Reply to reviewers, Chemical and isotopic composition of secondary organic aerosol generated by alpha-pinene ozonolysis by Meusinger et al.

Referee comments are written in **bold**, our answers in *italic* and the resulting changes in text are quoted in quotation marks “”.

Anonymous Referee #1
The paper reports a study for secondary organic aerosol (SOA) produced in a large continuous-flow chamber by ozonolysis of a-pinene. SOA was produced by the chemical reaction(s) of a-pinene with ozone in the gas-phase, and the produced SOA was sampled on fiber filters, and followed by analysis using a thermal desorption (TD) system coupled with a proton-transfer reaction ionization mass spectrometry (PTR-MS) for product identification/quantification of fragment ions from SOA components and with a stable isotope ratio mass spectrometry (IRMS) for their stable carbon isotope ratios (d13C). SOA substances on the filter samples were heated to six (or seven) different temperatures in the TD apparatus to desorb the SOA components, and the evaporated substances/fragments of SOA components at each isothermal stage were analyzed by PTR-MS. Independently, d13C of the evaporated organic carbon at each stage was analyzed by the TD apparatus coupled with the IRMS. The study for isotope fractionation possibly provides valuable information to elucidate vailed production/sink processes of ambient SOA, which is one of hot topics in the subject of atmospheric science. Therefore, I think the topic is appropriate for an article of ACP.
Thank you.

General comments
After reading the manuscript, I had impression that points the authors argued were unclear: pieces of discussions seemed to be fragmented.
The discussion was overhauled and there is now a separate section 'Discussion' to allow a clearer distinction between results and discussion. Furthermore, a reaction scheme (new FIgure 1) was added as suggested and used to guide the reader through the paper.

I also had impression that some information and discussion (e.g., already studied C:O ratios and natural processes with isotope fractionations) were very detailed, and some (e.g., chemical reactions that lead to formation of low volatility products, calculation for predicted d13C in Table 5) were insufficient.
We have shortened the former and expanded the latter. The calculations leading to the numbers shown in Table 5 are now illustrated with an example and Table 5 was overhauled. The new reaction scheme highlights the reaction pathways that lead to the calculations in Table 5.

In addition, the authors may want to make more focus on what they can conclude from the data they gained. For example, the position-specific isotope analysis (PSIA) sounded a key achievement in the abstract. However, if my understanding is correct, the PSIA was performed only on the unreacted a-pinene. I did not get what conclusion the authors were

going to draw from the comparison of this information with d13C of step-wisely evaporated OCs, each of which is still possibly a complex mixture of multiple substances as indicated by more than 400 of fragment ions in the table in S4 of SI. If the authors could identify a specific product possessing enriched/depleted 13C atom at a specific position, which may have originated from a specific position of a-pinene, they should make discussion with the observed evidence (e.g., the difference in d13C between the different samples).
Thank you for your comment. It is correct that PSIA was performed on the unreacted a-pinene only. PSIA on single components of the SOA mixture is not possible at this moment. The argument is that if one dominant reaction channel prefers a certain reaction site on the alpha-pinene, then the position specific isotope distribution might govern the overall isotope signature. However, we cannot fully conclude that. PSIA on a-pinene was performed for the first time and we believe that this is an important result for future research and therefore chose to leave it in the abstract. Other parts of the abstract and large parts of the introduction were rewritten. A reaction scheme was added to better guide the reader in the introduction specifically when it comes to the idea that PSIA could play a role in the 'bulk' isotopic composition. This part reads now as:
"The position-specific isotope composition could yield unexpected isotopic fractionation in atmospheric aerosol. For example, the C9-atom in α-pinene is found in many small, volatile ozonolysis products as it is expelled preferentially solely due to its position during fragmentation reactions (see blue squares in Fig. 1). If for example the C9-position was depleted in 13C this could lead to depletion of the gas phase not caused by kinetic fractionation."

Lack of reaction mechanism for production of SOA from ozonolysis of pinene was also a problem to follow the discussions.
Thank you for your comment. We made a new figure (Fig. 1) that identifies how the site-specific α-pinene d13C values propagate through the reaction mechanism highlighting some key arguments of our paper. The following text was added:
"The ozonolysis of α-pinene is often used as a test system for formation of SOA; it is fairly well studied. Figure 1 shows a reaction scheme for α-pinene ozonolysis, based on the Master Chemical Mechanism (MCMv3.1) as described by Camredon et al. (2010). In the first step ozone adds into the double bond of the molecule resulting in two branches depending on the usual Criegee mechanism. These two branches proceed by stabilisation, and subsequent fragmentation and isomerization, and subsequent reaction with RO2, HO2 and H2O to yield a wide range of oxidation products from CO, HCHO and acetone, to many larger oxidised low volatile molecules like pinic acid and pinonic acid and pinonaldehyde. The figure shows only formation of first generation products. Further reactions including dimer formation (Kristensen et al., 2016) and oligomerization reactions are not shown."

