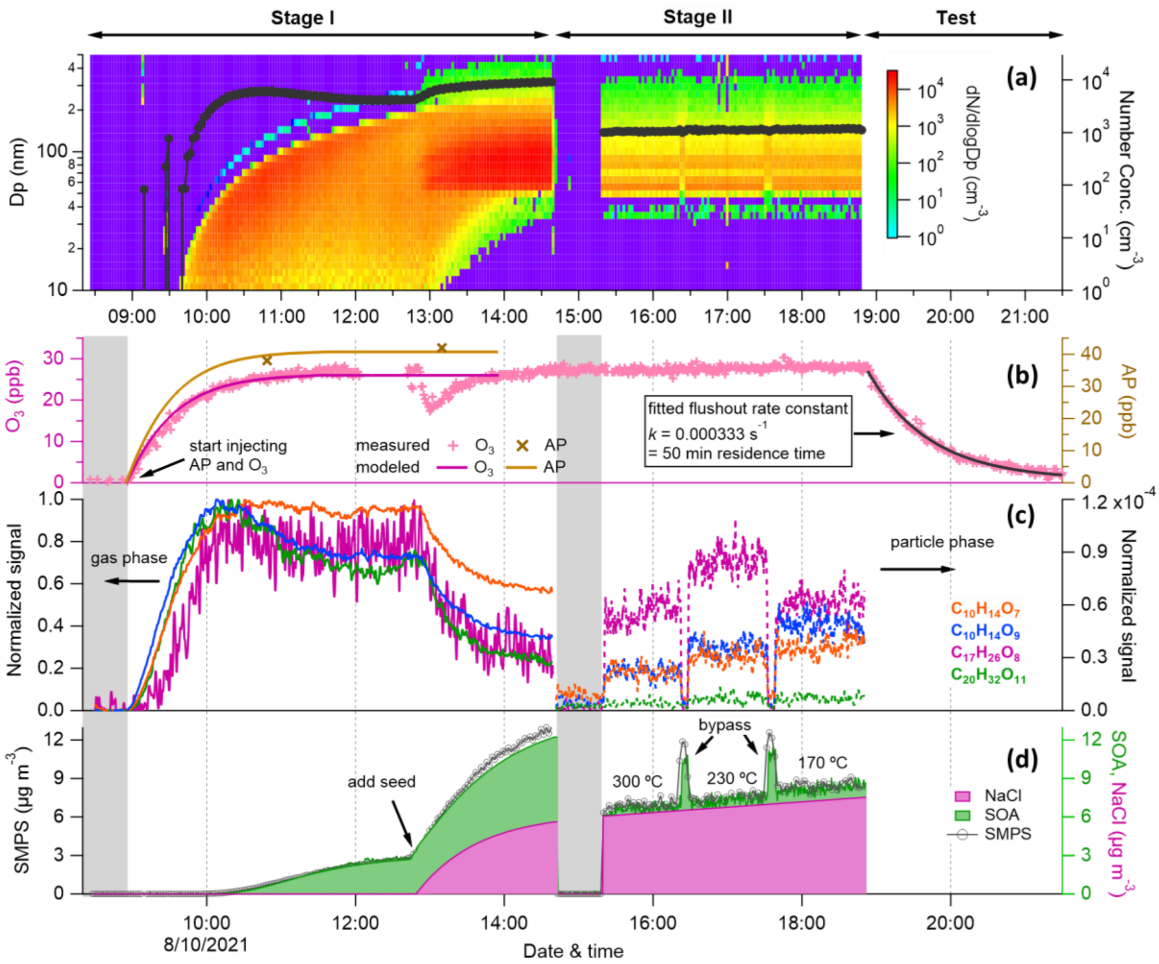
Comment #5 & #6:

Figure 2c: Were the raw signals normalized to reagent ions or total ion count. If not, why not?

Figure 2d: One could sacrifice the same scale as for the SMPS data and enlarge the data in right hand panel. Finally, you refer to details in this panel in the text.

Response:

The raw signals were not normalized to reagent ions or total ion counts. Although the signal of reagent ions was quite stable, we should have normalized the particle-phase measurements to the reagent ions. Thus, we made corresponding changes in Figure 2c. Also, we modified Figure 2d following the reviewer's suggestion. The updated Figure 2 is attached here and replaced the one used in the manuscript.



