Answers to referees' comments for "Elemental composition and clustering of α-pinene oxidation products for different oxidation conditions" (acp-2014-883)

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The authors would like to thank all three anonymous referees for their helpful and thoughtful comments and suggestions in order to improve the manuscript quality. Each specific point is addressed below. Referees' comments are in plain text and the authors' answers are in italics.

Anonymous Referee #1

General comments

First of all, more detail is needed in the experimental section for a paper where the results will be dependent on the conditions. Below you will find specifics. Second, there are a number of places within the results and discussion where interpretation is based on small differences with no mention about uncertainty or reproducibility (most notably average oxidation state discussion and time series), this should be addressed. For instance, the section on average oxidation state, as the mass spectrometry techniques are not calibrated versus all products and sensitivity will vary depending on the functional group, number of functional groups on a molecule, and the size of a molecule how do you find an average oxidation state? More detailed discussion on each section is below.

Comments on each section:

2. Experimental

Please talk about the source of NH3 and (C2H5)2NH, was it from trace contamination or were they explicitly added?

Ammonia and dimethyl amine – $(CH_3)_2NH$ – were present as trace contamination in the runs presented in this study. It is now mentioned unambiguously in the experimental part: "Despite the cleanness of the chamber, ammonia (NH_3) and dimethyl amine (C_2H_7N) are present as trace contaminants." References have also been included earlier in the text (see also comment by Anonymous Referee #2).

You only state that you use UV light to initiate photooxidation. Looking at the paper cited it indicates that the light provided could be from 300 nm and above or below 300 nm (down to 200 nm or possibly lower) please provide a more through description of the light irradiation, especially the "UV-sabre". This is important because UV light (especially intense UV light) can result in photodissociation of conjugated molecules, many organics with oxidized functional groups (carbonyls, hydroperoxides, peroxyacids…) as well as α-cleavage of alkenes. Please provide a better description of your light source. If intense UV light below 300 nm was used was potential photodissociaiton studied?

The lamp used for the "UV sabre" is a Philips TUV 130W XPT producing 50W power, essentially monochromatic at 253.7 nm. It is installed in a quartz tube inside the CLOUD chamber. This information is now included in the manuscript.
The potential photo-dissociation resulting from this source of UV light has not been studied. However, we believe that this would not influence the results presented in the manuscript. It would enable new reaction pathways and products (e.g. from aldehydes or peroxides), but the observed

products containing 10 and 20 carbon atoms ("C_{10}" and "C_{20}") would still be observed (at lower concentrations, though). However, as the manuscript does not contain quantitative comparison between both experimental conditions, conclusions remain unaffected by potential photo-dissociation. To illustrate this statement, we include here similar bar plots as in the manuscript for Run 1085.02 (Figure 1, see experimental conditions in Table 1). The signals are much lower due to the low OH concentration (see comment from Anonymous Referee #2) and that is the reason why C_{20} compounds are not included in the plot. This is because most OH reacts with SO_2 that is present at high concentration. However, the qualitative picture remains the same.

Table 1. *Experimental conditions for run 1085 (without UV sabre, presented here) and 1100 (with UV sabre).*

Run	[α-pinene] (pptv)	[O_3] (ppbv)	[SO_2] (ppbv)	[HONO] (ppbv)	[H2] (%)	UV	[H2SO4] (cm^{-3})
1085.02 (here)	1250	0.0	70	0.44 ± 0.01	-	yes (40% UV fibre)	1.52e7
1100.02 (manuscript)	1250	0.8	1.1	1.6 ± 0.2	-	yes (fibre and sabre)	1.03e7

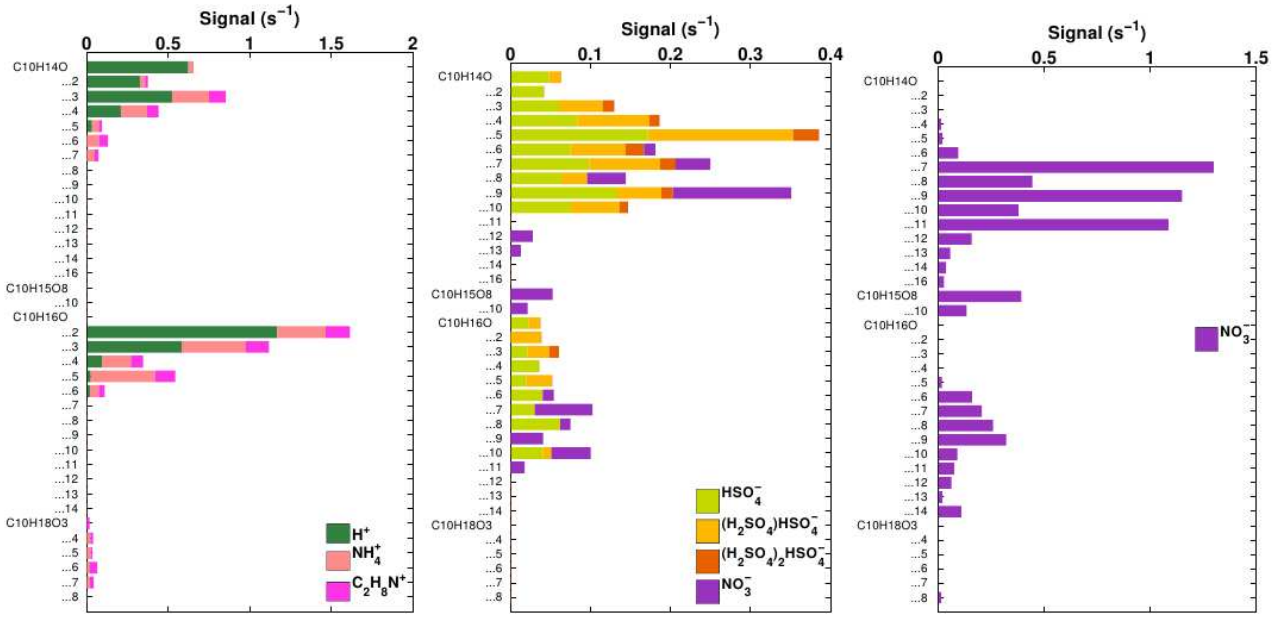

Figure 1. *Stacked peak area for observed clusters containing $C_{10}H_bO_c$ according to core ion(s) of positive (left column), negative (middle column), and neutral (right column) clusters obtained from α-pinene oxidation by OH only (without use of UV sabre).*

In the experimental you explicitly mention the ability to remove or add more ions to the chamber; did you do either of these? Would either produce different results to those reported?

The runs presented were conducted under elevated ion concentration due to the use of the Proton Synchrotron pion beam (π^+). This is now clarified in the experimental part: "The use of the pion (π^+) beam from CERN's Proton Synchrotron increases the amount of ions present in the chamber up to ca. 4000 ion pairs cm^{-3} for the experiments presented in this study."