At last, I was impressed that the goal of this study the authors state at the end of introduction was not convincing to me.
The larger question is if stable carbon isotopes can be used to trace the origin of SOA and its formation mechanism. The goal was reformulated and now the last sentence of the introduction reads:

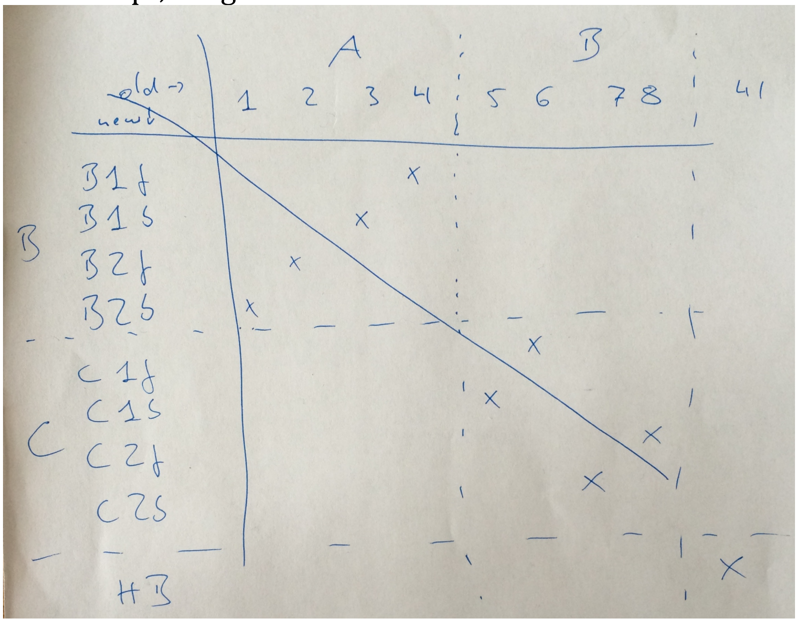
"The goal of this study was to provide detailed isotopic and chemical characterization of newly formed α-pinene SOA and to shed light on the mechanisms that govern isotopic fractionation in the formation of fresh SOA."

The authors may want to thoroughly revise the manuscript, including these points.

We thank the reviewer for the general comments. We adapted the manuscript according to the raised issues and thoroughly revised the manuscript. As part of the overhaul, the experiments and the filter ID's were renamed. Experiment B (former A) is the one using 1-butanol, and experiment C (former B) is the one using cyclohexane as OH scavenger. The new filter ID should make it easier for the reader to remember what as loaded initially on the filter. An explanation of the new Filter ID is given in Table 2 and in the text. It reads:

"Filter ID's are composed of a capital letter denoting the scavenger used, a number counting experiments using that scavenger and a small letter indicating the filter position: 'b' for back filter and 'f' for front filter."

In case the reviewers have their own notes on the previous version of the manuscript, we give a matrix on how the filter names were re-assigned:



		A				B				
	old → new ↓	1	2	3	4	5	6	7	8	41
B	B1f				x					
	B1b			x						
	B2f		x							
	B2b	x								
C	C1f						x			
	C1b					x				
	C2f								x	
	C2b							x		
	HB									x

Specific comments

P3l2-3: the statement "Typically. . ." does not sound right. As long as I know, the direction of condensation/evaporation isotope fractionation depends on substances.

The sentence was omitted.

P3l10: The authors may want to use a symbol of alpha instead of epsilon for the expression of fractionation factor.

We rewrote the section in question and now describe the Kinetic Isotope Effect (KIE) using ε values, as is common practice. We believe this makes the explanation easier to follow and more clear. The replacement of ε by α does not change the manuscript as they are simply related by $\varepsilon=\alpha-1$ which is common knowledge within the field of isotope research (see for example Coplen, 2011). The new text now reads as:

“Kinetic fractionation results from isotope-dependent differences in reaction rates. Let 12k denote a reaction rate constant for a reaction involving a compound containing only 12C and let 13k denote the reaction rate constant for the reaction involving a single-substituted 13C isotopologue; the kinetic isotope effect (KIE) can be written as ε = 13k/12k−1. It is common to distinguish "normal" and "inverse" KIEs.”

P4l20-29: The objective the authors seems to be available without PSIA. The authors should state more clearly why they need PSIA. Referring to the PSIA study for isotope fractionations by NMR, Singleton et al. (1995, JACS, doi: 10.1021/ja00141a030) should be included. I recommend to reorganize this paragraph.
We did not add this reference because it is an old article where the relative position-specific isotopic composition was determined based on elaborate calculations, but without determining delta values. Since about 10 years now, we are able to directly access the delta values using NMR. For the sake of completeness, we follow the reviewers comment and added the citation to the SI, near to the methodology references of the irm-13C NMR protocol (Tenailleau et al. 2007 and Caytan 2007).
The paragraph in question was rewritten (quoted above). Since the reaction scheme was added as Figure 1, the line of argument was sharpened. It should now be easier for the reader to follow our line of thought on why PSIA could play a role by following single C-atoms. We also added calculated examples in the results section, see below.

