

We are extremely grateful to both reviewers for their constructive comments to improve our manuscript. Below are point-by-point responses to both reviewers. Reviewer comments are in red, author replies in black.

Reviewer 1:

This manuscript presents elemental composition data of highly oxidized compounds as clusters of nitrate ion, NO_3^- , and biogenic volatile organic compounds, especially α -pinene, oxidation products. The authors present a brief description of the APi-ToF instrument and mass calibration procedure for a large mass range, followed by comparison of mass spectra from Jülich chamber and the Hyytiälä field site along with a hypotheses for the formation mechanism of the highly oxidized compounds. Finally, the authors estimate the concentration of neutral molecules from the observed ion clusters. The data presented is very convincing and the manuscript is suitable for publication in ACP after the following comments are addressed.

General comments:

1. Methods: Can the authors provide a quick statement as to why the experiments were conducted at the specific conditions reported? Where these the conditions at Hyytiälä when the field data was collected?

The conditions were selected based on previous measurements, mainly Mentel et al. (2009), in which they showed that new particle formation events similar to those observed in the boreal forest could be obtained under these conditions. The temperature and RH can be considered typical summertime conditions in Hyytiälä, though of course the conditions were highly variable over the course of the longterm measurement campaign conducted (May-November). The ozone concentration used in JPAC was about twice that which is typically measured in Hyytiälä, but due to the shorter residence time in the chamber (~50 min), oxidation needs to happen somewhat faster than under ambient conditions.

During the specific time period plotted in Fig. 1, the conditions were more autumn-like, with values around $T = 5\text{C}$, $\text{RH} = 80\%$ and $\text{O}_3 = 30\text{-}35\text{ ppb}$. However, the HOMs were detected throughout the campaign with a very similar pattern under many different conditions.

Action: A sentence was added to the manuscript, stating why the specific conditions were chosen.

Last paragraph of the “Data analysis and APi-TOF mass calibration” section. This paragraph needs further improvement. In its present form, it will confuse the reader. I suggest deleting this paragraph and adding a sentence at the end of the previous paragraph stating that throughout the iterative process of adding new ions for mass calibration, the difference between the 3-parameter fit and the exact mass of each ion was within the 20 ppm instrumental accuracy.

We thank the reviewer for this very good suggestion, which helped to shorten and clarify the text.

Action: The paragraph was removed, and a sentence added to the previous paragraph in line with the suggestion of the reviewer.

2. Identification of elemental composition: Pg 4601/line 12. The authors use exact mass of the proposed ion and the 10 ppm mass accuracy to calculate the different elemental composition that

are within this mass range. Rather, wouldn't it be more appropriate to use the measured mass of the ion at 340 Th and the mass accuracy to identify the compound that best fits this peak?

The problem with the approach suggested by the reviewer, though it would be more intuitive, is „the measured mass of the ion 340 Th“. As discussed in the paper, we can only measure a time-of-flight, which needs to be attributed to a mass using the mass calibration. In our case, we used the ion at 340 Th, together with its proposed composition, in the calibration. To minimize the possibility of circular reasoning, we wanted to show that no other „reasonable“ ions at this mass would fit the calibration within the instrumental accuracy.

Action: We prefer to keep the original method, but it was clarified in the text that this mass was used for the calibration itself.

3. Possible formation mechanism: Where there any chamber experiment done at low RH, that can be compared to the experiments discussed here and provide an insight into how important gas-phase hydration is? Also, clearly stating that α -pinene oxidation products that have aldehydes and ketones, along with carboxylic acids, are possibly hydrated in gas-phase, thus producing products that have high O to C and H to C ratios would clarify the argument for a reader. Another hypothesis that is presented is hydroperoxide formation. Can the authors refer to any past studies that provide an indication to the yields of hydroperoxides from α -pinene ozonolysis? It would be helpful for the reader if the hypotheses are clearly stated at the start of the section followed by the reasoning for each one.

The humidity and temperature were both kept constant throughout the chamber experiments to allow comparability to previous measurements. Unfortunately, this prevents us from analyzing the impact of different humidities on HOM formation. During the ambient measurements in Hyytiälä, the major peaks at 308, 340, 342 and 372 Th peaks ($C_{10}H_{14}NO_{10}^-$, $C_{10}H_{14}NO_{12}^-$, $C_{10}H_{16}NO_{12}^-$ and $C_{10}H_{14}NO_{14}^-$, respectively) dominated under a wide range of conditions. However, night-time relative humidities below 50% are very rare in Hyytiälä.

It was clarified in the text that the geminal diol and hydroperoxide functional group hypotheses were suggested due to their ability to increase O/C while retaining the H/C ratio.

Related to comments by reviewer 2, some references were added for hydroperoxides detected in SOA. E.g. Chen et al., 2011 discuss measured and modelled SOA yields of hydroperoxides.

Chen, Q., Liu, Y., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-phase chemistry of secondary organic material: Modeled compared to measured O:C and H:C elemental ratios provide constraints, Environ. Sci. Technol., 45, 4763–4770, doi:10.1021/es104398s, 2011.