Results not included in this study suggest that mainly the signal in APi-TOF mass spectrometers decreases with lower ion concentration, without influencing the oxidation chemistry. CI-APi-TOF spectra do not show a difference in the signals from organic compounds between experiments with and without ions present.

With the discussion presented later in the paper, a section on what types of molecules (i.e. with what functional groups) are detected with each mass spectrometric technique is needed. In addition, can you comment on the sensitivity of each technique to different compounds (functionality, multifunctional, large molecular weight). This last part is especially important for the oxidation state and elemental composition discussions (sects. 3.2 and 3.3).

APi-TOF both in negative and positive mode measure any charged species up to about 2000 Th. Ionization selectivity is, indeed, an important aspect of discussion about OS_C*. The fact that nitrate chemical ionization is more selective towards more oxidized organic compounds was not known a priori and is one of the outcomes of this study. We modified the manuscript and its title ("Elemental composition and clustering behavior of α-pinene oxidation products") to emphasize this and the discussion about* OS_C *has been revised (see comments from Anonymous Referee #3 as well). Nevertheless, recent studies (Rissanen et al., 2014 and 2015) suggest that hydroperoxy functionalities bind to nitrate.*

Results and discussion
3.1 Mass defect

In figure 2 and the discussion on page 30807 you discuss that there are organonitrates present in the OH oxidation experiment due to the presence of NOx, my question is why is there organonitrates present in the ozonolysis experiments when no NOx was added? In addition, where does the nitric acid come from?

It is true, that we do not expect organonitrates forming in the ozonolysis experiment due to the very low NO_x *regime. The mentioned points from Fig. 2 (APi-TOF) are likely small background peaks that have a mass very close to the one of potential organonitrates, but have been mislabeled. Their mass/composition was checked again and the figure improved accordingly. Even if we cannot exclude the presence of low levels of organonitrate compounds due to the presence of background* NO_x *and nitric acid, these compounds definitely do not dominate the spectra. In the case of the CI-APi-TOF mass defect plot, these peaks should have been labelled* $(OxOrg)(HNO_3)NO_3^-$*, which can have the same composition as* $(Organonitrates)NO_3^-$*. The* $(HNO_3)NO_3^-$ *comes from the chemical ionization and binds to oxidized organic compounds. The following sentence has been added to the manuscript: "In the CI-APi-TOF spectra, such compounds share the same elemental composition with oxidised organics bound to* $(HNO_3)NO_3^-$ *from the CI. Even if they have been labelled so, one may not totally exclude the detection of organonitrates bound to* NO_3^- *by the CI-APi-TOF."*
In the chamber, nitric acid is expected to form from the reaction of NO_2 *and OH. In the ozonolysis only experiment, a small amount of* NO_3^- *can be seen in the negative APi-TOF spectra, showing that some* NO_x *(and consequently nitric acid) is present, but not present in sufficient amount to compete with bisulfate during the formation of clusters. In the CI-APi-TOF nitric acid is used as ionization reagent.*

3.2 Average carbon oxidation state

As the mass spectrometers are not calibrated and could potentially have different sensitivities to different types of molecules doe a small difference in the "average oxidation state" between positive and neutral detected compounds in figure 3 mean anything? It is hard to determine how you determined the average oxidation state; did you sum up all the signal at a given number of carbons from each of the mass spectrometric techniques? If so, how does this represent the average oxidation state if you do not know functionality of the compounds and thus the sensitivity in each mass spectrometric technique?

As replied to an earlier comment, APi-TOF instruments are not sensitive to compounds' functional groups and even if the transmission in the mass spectrometer may vary depending on the tuning of the instrument, no dramatic change in transmission is expected on the m/z range where each group of compounds has been averaged (typically around 100 Th).
We agree that our manuscript contained a misleading sentence ("The results from all three instruments are combined.") that has been replaced by "OS_C *has been derived by averaging all peaks with retrieved elemental composition, weighted by signal intensity, for group of compounds (e.g.* C_{10}, C_{20}*) and for each instrument separately. Weighted averages and standard deviations for bands for each instrument are shown as large gray symbols and bars, respectively."*
This, of course, leaves the question of the functionalities. This is why we stated (page 30808, line 18-21 of the original manuscript): "Note that OS_c *neglects the effect of peroxide functionalities, which one expects to be abundant for low* NO_X *levels as it is the case in the ozonolysis-only experiment. Taking this effect into account would lower the averaged* OS_c *values for this experiment, reducing the difference between the oxidation conditions." This has now be revised and Fig. 3 shows now additional values lowest limits of* OS_C*, maximizing the amount of hydroperoxide functional groups compounds with exactly 10, 20, 30, and 40 carbon atoms. These values remain close to the* OS_C *values derived from the operational definition. The manuscript now reads: "Note that the operationally defined* OS_C *neglects the effect of peroxide functionalities (-OOH), which one expects to be abundant for low* NO_x *levels as it is the case in the present experiments. We derived a formula to estimate the lowest value of* OS_C*, maximizing the amount of hydroperoxide functional group for compounds with exactly n*10 carbon atoms (*$OS_{C,max(OOH)} \approx n*0.8 + O:C - 1.5\ H:C$*). It derives from the minimum amount of carbonyl (C=O) functionalities required based on the amount of hydrogen atoms, knowing that the elemental composition of α-pinene, the starting material is* $C_{10}H_{16}$*, so that it cannot be generalised. This remains an approximation, as one cannot precisely derive* OS_C*, without knowing the exact structure of the analysed compounds. This is represented in Fig. 3 by light gray bars and symbols and these values vary marginally from operationally defined* OS_C *values for ozonolysis. The variation is slightly higher from compounds with 20 and 40 carbon atoms in the OH oxidation experiment."*

3.3 Elemental composition

Are the numbers in figure 1 reaction partners or numbered reactions? In your discussion on page 30810 (lines 20-28) you seem to use them for both.

The numbers in Fig. 1 describe 5 possible reactions of peroxy radicals (and acylperoxy radicals) and not the reaction partners. The sentence in the discussion has been reformulated and now reads: "Despite different mechanisms in the early steps, peroxy radicals are produced under both oxidation conditions and will react in a similar way with various present reaction partners independent of their formation pathway (reactions 1 to 5)."

4 Clusters time series

For the figures (6-8) were the results reproducible? Was this one run or the average of many runs?

The results presented are only from one run. Unfortunately, most CLOUD runs differ in several ways (e.g. vapors concentrations, use of scavenger) so that it is a difficult task to group them. Therefore, we preferred to present one run that we believe is representative for the mentioned conditions, rather than averaging several runs, which would require more extensive discussion to explain the cause of the variations between them.
Table 2 presents two runs that are similar to the ones presented in the manuscript. Run 1068 (ozonolysis only) had to be stopped after 11:33 as the beam was interrupted. Figure 2 reproduces a similar figure to Fig. 6 from the manuscript and Figure 3 a similar one to Fig. 7 from the

manuscript. The similarity of the results illustrates how the runs that we selected are representative for the given conditions and the repeatability of the measurements.