Section 2.1: a-pinene from different suppliers presented in Table 1 should be stated. Also, I recommend to present a figure for the chemical structure with carbon number for a-pinene here.
The manufacturers names were included in the text.
A figure showing the numbering of the C atoms was included in Table 1.

P5l10: the published year of the reference is missing.
“Viessmann” is not a reference but the name of the company that manufactured the temperature controlled room. In order to make the distinction more clear, we now write “Viessmann A/S” (full danish company name).

P5l13: What did they feed through the flange?
The flanges connect the inside of the bag with the surrounding. We decided to simplify the description and leave out the flanges. We hope that Figure S1 helps illustrating the setup. The text now reads:
“Reactant and sampling gasses are fed through the insulating walls on opposite sides and provide numerous ports for injection and sampling.”

Section 2.2.: I recommend to present an experimental scheme for flow chamber experiment.
Thank you for the comment. A flow scheme was Inserted in the SI and is the new Figure S1. The Figure was referenced wherever suitable.

P6l6: Provide the information of sampling flow rate. The information may give readers some idea of magnitude of artefact.

The sampling rate is given in the sentence at the beginning of the paragraph. In order to improve the reader's flow, we rearranged the paragraph and placed the last sentence after the first. Thus, sampling time and rate are mentioned next to each other:

"On the outlet side, the generated aerosol was sampled after an ozone scrubber on doubly stacked quartz-fibre filters (4.7 cm diameter, QMA 1851, Whatman) for offline chemical and isotope analysis at 10 L/min. Collection times were around 1-2 days in order to provide sufficient amounts of carbon on the filters for isotope analysis, see Table 2. "

P6l20: The authors may want to rewrite the sentence like "Experiments were performed with two different OH scavenger: Experiment A with 1-butanol and Experiment B with cyclohexane."

Thank you for the comment. We replaced the sentence with the one you suggested, except that the experiments were renamed.

Section 2.3.: The information presented here is the initial condition. It is preferable to present the information of extent of reaction of pinene because SOA's O:C and d13C possibly depends on it.

Thank you very much. We followed your suggestion and moved the first paragraph of section 3.1 here.

P7l13: delete "with time-of-flight detector" because PTR-MS is already defined as PTR- time of flight MS.

Thank you for spotting the redundancy. We followed your recommendation and removed it.

P7l20-12: Why did the authors combine the data from the front and back filter analysis together? Please state a reason using a sentence or so.

There is a technical explanation for this as explained in the referenced paper (Holzinger et al., 2010a): "the derived mass for a detected ion may vary a few mDa from file to file due to statistical uncertainty and the limited mass resolution of the mass spectrometer. The homogenization routine creates a "unified-peak-list"; the overall mass accuracy of the detected ions is improved."

"Unified mass list" was replaced througout the text by "unified-peak-list". The text in question now reads: "For each experiment (B or C), the ions detected on the front and back filters were combined in a unified-peak-list to minimise statistical uncertainty and improve overall mass accuracy (Holzinger et al., 2010a). "

P8l30: Equation (3) seems to use inconsistent acronym used in Table 1. Please make those consistent.

We can't see an inconsistency here. Table 1 lists the a-pinene samples, their bulk isotopic values $d^{oj}_{TC}(^{13}C)$*, and their position specific isotopic difference,* $\Delta_i(^{13}C)$*. "j" is just a counter to distinguish the different manufacturer samples. The last sentence in 2.7 gives the formula for the position specific isotopic difference, which is restated in the table's header. This formula is similar but not identical to equation 3, which states how the "bulk" isotopic difference was calculated. We choose not to use the word "bulk" as we discuss different fractions evaporating at different evaporation temperatures.*

P9l1: Present the size and the supplier's name for tin capsules used.

For the bulk measurements alongside the PSIA we used capsules of size 2x5 mm, from Thermo Fisher scientific. For the bulk analysis of the other samples, we used 4x6mm capsules from Lüdi AG (Flawil, Switzerland). The corresponding text passages were added to the manuscript:

"The α-pinene used in the smog chamber experiments and selected filters (cf. Table 2) were transferred into tin capsules (4x6 mm capsules from Lüdi AG, Flawil, Switzerland), weighed and analysed for total carbon isotopic composition, $\delta_{TC}{}^{13}(C)$ in the ISOLAB of the Max-Planck-Institute for Biogeochemistry in Jena, Germany. "

"A precision balance (Ohaus Discovery DV215CD) has been used to introduce 0.5 mg of pure α-pinene into tin capsules (2 x 5 mm, Thermo Fisher scientific), before loading them into the elemental analyser."

P9l16: replace "mix" with mixture.

Thank you, we followed your suggestion.

P10l3: "(1/e)" does not make sense. Readers will appreciate if the authors define the lifetime more specifically.