"Figure 2. Overview of experiment No. 1 (input flow with 53 ppb α-pinene and 33 ppb O_3). (a) Particle number concentration and size distribution sampled by SMPS as a function of time. Time series of (b) measured and modeled ozone and α-pinene concentration (1-min averaged) in the chamber, (c) gas-phase (solid lines, normalized to reagent ions at first and then to their maximums) and particle-phase (dashed lines, normalized to reagent ions) HOM species (10-s averaged), (d) total aerosol, organics, and sodium chloride mass concentrations from SMPS (2.2-min averaged, black circles) and AMS measurements (20 s averaged). The first and second shaded areas are gas phase and particle phase background measurements, respectively. Note that the time series of NaCl was estimated using the method explained in the supplementary owing to the lack of measurements, and no measurements given above were corrected for chamber wall loss."

Comment #7:

Line 192: I think that the logic of this sentence is somewhat odd. Or did you mean more volatile components decrease already at the "lowest" temperatures?

Response:

Yes, it may be the case that more volatile components decrease already at the "lowest" temperatures as the reviewer suspected. Based on our previous results by Häkkinen et al. (2022), we found that the sum of HOM monomers peaks at 120 °C.

Here, we were trying to convey that the temperature that was chosen for the measurements could largely affect the distribution of observed HOM compounds. Although we focused on the results obtained at

230 ^{o}C, which detects the largest fraction of SOA mass, higher temperatures may falsely "concentrate" dimers because 230 ^{o}C is not optimal for monomer measurements (lower by a factor of ~1 vs. 120 ^{o}C for monomers). This bias needs to be kept in mind when interpreting the particle-phase HOM mass spectra. In order to make this point clear, we rewrite this sentence as follows:

"However, as shown in Fig. 2c, larger molecules (C_{17} and C_{20} compounds) were found to evaporate more efficiently at 230 ^{o}C, while signals of more volatile molecules (e.g. C_{10} compounds) were already decreasing at this temperature. This effect, where the choice of evaporation temperature significantly impacts the distribution of observed species, is consistent with the previous results reported by Häkkinen et al. (2022) and needs to be kept in mind when interpreting the particle-phase HOM mass spectra."

Comment #8:

Line 214: I don't understand what you want to say here.

Response:

By showing that the nitrate dimer ($HNO_3 \cdot NO_3^-$) charged signals contributed only a small fraction to the total signal (4.3±1.5%), it would be safe 1) if we only focus on the HOM_{CHO} species in the experiments without NO_x addition, and 2) to assume that the N-containing HOM_{ON} species measured in the NO_x experiments were mainly formed through NO/NO_3 reactions instead of nitrate dimer changed HOM_{CHO} species. To make this point clear, we modified this sentence:

"Note that a relatively low contribution of nitrate dimer ($HNO_3 \cdot NO_3^-$) charged signals to the total signal (4.3±1.5%) was observed for α-pinene ozonolysis experiments. Thus, we only focused on HOM_{CHO} compounds in the experiments without NO_x addition and the HOM_{ON} species measured in the NO_x experiments were mainly formed through NO/NO_3 reactions instead of nitrate dimer charged HOM_{CHO} compounds".

Comment #9:

Line 450: There is probably not much NO left in the NO_3 case, therefore no termination with NO. "All" NO_X should be NO_2, or?

Response:

Yes, the reviewer is correct. In the NO case, photolysis of NO_2 was used to introduce NO into the chamber. On the other hand, in the NO_3 case UV lights are off during the entire experiment, thus all NO_x should be NO_2.

Comment #10:

Line 454: "Here", and "in this work" is redundant.

Response:

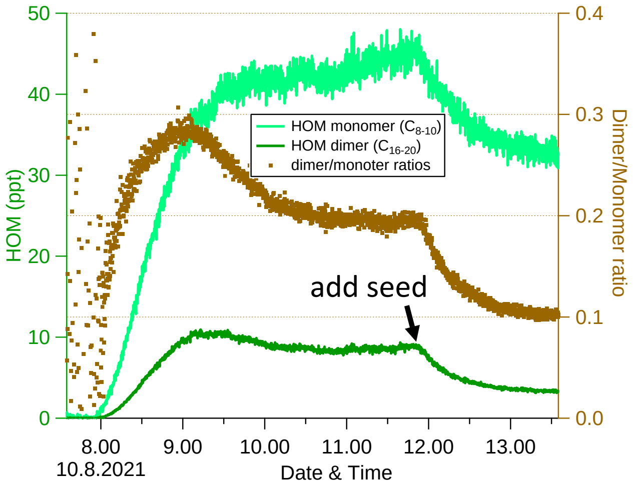
We deleted "Here" and left "in this work" in the manuscript.