Table 2. *Experimental conditions for run 1068 (ozonolysis only) and 1102 (OH oxidation), similar to the runs presented in the manuscript.*

Run	**[α-pinene] (pptv)**	**[O_3] (ppbv)**	**[SO_2] (ppbv)**	**[HONO] (ppbv)**	**[H2] (%)**	**UV**	**[H2SO4] (cm^{-3})**
1068.02	620	22	69	0	0.1	no	1.91e7
1102.02	1250	2.0	1.8	2.1 ± 0.2	0	yes (fibre and sabre)	1.61e7

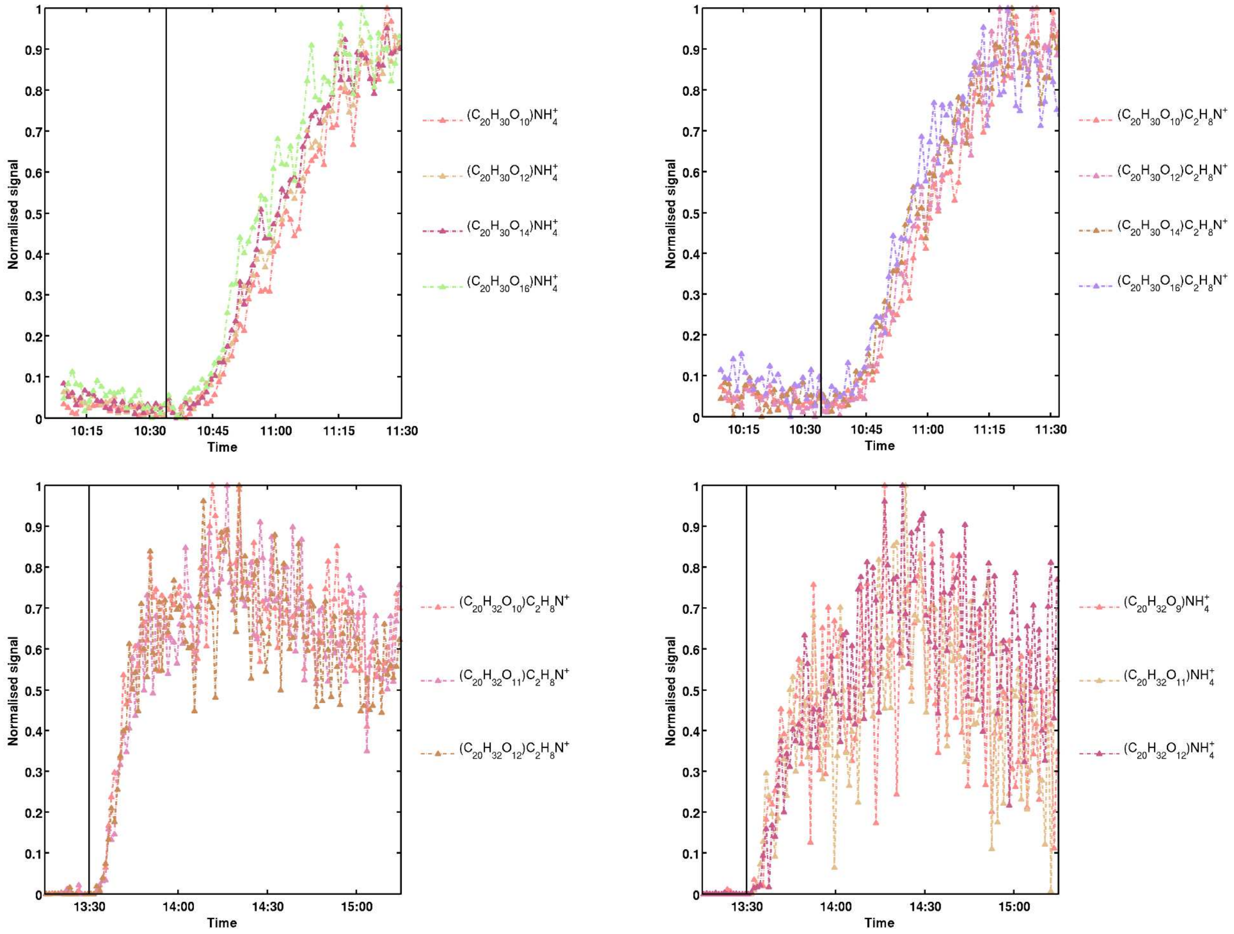

Figure 2. *Time series of observed positive clusters containing $C_{20}H_{30,32}O_z$ oxidised compounds bound to NH_4^+ (left) and $C_2H_8N^+$ (right) for α-pinene pure ozonolysis (top row) and pure OH oxidation (bottom row). The vertical black line marks the beginning of the experiment.*

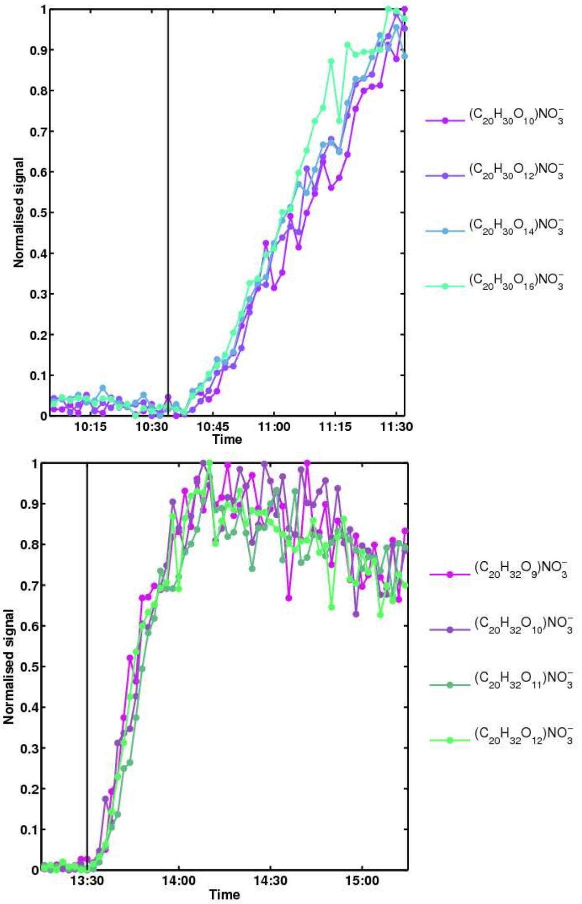

Figure 3. *Time series of observed neutral clusters containing $C_{20}H_{30}O_z$ oxidised compounds for α-pinene pure ozonolysis (top row) and $C_{20}H_{32}O_z$ for pure OH oxidation (bottom row). The vertical black line marks the beginning of the experiment.*

You state on page 30813 lines 5-6 that the positive signal (fig. 6) from the most oxidized species decreases after it reaches its maximum while the other signals become stable (for ozonolysis). I am not sure I see what you mean. First of all in the first panel you should zero out the single at time zero if you are also going to normalize to maximum signal as you are only giving about 90% decimation of the green line (starting at _0.1) as the pink line (starting at 0). Second, as I am assuming that the fluctuation in signal after 23:30 is an indication of the noise. Given this noise level, all signals appear to show the same trend within error or noise.