Thank you. We meant the e-folding time assuming a batch experiment with a single VOC injection and changed the sentence to:

"The e-folding time of α-pinene with respect to loss to ozone is $\tau_{O_3}=(k[O3])^{-1}=$ 40 min based on an ozone concentration of 150 ppb and a second-order rate coefficient of $k = 1.1\times10^{-16}$ cm^3 $molecule^{-1}s^{-1}$ (Witter et al., 2002)."

P10l12: replace "is" with was.

Thank you, we followed your recommendation.

Also "Fig.S1 and S2 in the SI" probably means the two figures in Fig. S1. Please check.

We meant to include only figure S1 (now S2) and panel a of Figure S2 (now S3). the text was changed accordingly.

P10l13: state more specifically what "that point" is.

"That point" refers directly to the sentence before where the only time is given in this context: "ca. one day after start of the experiment ". We modified the sentence in question to: "Sampling on filters was started ca. 24 h after start of injection of VOCs into the chamber. "

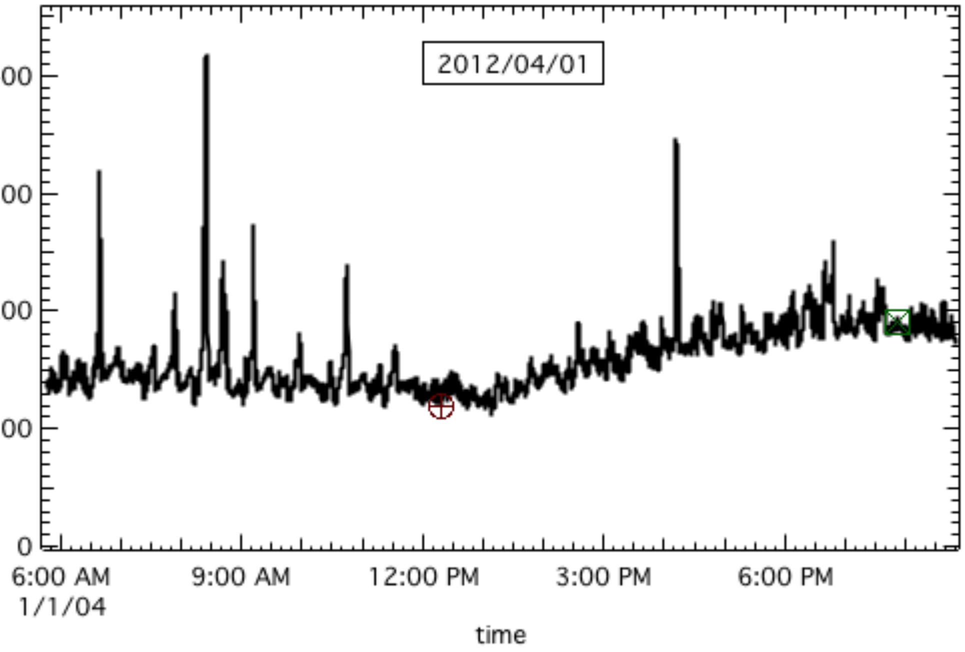
P10l13-14: The sentence with "good agreement" should be discussed with numbers: do they agree within their own uncertainties or standard deviations?

We want to avoid a detailed discussion about different techniques to determine CCN activity and their associated errors as it exceeds the scope of this paper. The important point is that the SOA generated in our experiments is similar in its physicochemical properties to SOA generated by other authors.

Our statement was changed to: "The measured CCN activity of SOA generated in this study resembles literature data for α-pinene SOA generated in batch mode chambers (panel b in Fig. S3 in the SI)."

Section 3.1.: The authors may want to present an example time series plot of ozone mixing ratios and pinene concentrations.

Among authors we discussed providing a plot of the ozone mixing ratios but decided against it. The main reason against it being an interference of organic vapours on the ozone detection system yielding spikes of the ozone mixing ratios. This was tested and confirmed in extra experiments, but with no conclusion / suggestion on how to resolve the issue or how to correct our data for it. An example plot is given here (Experiment B):



In order to avoid an extended discussion on operation and detection mechanisms of ozone monitors, we opted to leave the plot out.
The pinene concentration was not measured.

P10l19: What is "(#41)"?

"#41" denotes the filter number. As all other filters, also the blank filter has an ID, and was simplified now to 'HB' for handling blank. The text in question was changed to: "Very low surface loadings (0.23μg/cm2) were found on the blank filter (HB), cf. Table 2."

P10l31: replace "contain" with contained.

Thank you, we corrected the mistake.

P11l3-16: The discussion in this paragraph is critical. Possible problem(s) causing the discrepancy between the mass conc. by filter sample/PTR-MS and by SMPS may be narrowed down using the references the authors referred. The authors should present the recovery of filter/PTR-MS measurements here.