4. Estimation of neutral HOM concentrations: Can the authors provide a reference for the ion lifetimes used in the calculation of the HOM concentration. Although the HOM concentration is a lower bound estimate, have the authors considered ion transmission difference between NO_3^- ion and HOM $\tilde{A}^+cNO_3^-$ clusters as a function of mass/charge? I would assume that this correction will be less than an order of magnitude but accounting for this difference would nevertheless be useful.

In addition to the already included Eisele (1989), we added a reference with typical condensation sink values from Hyytiälä.

The two quadrupoles in the atmospheric pressure interface of the API-TOF will skew the transmission towards larger or smaller masses depending on the tuning. Typically the tuning is aimed to produce a

compromise with transmission in a wide mass range. Calibrating the APi-TOF, especially in the field, is, however, extremely difficult, and was not done during this campaign.

Action: Additional reference on ion lifetime added, and a sentence discussing the transmission were included.

Specific comments (page/line)

4591/14 – remove “can”

Text changed in accordance to reviewer’s suggestion.

4592/1-4 – These two sentences seem out of place. Also, absorptive partitioning theory was proposed by Pankow (1994) and not by Robinson et al.

The reviewer is correct, and the sentences were removed, together with the reference.

4592/13 – Add Smith et al (2010) reference

This paper only discusses early growth of nanoparticles, whereas the references in our manuscript made nucleation studies. Therefore we prefer not to include the suggested reference.

4594/13 – Correct Thompson to Thomson (Th)

Corrected.

4594/23 – Change “running” to “operating”. Please change similar wording in other places, example 4594/28 change “run” to “operated”.

All four instances of run/running were changed.

4595/2 – Add reference for the transmission numbers quoted here.

4595/6 – Remove “so”

4595/25-26. The authors quote the α - and β -pinene concentrations in the figure captions but please also mention them here.

4596/10-11 – Please remove the wording “it cannot be stressed enough” and I suggest the authors rather use “therefore”.

All above changes made.

4597/12-14 – Please re-phrase the sentence. As worded, it does not provide any information.

The reviewer is correct, and the sentence was incorporated into the previous one.

4597/15 – Remove “the”.

Removed.

4598/11 – Remove “practically”.

„Practically“ was changed to „almost“, as the previously reported ions were not abundant every single night during the 6-month measurements.

4598/11-12 – Please reword “under field conditions with frequently changing conditions”. I suggest, “However, with frequently changing ambient conditions : : :”.

4598/24 – Change “comes off” to either “desorbs” or “evaporates”.

Above changes made.

4599/29 – Change “look” to looks.

„look“ refers to the plural „spectra“, and should therefore not be changed.

4600/17 – Remove “truly”.

4600/19 – Reword “still next to identical”. I suggest “largely consistent”.

Above changes made.

4600/22 – Authors mention that 341 Th is different in chamber and field data, but Fig 2c does not show any difference. Please clarify?

Although not as obvious as the difference in peaks 541 and 543 in Fig. 2d, the JPAC red trace in figure 2c does show a shoulder on the left side of the peak that is not visible in the green ambient trace. For example at 343 Th the peaks overlap each other almost completely. The 341 peak is also re-plotted in Fig. 4 where the difference becomes much clearer.

4602/21 – Change “were” to “are”

4605/13 – Please add the reference for ester formation.

4606/12 – “water to the carbonyl groups”

4610/22 – Remove “at night”

Above changes made.

Figures

Fig 1 and 2: Please offset the spectra from the origin slightly and add intermediate ticks. Also, increase the font size for the axes labels.

The ticks and font size were changed to make the figures more readable.

However, we do not see how offsetting the spectra from zero would improve the graphs. Currently in Fig. 1, all signals down to $\sim 0.05\%$ of the total signal (corresponding to roughly $0.1\text{--}0.5\text{ ions/cm}^3$) are visible above the „zero line“. The results we wish to present in the figures are now clearly plotted, and we feel that adding offsets would only serve to make the figures more complicated, while not adding any new information.

Figure 3: Increase the font size for the axes labels and legend.

Fig 4: Please label these as (a) and (b) rather than left and right so that it is easier to refer them in the main text (see pg 4603/ line 1). X-axis label missing. Also, increase the font size for the axes labels and legend.

Fig 5: Increase the font size for the axes labels and change E.g., to e.g. in the caption.

All of the above changes were incorporated.

Pankow, J. F.: An Absorption-Model of the Gas Aerosol Partitioning Involved in the Formation of Secondary Organic Aerosol, *Atmos. Environ.*, 28, 189–193, 1994.