The normalization in the first panel has been improved, so that now all the signals start at 0. The signal after 23:30 is not only indicative of the noise. There are some real signal fluctuations that are also seen by the Air Ion Spectrometer (see also comment on technical corrections and comment on oscillations by Anonymous Referee #2). The reason for the fluctuations is not clear but is very likely related to the use of an ungrounded mixing fan.
Also comparing this panel, with the lower left panel, where despite the noise in the steady-state conditions, the signals are matching very well with each other when increasing, much more than in the ozonolysis experiment.

Second, and potentially more important, comparing the two ozonolysis panels (addition of NH4+ or C2H8N+) why are the trends different, even with species with the same molecular formula? There is no discussion about this. Why does the species that it clusters with have a much greater effect on its time trace than the molecular formula? Are they being converted from the ethyl ammonium species to the ammonium species? Why is this trend not observed from OH oxidation? Please provide a discussion.

The behavior of naturally charged species is complex. It is for instance possible that, while a neutral molecule concentration increases, the concentration of charged clusters containing this molecule may decrease due to the presence of other species competing for the available charges and forming more strongly bound clusters with the same molecule.
Also, species with the same elemental composition do not have to be one unique species. Several compounds with the same elemental formula may have different structures with different functionalities. This adds further to the complexity of the signal behavior and its interpretation.
We added this sentence to the manuscript to clarify this observation: "The different behaviour of oxidised organic compounds with the same elemental composition bound to NH_4^+ *and* $C_2H_8N^+$ *can be explained by either the different formation rates of these clusters (both cations competing and* NH_4^+ *seemingly forming more stable clusters) or by the fact that there can be various compounds with the same elemental composition but different chemical properties." (see also comment by Anonymous Referee #3).*

For your discussion on the time trace of the negative signal for ozonolysis (figure 8 top panel) you state that this figure indicates that species with two sulfuric acids are produced later that with one sulfuric acid (page 30813 lines 26-28). The noise level from the species with one sulfuric acid molecule makes this claim hard to evaluate. The trace with one sulfuric acid shows signal of up to 0.4 prior to oxidation (black vertical line) and does not surpass that again until the other signals (ones with two sulfuric acids) begin to rise as well. With the amount of noise it is tough to draw any conclusion on this time trace. Again it must be asked, where these results reproducible or is this from one experiment?

The results presented are from only one experiment. We agree with the reviewer that the noise level for species with only one sulfuric acid molecules is large and that the claimed conclusion needs better experimental evidence. Due to the lack of comparable run to explore the results reproducibility in the ozonolysis only case, we decided to remove this figure and the related conclusions.

Technical corrections

Please letter (A, B, C..) each sub figure, this will make it much easier to follow.

This has been done.

Provide a distinction between product classifications and reactions (Figure 1 and discussion thereof). In the text or figure 1 please provide a reaction scheme for reactions 4 and 5.

We are not sure if we understand the comment from the reviewer. Boxes in Figure 1 have been used to group various products of the same reaction or compounds that may react according to the same reaction pathways. No product classification has been made and reactions happen following arrows. The figure caption has been improved to reflect this.
Reactions 1 to 5 depict possible reaction from peroxy radicals with various species. Reaction 4 depicts the following possible reactions:

- $RO_2 + NO \rightarrow RO + NO_2$
- $RO_2 + RO_2 \rightarrow 2\ RO + O_2$

As mentioned in the main text it is unknown which H atom is abstracted during intramolecular reaction 5, so we decided to not depict an example to not confuse readers.

Figures 4 and 5 are very hard to read, I had to put the pdf on 300% magnification in order to read the molecular formulas.

We are aware of the fact that the molecular formulas are not easy to read, especially for these figures. However, we do not really know how to label these figures in a better way. We improved as much as we could the readability and expect the figures in the final ACP manuscript to be wider *in order to further enhance readability. It seems that the format of the discussion paper was hindering the publication of larger figures.*

Figure 6 first panel, you should zero out the response at time zero (vertical line) so that the normalized response from each mass spectrometer can be compared.

In this case the normalization did not work properly due to a short beam interruption before time zero (leading to no signal in the APi-TOF as the "dip" about 22:30 was indicating). These data have been filtered out and this panel replaced by a new version (see also comment on section 4).

Anonymous Referee #2

General Comments:

Praplan et al describe a series of measurements of a-pinene oxidation products made in the CLOUD chamber at CERN. The measurements described are primarily from three API-ToFs (+ mode, - mode, nitrate chemical ionization). Oxidation of a-pinene was studied under two different conditions: 1) dark, in the presence of O3, and 2) light, in the presence of UV light, OH, NO, and trace O3. As has been well established over the past decade, the oxidation mechanism is a strong function of oxidizing conditions and it is not unexpected that the resulting oxidation products from these two scenarios would differ in their oxidation state (among other metrics of their volatility). The manuscript provides helpful mass spectral tools for understanding these mechanisms and contributes to the growing number of publications from this group on the topic.
However, the manuscript is very observation based for the two select conditions studied here. A case has been made that these two oxidation scenarios correspond to O3 vs OH oxidation. This may very well be the case, however the difference in other experimental factors between the two experiments (UV, NOx) make this direct comparison quite challenging. More detail on the experimental conditions and a discussion of how they may impact the results would be very helpful.

Specific Comments:

Page 30799: I am surprised to see an author list of 33 for a manuscript that appears to be reliant on three instruments. Perhaps the authors can briefly elaborate on the contributions on the groups to the data and analysis?

The CLOUD project is a large collaboration of many groups from various research institutions and each campaign requires a lot time and manpower. Even if the focus of this paper is set on actually four APi-TOF mass spectrometers (Helsinki, PSI, Frankfurt, Aerodyne Inc.) – there were two CI-APi-TOF instruments – and a small subset of experiments, these could not have been conducted without the participation of all the groups. This includes preparation (e.g. testing, planning of experiments), execution (running the chamber and the instruments, as well as data analysis). supervision, and interpretation of the results. Other instruments mentioned only briefly were necessary to monitor various species such as O_3 and SO_2 (Frankfurt), α-pinene (Innsbruck, Ionicon Analytik), H_2SO_4 (Frankfurt).