We were contemplating earlier to include the ratio of SMPS/PTRMS total masses, but didn't follow up on it since both measurements come with severe restrictions: the cut-off diameter of the DMA and the general issues of the PTRMS detection (filter extraction, fragmentation, charring, too low maximum extraction temperature, …). We included an earlier study to comment on the typical recovery *of such an extraction / detection system. The section was also trimmed a bit to make our points more clear (based on the references). It now reads:*

"An earlier study using an impactor-based thermal-desorption PTR-MS concluded that the total aerosol mass measured was typically 20 % lower than the total aerosol mass measured with an SMPS (Holzinger et al., 2010b). The authors estimated conservatively that their PTR-MS setup detected 55-80 % of the total aerosol mass. Filter sampling losses of up to 10 % were attributed to negative sampling artefacts, i.e. evaporation from the filter, during sampling times of 24 h or longer in earlier work (Subramanian et al., 2004). The maximum desorption temperature during chemical analysis was only 350°C and previous studies on β-pinene ozonolysis and photo-oxidation of terpenes also showed significant remaining volume fractions at desorption temperatures exceeding 400°C (Emanuelsson et al., 2013, 2014). Finally, charring and fragmentation in the PTR-MS can additionally lower PTR-MS derived total mass concentrations. Section S3 in the SI describes these processes in more detail, as well as other aspects relevant to PTR-MS data interpretation."

P11l17-24: the discussion is confusing. I do not get the point of argument in this paragraph. Additionally, the digits of masses presented are inconsistent. Please correct those.

Thank you. We overhauled the paragraph. The last sentence was moved and the detials on single masses omitted. The following paragraph (see next item) was removed, and the paragraph after that was completely rewritten in order to simplify the discussion. The main point was to explain the difference between detected mass and inferred compound, but we agree that this is not central to our main arguments and maybe too common.

The section now reads:

"Figure 3 shows ion concentration thermograms of specific compounds desorbing from front filter C1f. Table 4 complements information in Fig. 3 and Sect. S6 in the SI gives the full list of ions detected by PTR-MS from filter C1f. In Fig. 3 most ions 5 show the highest concentrations at a desorption temperature of 150°C, in agreement with Fig. 2, but also show significant concentrations at other temperature steps.

A pure compound is expected to desorb from the filter at temperatures between its melting and boiling temperatures. Dusek et al. (2013) observed this on the same analytical setup for dicarboxylic acids. Such a pure compound should in principle be detected by the PTR-MS as an ion of similar mass and only in this temperature window. There are several possible reasons, why the same ion is observed over a range of temperatures. Since fragmentation of chemical compounds can occur during thermal desorption in the oven and ionization in the PTR-MS (see Sect. S4 in the SI) a fraction of the detected ions are likely fragments of larger (heavier) compounds. This fragmentation can occur at all desorption temperatures and consequently fragments are detected over a range of temperatures. Moreover, an SOA particle usually does not consist of a single compound, but a complex mixture of compounds (Cappa et al., 2008). A specific compound in this mixture will only desorb significantly, when the melting point of the mixture is reached, which might differ from the melting point of the single compound. Specifically, the detection of small ions that are not likely to be present in the particle phase by themselves over a wide range of desorption temperatures indicates oligomers. Recent studies show that high molecular weight dimer esters contribute significantly to SOA from the ozonolysis of α-pinene (Kristensen et al., 2016). These low volatile compounds are believed to form from gas-phase reactions of the α-pinene derived Criegee Intermediate with abundant α-pinene oxidation products such as pinic acid. Decomposition of the dimer esters such as those reported in Kristensen et al. (2016) and subsequent volatilization of the carboxylic acid moieties could at least partly explain the detection of specific ions over a range of desorption temperatures."

P11l25-31: Similarly to the previous paragraph, I do not understand the point of this paragraph. The statements are kind of common sense within chemists.
The paragraph was omitted, see previous item.

P11l32: replace "significantly" with appreciably or considerably. If you use stats in your argument, significantly would be more appropriate.
This sentence was omitted, see previous items.

P12l11-12: "The reaction of OH. . ." seems to suggest contribution of scavenger to SOA or SOA reactions. Any discussion with references?
In the same paragraph that contains this sentence, we discuss our result briefly in light of other publications, e.g. Docherty and Ziemann, 2003, Keywood et al., 2004, Jenkin, 2004, Shilling et al., 2008. As we don't feel this discussion will lead to any major insights concerning the isotopic fractionation, we did choose not to deepen it further. However, in order to strengthen this point we added the following sentence:
"However, the most abundant reaction products were not affected."