Comment #11:

Line 473: Is Fig S7D correct here?

Response:

Yes, it is the time series of gas-phase HOM monomers and dimers as well as the dimer/monomer ratio during an experiment. Both the HOM monomers and dimers decreased after the addition of NaCl seed particles, but the relative change of the dimers was larger, and therefore the dimer/monomer ratio also decreased. The right y-axis may have been a little confusing, so we changed it to a linear scale.



"Figure S7. (d) Time series of gas-phase HOM monomers and dimers as well as the dimer/monomer ratio measured in experiment No. 1 (input flow with 53 ppb α-pinene and 33 ppb O_3)."

Comment #12:

Line 523: detected

Response:

We replaced "detect" with "detected".

Comment #13:

Line 536: "are" compared ?

Response:

We added "are" in front of "compared".

Comment #14:

Line 539: more in between O8 and O9 !

Response:

We changed "$C_{10}H_{15}O_8$" to "$C_{10}H_{15}O_{8-9}$".

Comment #15:

Line 621: much “shorter” ?

Response:

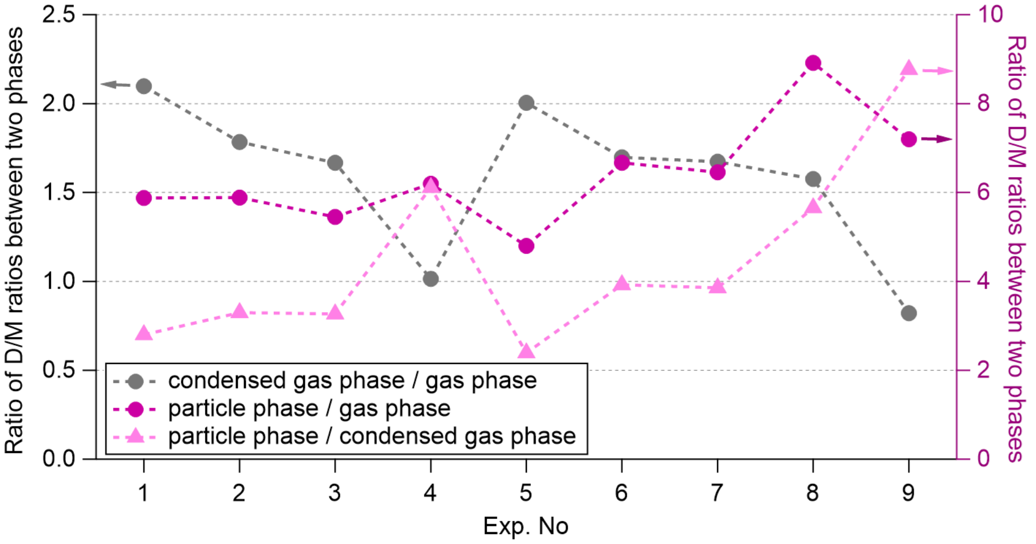
We replaced “short” with “shorter”.

Comment #16:

Figure S8: On which axis read the pink triangles?

Response:

The pink and purple markers share the right axis. We changed this figure to make it clear.



“Figure S8. Ratio of D/M ratios obtained between different phases (using the same dataset as used in Figure. 8c).”

Comment #17:

Table S2 and S3: The readability of these tables could be possibly improved by comparing only the same CxHy in one line, allowing for gaps where other methods did not find this class of compounds.

Response:

We changed Table S2 and Table S3 as below according to the reviewer’s suggestion.

“Table S2. Comparison of main particle-phase compounds (by α-pinene and O_3 reactions) identified by a NO_3-CIMS used in this work and other techniques. The chemical formula of main monomers and dimers are roughly listed according to their relative abundance in SOA (e.g. O numbers), if the concentration was measured/reported.”