Page 30801: The manuscript discusses in general terms the difference between oxidation products for a-pinene oxidation under to different scenarios. In the abstract these two scenarios are painted as OH and O3. However, the scenarios differ in many other (potentially even more important) way (e.g., NOx, hv). This should be mentioned in the abstract. It would also be of help to the reader to understand what the broader implications of these observations are. For example, is the point of this manuscript to provide molecular markers for oxidation pathways that could then be looked for in field observations? Is the primary point that the oxidation state of the resulting oxidation products between the two scenarios is different?

We improved the manuscript's abstract taking the referee's comments into account. The study covers two aspects: firstly the difference between the two oxidation pathways, but also the clustering behavior of the oxidation products. We modified the title to emphasize this (see comment from Anonymous Referee #1). Even if the direct comparison of the selected experiments is not straightforward, the manuscript presents valuable information regarding the clustering behavior of various oxidation products, both from ozonolysis and OH oxidation pathways.
It appears, as stated in the conclusions, that even if the early steps may differ and lead to different oxidation products, once peroxy radicals are formed in both pathways, the reactivity is similar, leading to large multifunctional oxidation products that show a very similar clustering behavior towards various types of ions. The improved abstract reflect this with this first sentence: "This study presents the difference between oxidised organic compounds formed by α-pinene oxidation under various conditions in the CLOUD environmental chamber: 1) Pure ozonolysis (in the presence of hydrogen as hydroxyl radical (OH) scavenger) and 2) OH oxidation (initiated by nitrous acid (HONO) photolysis by ultraviolet light) in the absence of ozone."

Page 30803: Were any of the unique features of the synchrotron utilized in this study? Or was the CERN chamber primarily utilized because of its low background?

As previously stated in our answer to anonymous referee #1, the presented data were acquired under "charged" (π^+) conditions, i.e. using the pion beam of the CERN's Proton Synchrotron. This is now explicitly mentioned in the main text. The sensitivity of the negative and positive APi-TOF mass spectrometers is improved when the ion concentration is higher in the chamber. The low background of the chamber is even more important and therefore has been stressed so far.

Page 30804: What does "decrease contaminant levels to a minimum" mean? What contaminants are of importance to this study, and what defines a minimum? These details should be added here.

As requested, we mention now explicitly which contaminants are of importance. The sentence now reads: "Thorough cleaning with ultra-pure water and heat (373 K) decreases contaminant levels such as ammonia and amines to a few pptv, and volatile organic compounds to below 1ppbv (Praplan et al., 2012; Schnitzhofer et al., 2014). However, only heating and flushing with ultra-pure air of the chamber has been performed between experiments with ammonia and dimethyl amine and the experiments presented in this manuscript, which is slightly less efficient than the use of water."

Page 30804: What does "trace gases are carefully adjusted and monitored" mean? Which ones, what is the control on those of importance? For example what is the confidence in the initial HONO concentration and the time decay in OH?

We have now clarified the cited sentence: "Trace gases, such as water, sulfur dioxide (SO_2), O_3, and α-pinene are carefully injected to desired levels and monitored. Time resolutions vary from seconds to minutes." Ammonia and dimethylamine can be injected in a controlled fashion and monitored with ion chromatography, but this has not been done here and is therefore not explicitly mentioned in the main text.
The confidence in the initial HONO concentration is given in Table 1 and is about 20%. Calculations with the MCMv3.2 model taking into account dilution and the light spectrum in the CLOUD chamber show that [OH] peaks at about 9.3×10^5 cm^{-3} after ca. 15 min and decays to about 8×10^5 after 3 hours of oxidation.

Page 30804: Please add more details on the light source and intensity and how this translates into OH concentrations. Does using the "UV sabre" mean that 1.9 ppbv OH is generated at t=0? Again, what does "increase OH levels" mean quantitatively? Was O3 or NO measured in time? Was OH calculated from hydrocarbon concentrations?

As requested by Anonymous Referee #1, we improved our description of the "UV sabre" in the experimental section. As an answer to the previous comment, we discussed that using the UV sabre doesn't mean that 1.9 ppbv OH is generated. OH levels vary between 8 and 9.5x10^5 *cm*$^{-3}$ *during the first three hours of the experiment, based on model estimates (Master Chemical Mechanism v3.2 with UV sabre parametrization). We mention this now explicitly in the experimental section of the manuscript: "A model estimation based on the Master Chemical Mechanism (v3.2) and parametrization of the UV sabre estimated the OH concentration to vary between 8 and* $9.3 \cdot 10^5$ *cm*$^{-3}$*."*
Without UV sabre OH levels are at least one order of magnitude lower (about 10^4 *cm*$^{-3}$*).* O_3 *was measured but lower than the detection limit (0.6 ppbv), but NO was not monitored for the presented experiments (also see comments by Anonymous Referee #3).*

Page 30806: How confident are the author that these C20, C30, and C40 compounds are actually gas phase molecules and not formed in the expansion in the API-ToF? I am sure that this has been asked in the review of other nitrate ion CIMS. As such, perhaps a reference will suffice.

We are very confident that we detect actual molecules and not purely clusters formed in the expansion into the APi-TOF. Even though the sample will cool considerably upon expansion into the APi-TOF, the reaction times are short (on the order of µs), which in turn would require very high concentrations of C_{10} *molecules in order to be able to collide and cluster during the expansion. Water molecules are abundant and therefore expected to attach to the ions entering the APi. However, the ions will heat up again as they traverse through two quadrupole ion guides at pressures of ~2 mbar and* 10^{-2} *mbar. During this phase, the water molecules re-evaporate and we therefore very rarely detect water clustered to ions. In fact, although the reviewer expects that the question of clustering inside the APi-TOF would have come up before, the more common question has been whether we are fragmenting clusters inside the instrument.*
Additional support for the signals being molecules and not clusters can be found in Ehn et al. (2014, see especially Extended Data Fig. 10), where they saw that by adding 1 ppb of NO to their chamber, they were able to remove all C_{20} *compounds from their mass spectra. This was explained by the NO limiting* $RO_2 + RO_2$ *reactions. This result could not be explained by the* C_{20} *(and larger) molecules forming from* C_{10} *molecules clustering in the APi.*

Page 30807: What is the source of sulfuric acid, NH3, and amines in this experiment? Are these contaminants? Were they added intentionally?

Ammonia and dimethyl amine have been added intentionally in the CLOUD chamber for experiments before the ones presented here. The chamber was cleaned by overnight heating to 100ºC before starting experiments with α-pinene. This removed most of ammonia and amines, but the chamber walls were not cleaned with water as this procedure takes time and is not convenient to perform during a campaign. Therefore, ammonia and dimethyl amine remain present at very low pptv levels (see Praplan et al., AMT, 2012 in the present ACP/AMT CLOUD special issue). This is now better explained in the manuscript (see also comment from Anonymous Referee #1). We now mention explicitly that sulfuric acid is formed from the photo-oxidation of intentionally added SO_2 *in the chamber (see also comment from Anonymous Referee #3).*

Page 30808: Given that each ion detected (at least via nitrate CIMS) has a different calibration factor, what do these average oxidation state values mean? I would almost guess that the calibration factor for each molecule would be a function of its oxidation state. Also, what is the uncertainty in the -0.7 and -0.3 values that are reported?