Section 3.2.3: I am not sure how important the results of back filter analysis are. Figure 1 tells the amount in the back filters was very small relative to the front. How will the manuscript be without the section 3.2.1? If the results are necessary to justify a point of the authors' argument, they should write the point explicitly.
Thank you for your comment. We discussed this issue several times between authors. Due to your comment we decided to place the main part of this discussion in the SI. The backup filters support one of our main conclusions, namely if a-pinene is almost completely reacted, and particle phase is enriched, the gas phase must be depleted. This we see on the backup filters (which collect adsorbed gas-phase molecules). We consolidated the main results of the back filter analysis into one paragraph and now write in the main manuscript (first paragraph in Sect. 3.2.2):
"Figure 2 shows the sum of ion concentrations at each temperature step as measured by PTR-MS. All front filters (B1f, B2f, C1f, and C2f) show a similar profile with most of the mass desorbing at 150°C. The back filters (B1b and C1b) are used to characterize the positive sampling artifact, namely gas phase compounds that adsorb to the quartz fiber filters. Material collected on QBQ back filters can be assumed to mainly consist of adsorbed gas-phase compounds corresponding to a positive gas-phase artefact (Cheng and He, 2015). This is confirmed by the chemical analysis of back filters in this study, which differs considerably from that of the corresponding front filters, as detailed in Sect. S3 in the SI. The back filters show small mass loadings - roughly 6 and 13 % of the masses of their respective front filters. The large mass difference between front and back filters suggests efficient sampling of a dominant aerosol phase on front filters and a small positive sampling artifact. The front filters were not corrected for the sampling artifact."

P16l10-19: The calculations for prediction of d13C are not described, although the heading of Table 5 state "details in the text". Please provide

the way to calculate those as well as factors (i.e., epsilons) used in the calculations.

We now speak of maximum expected enrichment and added the assumption that branching ratios would not affect the isotopic distribution. We give examples of our calculation, but feel that no more details are necessary: please note that under the assumption that such an expulsion reaction ran to completion, the isotopic distribution is independent of any epsilon value, be it position-specific or not. We also found an error in our manuscript, as there are no reaction products composed of only 2 carbon atoms, but only 1 (e.g. CO) and 3 (e.g. acetone). Table 5 was updated and the text now reads:

"Some simple considerations regarding the maximum expected isotopic enrichment of α-pinene fragmentation products can be performed based on the Δi 13C profiles obtained from PSIA. Table 5 shows predicted maximal enrichments/depletions if a single carbon atom or reasonable combinations of three carbon atoms are split off the parent compound, based on the simple assumptions that such reactions run to completion and that other competing reactions (branching indicated by arrows in Fig. 1) have no effect on the isotopic enrichment. Based on the chemical reaction pathways presented in Fig. 1, volatile reaction products such as acetone, CO, and formaldehyde can in most cases be assigned as originating from specific sites of the parent α-pinene. The minor (potentially gaseous) expelled fragment is predicted to have an overall isotopic difference relative to the initial α-pinene, Δgas 13C, similar to the measured Δi 13C value for the carbon atom's former position as seen in Fig. 7. The larger fragment, which would partition to the aerosol phase, is predicted to have an overall Δaerosol 13C value equal to the average of the Δi 13C values of the remaining C atoms. For example, the pathway leading to formaldehyde in the sixth box in Fig. 1 is predicted to deplete formaldehyde by Δ9 13C = 6.7‰ relative to the initial compound and leave the corresponding major fragment (denoted as 'R' in Fig. 1) enriched by Δi 13C = 0.8‰. Here, [...]av(i=1−8,10) av(i=1−8,10) denotes the mean of Δi 13C values for C atoms 1-8 and 10. Expelled C-atoms from positions with small Δi 13C values, e.g. C7, will only have a small impact on the isotopic composition of the remaining fragment. For expulsion of C2, a depletion of -1.1 ‰ is predicted for the aerosol fragment relative to the initial α-pinene.

If three carbon atoms are expelled as in the case of acetone, the isotopic difference of the minor fragment relative to the initial α-pinene is calculated as the average of the Δi 13C values of the respective expelled positions C8, C1, C9 or C10, C1, C9, see Fig. 1. The formation of acetone involves methyl migration of either the C8 or C10 atom. The gaseous fragments composed of three carbon atoms are predicted to show Δgas 13C values of −0.7‰ and −2.0‰ and the corresponding Δaerosol 13C values for the larger fragment are 0.4 ‰ and 1.0 ‰, cf. Table 5. These calculations are based on the measured position-specific enrichment for sample 2 in Table 1, but the results and conclusions drawn do not change significantly when performing similar calculations for the other α-pinene samples were PSIA data is available."

In addition, according to Fig 7a, OC at 100 degree Celsius (□ 7% of TC) has the largest difference of -3 permil in d13C. Any discussion for this difference? Does this difference attribute to different isotopic composition of different chemical species? This is the part the authors should make deeper discussion, I think.

We suspect the reviewer was commenting on panel b of that Figure and will give our answer accordingly. The second last paragraph of section 3 discusses the strong enrichment observed at 100 C. However, the discussion has to stay vague as no clear conclusions can be drawn from the data. Unfortunately, no species or group of species could be assigned to this enrichment. We omitted the last part of the paragraph which dealt with the back filters and added another consideration based on oligomerisation. The text was changed to:
"The reason behind the enrichment in material desorbing from front filters at 100°C cannot be unambiguously identified. The chemical analysis did not allow to identify single compounds or groups of compounds that contributed significantly more to the total aerosol concentration at 100 °C than at 150 °C and therefore could lead to the observed enrichment. Isotope effects associated with sampling artefacts, which are generally not well known, provide room for speculation on how to interpret the enrichment at 100 °C. During the negative sampling artefact, isotopically light isotopologues re-volatilise from the ensemble of sampled compounds preferentially leading to an overall isotopic enrichment in compounds that are left on the filter. Re-volatilisation should have it's largest effect at 100 °C. Another explanation can be based on oligomerisation. Hall and Johnston (2012) observed significant evaporation of oligomers in a thermodenuder already at desorption temperatures below 100°C. The effect of oligomerisation on isotopes is not known, but if it leads to enrichment, the fragments of decomposed oligomers could be enriched and explain our observations."