This work	(Müller et al., 2009)	(Kristensen et al., 2020)	(Zhang et al., 2015)	(Pospisilova et al., 2020)
NO_3-CIMS	[a]HPLC/FTICR-MS	[b]UHPLC/ESI-qToF-MS	UHPLC/ESI-qToF-MS	[c]EESI-TOF

Monomer				
$C_{10}H_{16}O_{9,8,7,10,6}$	$C_{10}H_{16}O_{4,5,6}$	$C_{10}H_{16}O_{3,4,6}$	$C_{10}H_{16}O_{3,4,6}$	$C_{10}H_{16}O_{6,5,4,7,3,8}$
$C_{10}H_{14}O_{8,9,10,7}$	/	$C_{10}H_{14}O_{4,5}$	$C_{10}H_{14}O_{4,5}$	$C_{10}H_{14}O_{8}$
$C_{9}H_{14}O_{7,8,9}$	$C_{9}H_{14}O_{5,6}$	$C_{9}H_{14}O_{4,3,5}$	$C_{9}H_{14}O_{3,4}$	$C_{9}H_{14}O_{4,5}$
$C_{8}H_{12}O_{7,6}$	$C_{8}H_{12}O_{4,5,6}$	$C_{8}H_{12}O_{4,6}$	$C_{8}H_{12}O_{4}$	$C_{8}H_{12}O_{4}$
$C_{9}H_{12}O_{6,8}$	$C_{9}H_{12}O_{4}$	/	/	/
$C_{8}H_{14}O_{6}$	$C_{8}H_{14}O_{4,5}$	$C_{8}H_{14}O_{5,6}$	$C_{8}H_{14}O_{5}$	/
Dimer				
$C_{17}H_{26}O_{8,9,7,10}$	$C_{17}H_{26}O_{6,7,8}$	$C_{17}H_{26}O_{8,7,5,9}$	$C_{17}H_{26}O_{5,6,8}$	$C_{17}H_{26}O_{8,7}$
$C_{19}H_{28}O_{9,10,8,11}$	$C_{19}H_{28}O_{7}$	$C_{19}H_{28}O_{7,6,5,8,9}$	$C_{19}H_{28}O_{7,9}$	$C_{19}H_{28}O_{9}$
$C_{18}H_{28}O_{9,8,10,11}$	$C_{18}H_{28}O_{6,7,8}$	$C_{18}H_{28}O_{6,7,8,9}$	$C_{18}H_{28}O_{7}$	/
$C_{16}H_{26}O_{7,8,9}$	$C_{16}H_{26}O_{6,7}$	$C_{16}H_{26}O_{6,7,9,10}$	$C_{16}H_{26}O_{6}$	$C_{16}H_{26}O_{7}$
$C_{16}H_{24}O_{8,9,7}$	$C_{16}H_{24}O_{8}$	$C_{16}H_{24}O_{6,7,8}$	$C_{16}H_{24}O_{6,8}$	/
$C_{18}H_{26}O_{9,10,8}$	/	/	$C_{18}H_{26}O_{8}$	/
$C_{19}H_{30}O_{9,10}$	$C_{19}H_{30}O_{7}$	$C_{19}H_{30}O_{8,5,6,7}$	/	$C_{19}H_{30}O_{8}$
$C_{17}H_{24}O_{9}$	/	/	/	/
$C_{17}H_{28}O_{9,8}$	/	$C_{17}H_{28}O_{7,8}$	$C_{17}H_{28}O_{9}$	/
$C_{18}H_{30}O_{9,10}$	/	$C_{18}H_{30}O_{10}$	/	/
$C_{20}H_{30}O_{9,10,11,12}$	/	/	/	/
$C_{20}H_{32}O_{10,9,11,8}$	/	/	/	$C_{20}H_{32}O_{9,10,11}$

Notes:

[a] *HPLC/FTICR-MS: High-Performance Liquid Chromatography and Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry.*

[b] *UHPLC/ESI-qToF-MS: Ultra-High Performance Liquid Chromatography/Electrospray Ionization Quadrupole Time-of Flight Mass Spectrometry.*

[c] *EESI-TOF: Extractive Electrospray Ionization Time-Of-Flight Mass Spectrometer.*

[d] *Derivatization with 2,4-dinitrophenylhydrazine (DNPH).*

"Table S3. Comparison of particle phase N-containing compounds (by α-pinene and NO_3 reactions) measured by a NO_3-CIMS used in this work and other techniques. The chemical formula of main monomers and dimers are roughly list according to their relative abundance in SOA (e.g. O numbers), if the concentration was measured/reported."