Smith, J. N.: Observations of aminium salts in atmospheric nanoparticles and possible climatic implications, *PNAS*, doi/10.1073/pnas.0912127107, 2010

Reviewer 2:

General Comments

The manuscript describes ambient air and chamber studies using APi-TOF-MS (Atmospheric Pressure interface- Time of Flight Mass Spectrometry) measuring naturally charged air ions. Mass spectral pattern of α - and β -pinene chamber studies and night time ambient measurements at Hyytiälä are remarkably similar, both showing high molecular weight naturally charged air ions. High resolution enables to determine the elemental composition of those ions which seem to cluster with NO_3 and fluorinated acids in the chamber studies. Results from both, chamber and ambient air measurements, show remarkably high oxidized compounds with high O/C ratio and high H/C ratio, e.g. the compound $\text{C}_{10}\text{H}_{14}\text{O}_{13}$. Indeed the results reported are highly interesting, although no conclusive explanation of the possible structures of the compounds are given. The authors speculate on geminal diols and hydroperoxides to explain the experimental findings, however, several open questions remain. Our major concern is that there exists no potential reaction pathway to incorporate so many oxygen atoms into the carbon skeleton, without breaking the molecules apart (even if gem-diol and hydroperoxides are considered). However, for the observations reported even very small amounts of products (i.e. very minor formation yields of side products) would be enough to explain the experimental findings. Thus, the reported results might stimulate further detailed products analysis also on highly oxidized products. Consequently, the paper fits perfectly to the scope of the journal and it will contribute to understand the role of organic molecules in new particle formation. The paper is well written and might magnify the interest of the community towards organic speciation. We highly recommend publishing the manuscript in ACP, however, have some minor comments on the manuscript.

Comments: Page 4595: “Particularly water, which is believed to be clustered with most of the ions at ambient conditions, is typically so weakly bound that it evaporates from the ions before reaching the TOF region”. Is that pure speculation or based on observations? What if water molecules stabilize the cluster itself (creating an organic-water-NO₃-cluster) or in other words: without non-covalently bonded water the cluster (or more specific the negatively charged cluster) would not be stable? The argument that the major peaks are separated by 16 Th (O) and not 18 Th (H₂O) (page 4606) are not absolutely convincing since such a separation would not be expected when the underlying compounds would have different oxidation states, however, would all contain water (as a cluster stabilization precondition so to say). Obviously such an assumption is speculation too, however, would slightly reduce the pressure to define chemical reaction mechanisms and thermodynamically stable structures for intact C₁₀-backbone oxidation products with the composition suggested.

The water evaporation hypothesis is based on the fact that e.g. HSO₄⁻ is almost completely observed as the unhydrated ion, while e.g. Kurten et al. (2007) calculated that no unhydrated HSO₄⁻ should be present even at an RH of 20%.

Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H₂SO₄ and HSO₄, Boreal Environ. Res., 12, 431–453, 2007.

However, even if the water always evaporates from HSO₄⁻, it is of course possible that water forms particularly stable clusters with the HOMs, as the reviewer suggests. The issue still remains that if e.g. the HOM at 372 Th, C₁₀H₁₄O₁₁, would contain several water molecules in a cluster, this would produce an unreasonably low H/C before coming down to a more commonly accepted O/C for the HOM (C₁₀H₁₄O₁₁, C₁₀H₁₂O₁₀, C₁₀H₁₀O₉, C₁₀H₈O₈, C₁₀H₆O₇, C₁₀H₄O₆...).

Action: Additional clarifications on the possibilities of water clustering were added to the text.

Page 4597: Allowing the exponent n in Eq. (1) to vary, greatly improved the fit over the desired range. What does that mean instrumentally?

The nominal exponent value (n=2) follows directly from the exponent in

$$E = \frac{1}{2}mv^2$$

and therefore the instrument design cannot directly change this value. Instead, letting the exponent vary is adding one more free, and well-behaved, parameter. The main instrumental effect leading to a perceived change in n is the finite rise time of the orthogonal extraction pulse, during which lighter ions can already move significant distances. See e.g. Guilhaus, M., Selby, D., and Mlynski, V. Orthogonal acceleration time-of-flight mass spectrometry, *Mass Spectrom. Rev.*, 19, 65-107, 2000.

Action: We do not add more text on this into the manuscript as the variable exponent method is widely used, and the reference DeCarlo et al. (2006) discusses this issue.

P. 4599, L. 24: During which season were the measurements performed?

The measurements were performed from late spring to early winter (May-November). The spectrum chosen for Fig. 1d was during autumn.

Action: The measurement period was added to the beginning of section 2.2.

Page 4603, L. 7: The HOMs have lower proton affinities? You mean lower gas phase acidities!?

P.4605, L. 10: replace the capital 's' in HOMS.

These corrections were made.

P. 4606 L. 18: It would be advantageous to include citations of papers which indeed observed hydroperoxides in biogenic SOA (e.g. Chen et al., 2011, ES&T, 45 (11), 4763-4770; Reinnig et al., 2009, Rapid Comm. Mass Spectrom., 23 (11), 1735-1741))

We agree with the reviewer, and added the suggested references to the manuscript.

P.4609, eq. (6): $2.78 \cdot 10^6 \cdot \text{cm}^{-3}$

Corrected.