P16l2033: There are papers discussing site specific isotope fractionations. Why do the authors argue with reactive isotope fractionations using the reference of sorption isotope fractionation of vanillin?
There is not much literature available on the topic as the analysis technique is rather new. However, we now included the Botosoa et al., 2009b reference in the text and omitted speculations about bond length variations. The full paragraph reads now as:
"A more realistic set of possible explanations for the observed fractionation of SOA relative to α-pinene should include isotope-dependent changes in branching ratios in the reaction mechanism (Fig. 1) and incomplete reactions. These effects complicate the analysis significantly as new factors come into play, including most notably, kinetically-derived position-dependent isotopic fractionation. It has been shown previously in simple systems (e.g. evaporation of solvents and sorption of vanillin) that each carbon position can have its own isotopic fractionation and that different positions can show normal and inverse isotope effects at the same time (Höhener et al., 2012; Julien et al., 2015). In chemical reactions, the substitution of a 12C atom by 13C will affect isomerisation and stabilisation dynamics by changing vibrational frequencies with an associated change in zero point energies. Therefore, positions that are not reaction sites can also show isotope effects, which have been termed non-covalent isotope effects (Wade, 1999), as has been observed during the chain-shortening reaction for the bioconversion of ferulic acid to vanillin (Botosoa et al., 2009b). It is generally difficult to predict which position has which isotope effect, but it has been shown that isotopic substitution in ring structures at positions that carry functional groups leads to stronger position- specific isotope effects compared to positions that have no functional groups attached (Höhener et al., 2012; Botosoa et al., 2009b). Similarly, the C-atoms in α-pinene that are not part of the ring structure

might have large position-specific isotope effects. However as Höhener et al. (2012) note for the case of vanillin, and as we also show in Table 5 in a simplified scenario, such effects leave the bulk isotopic composition largely unchanged, making the use of PSIA in SOA studies beyond what has been done here potentially challenging."

P17l1-4: As long as I read, the authors never measured d13C of residual pinene and products in the gas-phase. The statements sound too speculative.

That is correct, we have not directly measured isotope ratios of gas-phase compounds. There should be no residual a-pinene left in the gas phase. The first sentence was omitted. See also next item.

Section 3.3.2: The section seems to discuss possible phenomena of isotope fractionations that products the authors observed may have undergone. But many of them are speculations. The authors may want to write the section more concisely.

We agree on the speculative nature of the section. First of all, we renamed it ("Discussion") and added an explanation in the beginning to highlight that there is no unambiguous conclusion possible. We therefore discuss a couple of options (fragmentation, partitioning, etc.) and how they would affect the isotopic composition. The section was completely rewritten. Here we only quote the new beginning of the section:

"SOA formation in α-pinene ozonolysis includes several chemical processes that influence the isotopic compositions of product species. The presented data does not allow unambiguous identification of the underlying effect that lead to enrichment of the aerosol phase with respect to the gas phase and this section discusses different possibilities to explain the observations."

Comments on Figures

The figure captions for Figure 1 and Figure 2: I do not know the difference between these figures by reading the figure captions. Please state what these are more specifically.

Thank you for raising this point. The caption and y-axis label of the first Figure now reads "Sum of ion concentrations" in order to ease understanding of the reader.

Figure 1: Why do the authors present the results for two back filters only? Likewise the front filters, the authors may want to present the results for all the back filters or to state a reason why not showing the rest of the results.

Data for filters is only presented when enough sample was available for multiple measurements. Some of the samples were 'lost' to adjusting the setup, etc. the following line was added:

"Data is only shown for filters when multiple measurements were performed."

The figure caption for Figure 3: I don't understand the sentence "The allows highlight. . .". Please rewrite it.

We mean that there are lobes of peaks present in the spectra and that they result from fragmentation patterns. The arrows highlight two elements in such a cascade of lobes. The text in question was changed to:

"The presence of lobes with specific periodicity is apparent. The arrows highlight

two detected fragmentation patterns that cause the periodicity: that of a CH2 group (light green arrow) and that of water (dark blue arrow), cf. Sect. S3 in the SI.”

Comments on Tables

I do not see a point presenting Table 3 because the authors do not argue with the information in this table.

Thank you for the comment. As the second reviewer pointed out that there is information missing on how the literature was selected, we feel the two reviewers differ in their opinion on this matter. We chose to include more information on the matter of choosing these publications and keeping Table 3 in the manuscript. See mored etails in the response to the second reviewer below.