This work, NO_3-CIMS		(Nah et al., 2016)	
α-pinene, monomer		[a]FIGAERO-I-CIMS	
lights off	lights on	b-pinene + NO_3	α-pinene + NO_3
$C_{9}H_{15}NO_{9,10,8,7}$	$C_{9}H_{15}NO_{10,8,9,7}$	$C_{9}H_{15}NO_{7,8,9,6}$	/
$C_{10}H_{17}NO_{10,11,12,9,8}$	$C_{10}H_{17}NO_{9,10,8,11}$	$C_{10}H_{17}NO_{8,7,9,6,5,4}$	/
$C_{10}H_{15}NO_{11,8,10,9,12}$	$C_{10}H_{15}NO_{8,10,9,11,12,7}$	$C_{10}H_{15}NO_{6,8,7,5,9}$	$C_{10}H_{15}NO_{6,9,5}$
$C_{9}H_{13}NO_{9,8,7,10,11}$	$C_{9}H_{13}NO_{9,8,7,10}$	$C_{9}H_{13}NO_{7,8,9,6}$	$C_{9}H_{13}NO_{6}$
$C_{10}H_{19}NO_{8,9,10}$	/	$C_{10}H_{19}NO_{5,6,7,8}$	/
$C_{8}H_{11}NO_{9,10,7,8}$	$C_{8}H_{11}NO_{8,7,9,10}$	$C_{8}H_{11}NO_{7,6,8,9}$	/
$C_{8}H_{13}NO_{9,10,7,8}$	$C_{8}H_{13}NO_{9,10,7,8}$	$C_{8}H_{13}NO_{7,6,8}$	/
$C_{10}H_{18}N_{2}O_{11,12}$	/	/	/
$C_{10}H_{16}N_{2}O_{12,13,14}$	$C_{10}H_{16}N_{2}O_{12,13,14}$	/	$C_{10}H_{16}N_{2}O_{7}$
/	$C_{10}H_{14}N_{2}O_{12,11}$	/	/
/	$C_{10}H_{13}NO_{9,8,10}$	$C_{10}H_{13}NO_{6,7,8,9}$	/
α-pinene, dimer			

$C_{19}H_{31}NO_{11,12,13}$			
$C_{19}H_{29}NO_{10,12,8}$			
$C_{20}H_{31}NO_{12,11,13,10}$			
$C_{17}H_{25}NO_{10}$			
$C_{17}H_{27}NO_{10,11,12}$			
$C_{18}H_{29}NO_{10,11,12}$			
$C_{20}H_{33}NO_{12,11,13,10}$			
$C_{20}H_{29}NO_{12,13,10,11}$			
$C_{19}H_{27}NO_{12,11,10}$			

Notes:

[a] *FIGAERO-I-CIMS: Filter Inlet for Gas and AEROsol – Iodide – Chemical Ionization Mass Spectrometer.*

Comment #18:

Table S3 header: listed

Response:

We replaced “list” with “listed”.

Comment #19:

Table S4: Not easy to read. It could help if you convert the references to symbols, which you list under the table and remove the line breaks in the columns with number ranges.