This has been mentioned as well by Anonymous Referee #1 (see also answer above). It concerns the CI-APi-TOF data and we agree that due to its selectivity towards higher oxidation states, it is not representative of the whole population of neutral molecules. However, because nitrate is an atmospherically relevant ion, the average oxidation state derived from CI-APi-TOF data is still an interesting parameter. The discussion has been extended: "Note that weighted averages for the CI-

APi-TOF instrument are not representative of the whole population of neutral molecules (see discussion in the next section). However, because NO_3^- is an important atmospheric ion, CI-APi-TOF results are also discussed in this section. Ehn et al. (2012) observed that oxidised compounds binds naturally to NO_3^- at low levels of sulfuric acid, for instance during night-time."

Page 30812: I would encourage the authors to think about how wall loss may be impacting the time series of the neutral compounds in the chamber. Specifically, isn't this a key to telling whether the C20 compound is actually covalently bound molecule with extremely low volatility (it would condense on the wall promptly), as compared with a C10 molecule. It would be interesting to quench oxidation and watch the decay of these compounds in the chamber to assess their volatility as compared to their measured oxidation state.

As the CLOUD chamber is used as a continuously stirred-tank reactor (CSTR), a steady-state is expected to be reached. This is the case for H_2SO_4, when sources and sinks are roughly balanced after up to 20 minutes. However, some time series for clusters containing C_{10} and C_{20} compounds reach a maximum before decreasing. As mentioned in the manuscript, this is due to a decrease in the production rate of the most oxidized organic compounds (and increase of the production rate of the less oxidized compounds) as the ratio between ozone and α-pinene is changing in the ozonolysis experiment and α-pinene concentration decreasing in the OH experiment. Moreover, particle formation and change in condensational sink (additionally to the chamber walls) also alter the loss term of the oxidation products. We modified parts of the discussion to reflect the fact that even used as CSTR, α-pinene concentration have not been constant during the experiment, leading to non-steady-state conditions (see comment by Anonymous Referee #3).
Only when reaching a steady-state oxidation quenching would be possible. However, as can be seen from the data, it can take up to several hours to reach a steady-state and usually no decay of oxidation products was recorded in CLOUD, but the chamber flushed and cleaned to start the next experiment as soon as possible. This may change in the future.
Ehn et al. (2014) also used a CSTR during their α-pinene oxidation studies, and they did exactly the tests the referee asked for (see Extended Data Fig. 6 in Ehn et al.). This was possible by studying C_{10} and C_{20} compounds that were products of OH oxidation, and the decay was monitored after turning off the photolyzing UV lights. They found that the molecules decreased according to their expected wall loss rates, and in fact the C_{20} compounds decreased slightly slower, probably due to slower diffusion of the slightly larger molecules. In their study, also the C_{10} compounds were thought of as extremely low-volatility.

Page 30831: Figure 6A, following peak concentration, there appears to be a 15min oscillation in the signal intensity. What is this caused by?

There is indeed a 15min oscillation appearing in Figure 6A. However, after verification we could not find a reason for it as the beam and the temperature were stable in the CLOUD chamber. However, this is also seen by the Air Ion Spectrometer (AIS), for instance (see Fig. 2). We suspect that the fans used for mixing of the air in the chamber (and ungrounded) may have caused these oscillations.

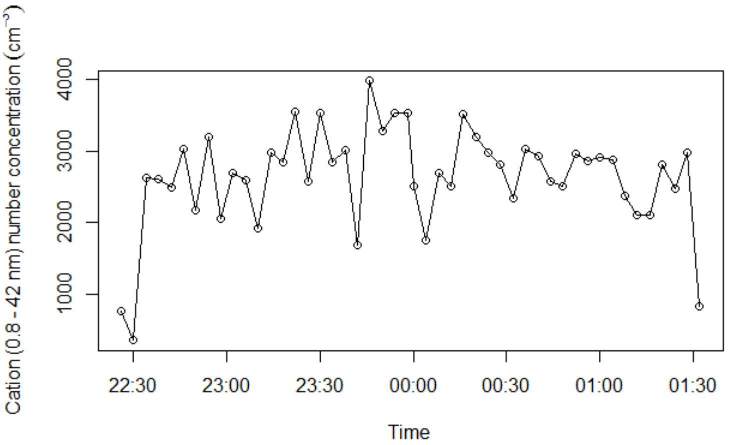

Figure 2. *Cation number concentration [cm^{-3}] in the size range 0.8 to 42 nm during ozonolysis-only experiment from Air Ion Spectrometer.*

Anonymous Referee #3

This study investigates the similarities and differences in the oxidation products formed from a-pinene ozonolysis and photooxidation. Experiments are conducted in the CLOUD facility at CERN. The negative ions, positive ions, and neutral molecules are measured with APi-ToF in the negative mode, positive mode, and NO3 as ionizing reagent, respectively. The distribution of the clusters, average carbon oxidation state, and the time series of the detected species are presented and discussed. It is found that the products from a-pinene ozonolysis showed a higher oxidation state than those formed in photooxidation. These novel measurements provide substantial amount of insights into the composition of the species formed in these oxidation experiments. The manuscript is generally wellwritten and will be of interest to the community. However, there are several aspects that weaken the manuscript and should be addressed.

Firstly, the authors need to substantially expand the experimental section. As noted in more details in the specific comments below, the authors need to include a discussion regarding the relative importance of peroxy radical reaction pathways, e.g., RO2+HO2, RO2+NO, in the context of the scavenger used and the NOx levels in the ozonolysis experiment and the photooxidation experiment. This is important as Ehn et al. (2014) showed that the products formed and measured by the CI-APi-TOF in a-pinene ozonolysis experiments are highly dependent on NOx levels. In essence, (just an example), a study comparing products formed from a-pinene ozonolysis in the presence of a large amount of NOx with those formed from photooxidation in the absence of chamber background NOx might have entirely different conclusions compared to the present study.

Secondly, while these measurements are novel, the manuscript is more focused on describing what the similarities/differences are in the oxidation products, rather than why and how. I feel that more discussions on the results are needed regarding what these results mean. I think that the manuscript will be greatly strengthened if the authors can include a discussion on the atmospheric implications of these measurements and results. Based on the data presented in this manuscript and the level of similarities between the oxidation products formed in ozonolysis and photooxidation, it seems like it would be a challenge to apply these results to ambient studies (i.e., it would be challenging to tell whether products detected in ambient measurements are from ozonolysis or photooxidation).