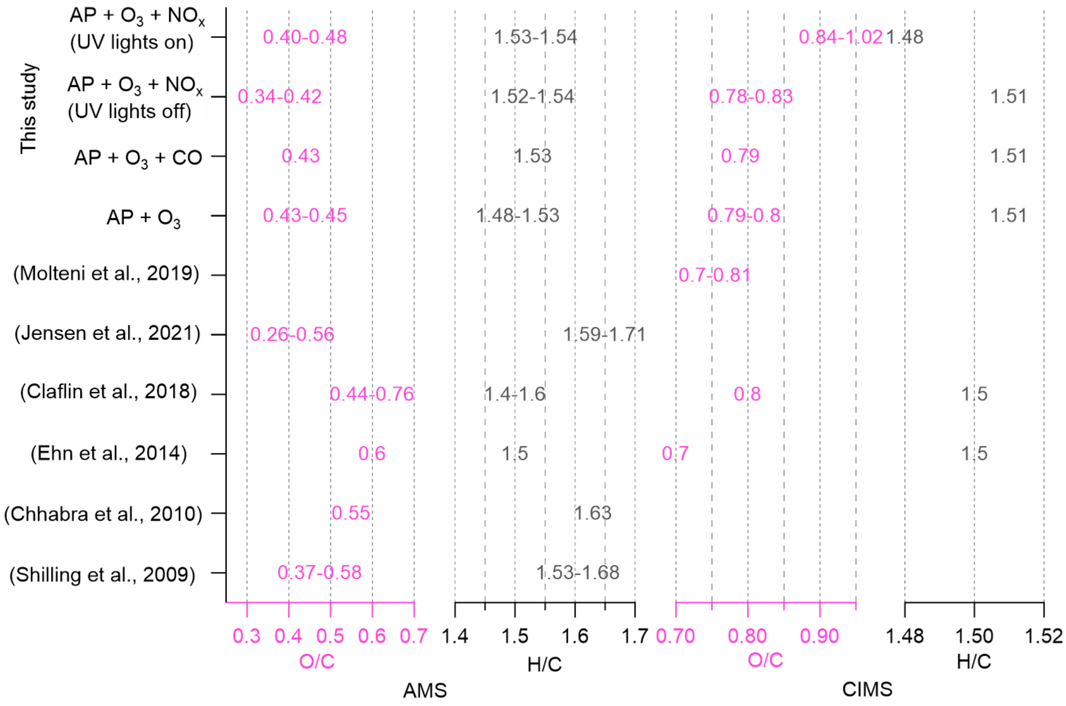
Response:

Thanks for the suggestion. We made some modification on Table S4 and made Figure S10 to clearly show the comparison between different studies.

“Table S4. Summary of elemental ratios of SOA and HOM (formed from ozonolysis of α-pinene under various conditions) measured in both the gas and particle phases.”

description	gas phase CI-APi-TOF		particle phase AMS				references
	H/C	O/C	H/C	O/C	SOA	method	
AP + O_3	/	/	1.38-1.51	0.29-0.46	0.5-140	AA	(Shilling et al., 2009)
	/	/	1.47	0.43	57-183	AA	(Chhabra et al., 2010)
	1.5	0.7	1.5	0.6	5-10	IA	(Ehn et al., 2014)
	1.5	0.8	1.4-1.6	0.44-0.76	/	IA	(Claflin et al., 2018)
	/	/	1.59-1.71	0.26-0.56	6-100	IA	(Jensen et al., 2021)
	/	0.7-0.81	/	/	/	/	(Molteni et al., 2019)
	1.51	0.79-0.8	1.48-1.53	0.43-0.45	3-15	IA	This study
AP + O_3 + CO	1.51	0.79	1.53	0.43	~10	IA	This study
AP + O_3 + NO_x	1.51	0.78-0.83	1.52-1.54	0.34-0.42	3-10	IA	This study (lights off)
AP + O_3 + NO_x	1.48	0.84-1.02	1.53-1.54	0.40-0.48	2-15	IA	This study (lights on)

“Notes: elemental ratios adopted from previous studies using the AA method (Aiken et al., 2008) were converted to IA methods by scaling an empirical factor of 1.27 and 1.11 for O/C and H/C ratios, respectively (Canagaratna et al., 2015), in Figure S10. SOA mass in above table was given in unit of ug m^{-3}*.”*



"Figure S10. Summary of elemental ratios of SOA and HOM (formed from ozonolysis of α-pinene under various conditions) measured in both the gas and particle phases. The detailed description is given in Table S4."

Reference:

Eisele, F. L. and Tanner, D. J.: Measurement of the gas phase concentration of H2SO4 and methane sulfonic acid and estimates of H2SO4 production and loss in the atmosphere, J. Geophys. Res.- Atmos., 98, 9001-9010, https://doi.org/10.1029/93JD00031, 1993.

Häkkinen, E., Zhao, J., Graeffe, F., Fauré, N., Krechmer, J., Worsnop, D., Timonen, H., Ehn, M., and Kangasluoma, J.: Online measurement of highly oxygenated compounds from organic aerosol, EGUsphere, 2022, 1-29, 10.5194/egusphere-2022-933, 2022.