Thirdly, the products formed from the ozonolysis of a-pinene have been measured by the APi-ToF in several previous studies (the authors cited them in the manuscript). The manuscript would benefit from a more thorough discussion in terms of how the results from this study compare to those prior studies.

The more specific comments are listed below.

1. Page 30802, line 14. The authors wrote “two oxidation pathways are known”. The nitrate radical oxidation of a-pinene does not appear to form much SOA (e.g., Hallquist et al., 1999; Griffin et al., 1999; Perraud et al., 2010). However, this is another a-pinene oxidation pathway and should be acknowledged.

As nitrate radical oxidation was not part of the study, it is true that it has been erroneously left out from the introduction. This has been now revised:
” Several oxidation pathways are known (see Fig. 1):
– Ozonolysis, […]
– OH or nitrate radical (NO_3) oxidation, in which the radical adds to the α-pinene double bond (or alternatively abstracts an hydrogen atom from α-pinene in the case of OH) resulting in the formation of an alkyl radical.“
Also, the legend of Fig. 1 has been revised and mention why the NO_3 oxidation scheme has not been included (“Oxidation by NO_3 has been omitted for the sake of clarity and because it is not relevant to the present study.”).

2. Page 30804 and page 30805. The experimental section needs clarification and additional information.

a. The authors should provide a general discussion regarding the fate of peroxy radicals, as this will affect the subsequent oxidation products and make it difficult to interpret any similarities/differences in the chemical composition observed in their ozonolysis vs photooxidation experiments.

i. Ozonolysis: what OH scavenger is used? Various scavengers (e.g., CO, cyclohexane, etc) will produce different amount of HO2 (Keywood et al., 2004) and affect the relative importance of the RO2+HO2 channel. What is the background level of NO and NOx? These will inevitably affect the fate of peroxy radicals and subsequent oxidation products in the experiment. For RO2+NO and RO2+HO2 reactions to compete, the mixing ratio of NO only needs to be in the order of ~40ppt. From figure 2, organic nitrates are also being formed in the ozonolysis experiment. Is this due to background NOx in the chamber?

The OH scavenger used was 0.1% molecular hydrogen (H_2). This was mentioned in Table 1, but not clearly in the main text of the experimental section. This has been corrected now. Jokinen et al. (2014, Fig. 2) showed that the signals of RO_2 radicals generated by limonene ozonolysis remain unaffected by the use of H_2 and propane as OH scavenger. Only the signals of RO_2 radicals attributed to OH oxidation pathways decreased. Therefore, we expect the same situation in our experiment, where the NOx levels are low (see below).
Regarding the organonitrates in the negative APi-TOF mass defect plot of the ozonolysis experiment, these particular data come from peaks with low signal and inaccurate mass-to-charge ratio and have been erroneously labeled as organonitrates. This has been addressed in the updated version of the figure (see also answer to Anonymous Referee #1).
In the CI-APi-TOF mass defect plot, these should have been labelled (OxOrg)(HNO_3)NO_3^-, that can be unfortunately isobaric with (Organonitrate)NO_3^-. This has been changed as well in the updated version of the figure.
NOx background levels were not measured. In the ozonolysis experiment, NO will be oxidized by ozone and yields NO_2. Based on MCMv3.2 model for the OH only experiment the NO_2 level does not exceed 20 pptv and NO level is smaller than a few pptv (see following comments).

ii. Ehn et al. (2014, extended data Figure 10) showed that the species measured by CI-APi-ToF in a-pinene ozonolysis is highly dependent on NOx. It is not clear what the NOx concentrations in the ozonolysis experiment in this study are, but the authors should comment and discuss this in the context of the results shown in Ehn et al. (2014). Are the results from this study consistent with the data shown in Ehn et al. (2014)? Please discuss.

Due to the very low levels of NOx, even using HONO as an OH precursor, we were not able to directly measure them, but remained low (see next comment).
These results are consistent with the results from Ehn et al. (2014, Extended Data Fig. 10c) and the role of NO_x *remains negligible in our experiments.*

iii. In the photooxidation experiment, what is the steady state concentration of NO and NO2?

As stated above, we could not measure directly NO and NO_2 *concentrations, but estimations done with MCMv3.2 show that* NO_2 *levels do not exceed 20 pptv and NO is less than a few pptv (see comment by Anonymous Referee #1). Note that due to the experimental conditions in the CLOUD chamber, steady-state is not reached before a few hours for both experiments presented.*

b. It seems that the a-pinene injection scheme is different in the ozonolysis vs photooxidation experiment? In page 30813, it was mentioned that the mixing ratio of a-pinene slowly reaches its equilibrium concentration towards the end of the run, however, for the photooxidation experiment, a-pinene concentration is high at the beginning. How would this affect the suite of products observed? Will the interpretation of the time trends of the products shown in Figures 6-8 be complicated by this

Yes, the α-pinene injection schemes differ between the two experiments and this is mentioned in the current manuscript, as stated by the referee. Even though it makes the comparison between both types of oxidation difficult (on top of other varying conditions), this enabled us to demonstrate the early formation of highly oxidized organic compounds (O:C up to 1.8).
The interpretation of time trends is difficult as we do not reach steady state conditions in the first few hours of the experiment (see comment by Anonymous Referee #2 and reply to comment 8 below). However, as mentioned above, other effects could be observed that we would not have seen under steady-state conditions.

c. Page 30806, line 9. Is the same amount of sulfuric acid added in the ozonolysis vs photooxidation expt the same? Is it added during the experiment? Or, it’s already at steady state at the beginning of the experiment?

Sulfuric acid is formed by oxidation of SO_2 *in situ. The* SO_2 *level is kept constant during each experiment and, while it differs for the presented experiments (69 and 1.1 ppbv, respectively), the achieved sulfuric acid concentration agrees within a factor 2 (as mentioned page 30807, line 14, and seen in Table 1). This is one of the reasons why these runs have been selected. This has been clarified in the experimental part and the discussion (see also comment by Anonymous Referee #2).*

3. Page 30806, lines 24-26. It is noted that “…based on previous studies, isotopic patterns, and assumptions on chemical reactions, the elemental composition of most compounds could be retrieved”. These need to be further elaborated. The corresponding previous studies should be cited. Also, what assumptions on chemical reactions have been made and how are those assumptions justified?

This paragraph has been rewritten (see further comment). Citations of earlier studies (Ehn et al. (2010, 2012), Junninen et al. (2010), Jokinen et al. (2012), Schobesberger et al. (2013)) are now included in the manuscript. We give examples on elemental composition attribution based on “assumptions on clustering behaviour”.

4. Page 30808. In calculating the “average carbon oxidation state”, did the authors assume that all the detected ions have the same sensitivity? Please clarify. If the authors did assume all the ions

have the same senility, please justify how this is the case. Also, what are the uncertainties in the "average carbon oxidation state" with respect to comment 3?

This comment has also been made by Anonymous Referee #1 and likely arose from the poorly formulated sentence: "The results from all three instruments are combined". Weighted means were derived from groups of signals (e.g. C_{10}, C_{20}*) individually for each of the instruments. This has been clarified now.*
In the submitted manuscript, the sensitivity of ions within the same group (e.g. C_{10}, C_{20}*) is assumed to be the similar in the APi-TOF. It is true that chemical ionization introduces further selectivity and that* OS_C *derived from CI-APi-TOF data may be biased. However,* NO_3^- *is an important atmospheric ion and even if CI-APi-TOF results do not represent the whole population of neutral molecules, they remain relevant. This is now explicitly stated in the manuscript. We are unable to draw any conclusions about ions' senility.*

5. Page 30809, line 22. If the attribution of composition in the negative spectra remains ambiguous (page 30809, line 22), how would this affect the comparison of composition between ozonolysis and photooxidation experiments? I assume this would also bring uncertainties in the calculation of the carbon oxidation state. Please discuss.

The authors mean that solely based on negative spectra, one cannot unambiguously tell if O_6 *or* SO_4 *is the correct assignment (e.g.* $(C_{20}H_{30}O_{12})HSO_4^-$ *or* $(C_{20}H_{28}O_6)(H_2SO_4)HSO_4^-$*). However, it became clear by combining these results with the positive APi-TOF and the nitrate CI-APi-TOF results (that suffer less from such ambiguity due to much less sulfur-containing compounds), that it would not make sense to observe* $C_{20}H_{28}O_x$ *compounds only in the negative spectra and not with the other instruments.*
The authors agree that this was not discussed in the manuscript and this paragraph has now been replaced by: "Attributing unambiguous elemental composition based solely on the negative spectra is challenging as O_6 *and* SO_4 *have nearly identical masses (95.969 and 95.952 u, respectively). Higher mass resolution would be required to distinguish between them. Nevertheless, based on previous studies (Ehn et al., 2010, 2012; Junninen et al., 2010; Jokinen et al., 2012; Schobesberger et al., 2013), isotopic patterns, and assumptions on chemical reactions, the elemental composition of most compounds could be retrieved. For instance it has been assumed that no organonitrate compound would form in the ozonolysis only experiment. For signals with low intensity, the elemental composition could sometimes be inferred by extending a pattern (e.g. increasing or decreasing the number of oxygen atoms or adding sulfuric acid molecules to* $(C_{10}H_bO_c)HSO_4^-$*). In the present study the comparison with positive and neutral spectra has been the key for the unambiguous attribution of elemental composition (see section 3.3). The composition* $(C_{20}H_{30}O_{12})HSO_4^-$ *was for example selected over* $(C_{20}H_{28}O_6)(H_2SO_4)HSO_4^-$ *as no* $C_{20}H_{28}O_6$ *compound was measured with the other instruments."*

6. Page 30812, line 15-20. The authors should provide more insights (from the mechanisms point of view) in terms of why the distribution of clusters in the neutral, positive, and negative spectra are more similar for C20 compounds which are independent of their formation pathways.

The author's interpretation on this issue can be found at page 30811, line 5-16 of the original manuscript (section 3.3.1) where they explain that specificity of chemical ionization fade out for C_{20} *compounds that are multifunctional ones and can therefore react with various ions, reducing the specificity of their interactions due to a limited type and amount of functional groups for* C_{10} *compounds for instance. This discussion has been clarified: "Below this size, compounds clearly behave differently depending on polarity and charger ion composition due to the limited type and amount of functional group, so that they bind selectively to specific ions."*

7. Page 30813, line 11-15. Shilling et al. (2009) has shown that the O:C for SOA is higher in a-pinene ozonolysis experiments with lower a-pinene levels. Also, Ng et al. (2010) showed that the initial products that condense to form SOA have the highest f44 (O:C) in a-pinene ozonolysis. Both

studies seem to be consistent with the results shown here and should be added to the citation. Please also include a citation for “the view that most oxidized organic compounds are formed only after long oxidants exposure time”.

The authors thank the referee to bring these studies to their attention. They are indeed consistent with the presented results and are now cited in the manuscript. Jimenez et al. (2009), Andrea (2009), and Kang et al. (2011) have also been added regarding the statement quoted by the referee.

8. Figure 6-9. It is not clear to me why some ions decrease faster than others. If I do not understand it wrong, the chamber is operated as CSTR. In this regard, how does one interpret decreasing signals over time – are they reacted away, are they lost to the chamber wall, etc that make them not reaching state steady? Please elaborate and comment on this.

It is correct that the chamber is operated as CSTR and sulfuric acid reaches a steady state usually after up to 20 minutes. Signals decreasing over time would indicate changes in formation/elimination rates that result in no steady-state. In the ozonolysis experiment, where this effect is more pronounced, this is due to a constantly increasing α-pinene mixing ratio and subsequent change in α-pinene/ozone ratio, which affects formation rates of the various oxidized organic compounds (see also Anonymous Referee #2’s comment). This is now clearly indicated in the manuscript: “This is due to the change in α-pinene: O_3 ratio, as the α-pinene mixing ratio slowly increases during the experiment, while the O_3 level is kept constant (no steady-state conditions). Therefore when α-pinene is very low, formation rates of the various oxidation products change because fewer termination reactions (with RO_2) happen, allowing further oxidation by successive intramolecular H-shifts as suggested by Ehn et al. (2014), see Fig. 1.”
We also added the following sentence in the following paragraph about OH oxidation results: “Note that the α-pinene concentration decreases during the experiment, so that steady-state conditions are achieved after about 3 hours of oxidation only. Moreover, various oxidised organic compounds compete to form stable clusters with the available ions.”

9. This is a more general comment: what is technically defined as ELVOC? With respect to the ELVOC discussed in Ehn et al. (2014), it would seem like pretty much all of the species detected in this manuscript can be considered as ELVOC?

The referee is partly correct: most C_{20} compounds in this manuscript are considered ELVOCs, and in general compounds detected by CI-APi-TOF. However, low oxidized species, mostly detected by positive APi-TOF, and C_{10} compounds are more likely low volatile organic compounds (LVOCs) or even semi-volatile organic compounds (SVOCs). This is due to the fact that even if the number of oxygen atom is large, they mostly belong to hydroperoxide functionalities, which do dot decrease volatility as much as two functional groups containing only one oxygen (hydroxyl, carbonyl).
Therefore the combination of all three instruments builds a volatility continuum. However, knowing the vapor pressure of each of these compounds is currently not possible. Donahue et al. (2012) gave a theoretical definition of ELVOCs as compounds with a saturation vapor pressure smaller than 3×10^{-4} µg m^{-3}.

10. Many of the figures are too small to read.

The authors are aware of this and made an effort to increase the final readability of the figures in ACP. They also expect that the figures in ACP can be made larger as already mentioned as an answer to Anonymous Referee #1.

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