Comments on Supplementary information

The authors may want to organize the SI more concisely. Please keep minimum to present extra figures and description even in SI.

Thank you for your comment, the SI was completely restructured. However, in order to slim down the main document, we had to move some parts to the SI that we feel should not be left out totally (e.g. chamber design, blank filter analysis). We hope that the SI still meets the high standards of ACP and the reviewer.

Anonymous Referee #2

General
This is a manuscript on an interesting small flow chamber study on the oxidation of a-pinene by ozone. Its highlight is the isotope analytics. The thermal desorption isotope analysis of filters is surely a nice and non-standrad method which should lead into new insights into VOC oxidation and SOA formation.
Thank you very much.

The paper is quite technical in a sense as it describes isotope techniques, the new chamber in detail.
Thank you. We feel that it is necessary to detail some of the techniques in the main document as they are non-standard in the field of aerosol science at the moment. On the other hand, we put some content (specifically on the chamber design and operation) in the SI in order to trim the main document.

What strike me is that there is a number of importants results all of which have to be put into the context of what is existing already. What is new here ?
Thank you for your comment, we think it is an important point that this is a source characterization study that can be used for the interpretation of ambient measurements. Some simple observation that we highlighted more clearly:

- *SOA formation from a-pinene is a mechanism producing material with typical desorption temperatures that are relatively low (100 – 150 C)*
- *The observed PTR-MS O/C ratio is in the range of 0.18-0.25*
- *d13C of formed SOA shows enrichment in the particle phase and stays relatively constant over different desorption temperatures*

Those points were more pronounced in the abstract and main text of the document. Some papers using the same analytical setup focussing on typical ambient spectra are unfortunately just in revision: Oyama et al., on tunnel aerosol, and Masalaite et al., on ambient aerosol collected in Lithuania. We hope that our paper provides the basis in future work to be used as a reference for SOA compounds.

What has been found already and is confirmed ?
We restructured the manuscript which now includes a general discussion section. Here, we present how different chemical processes might lead to the observed enrichment in the aerosol phase, and discuss these effect in light of other studies. The result section (former results and discussion section) stays closer to the data and compares our findings to other studies. We will not quote these extensive changes here, as they are too long to include but invite the reviewer to read the reformulated Sections 3 and 4.

I would suggest to go through the data of Table 4 and discuss each of, at least, the most important systems. The selection of compounds included into Table 4 is kind of rigorous as its elects 'the 20 ions with the highest concentrations'. There might be other important producst being identified when all the results are considered and a more detailed discussion of this

finding is warranted to make the paper a more substantial contribution to what is already know on a-pinene SOA from ozonolysis. I am aware that introducing such discussion of results puts a demand on the authors but I think the paper would gain much value and much better contribute to the science related to the system studied here.

Thank you for the comment. We followed your advice and included a Discussion section on its own, as described before. However, we must point out that the suggested task is very cumbersome and exceeds the scope of this manuscript (which is pretty long already). We hope that the presented work could be the basis of another paper comparing detected ions/compounds and their sources.

In order to better communicate our findings, we added a reaction scheme (Figure 1) and cross-referenced certain products that were found in our study, throughout the manuscript. Compounds predicted by the MCM can for example now be found in Figures 1 and 3, Table 4, and Section S6. The accompanying text in Sect. 3.2.2 reads now:

"Compounds predicted by modelling studies are noted by their capitalised Master Chemical Mechanism name in the description field in Table 4 and Sect. S6 in the SI, confirming the presence of several predicted species. These compounds include pinic acid (compound #72 in Sect. S6) and pinonic acid (#116 in Sect. S6) which are also shown in Fig. 1."

We added the following line to the caption of Figure 3:

"These are the same compounds as below the line in Table 4 and include those predicted by the MCM, e.g. pinic acid (187.093 Da) and pinonic acid (185.117 Da)."

I am missing a condensed assessment of literature available which then leade to the selection of Holzinger et al., 2005, 2010a; Winterhalter et al., 2003; Jenkin, 2004; Jaoui and Kamens, 2003 for comparison as listed in Table 3.

Thank you for your comment. In the second-last paragraph in section 3.2.2, we detailed some aspects of selecting literature to compare our results to. The main point was that the references presented detailed lists of detected constituents of particulate matter that allowed for direct comparison to our findings. Preference was given to such studies that also used PTR-MS and that were investigating α-pinene ozonolysis. The following sentences were added:

"The chosen references (cf. Table 3) preferably listed detected constituents of particulate matter to allow direct comparison with compounds found in the present study. Preference was furthermore given to such studies that also used PTR-MS and that were investigating α-pinene ozonolysis."

Overall, the paper warrants publiction subject to a revision somewhere between minor and mayor.

Thank you very much. We included both minor and major changes in the manuscript and hope the reviewer agrees with us that the revised version addresses most raised points. Please also see the reply to reviewer 1 for changes in filter ID's and experiment numbering - all of which are intended to ease the experience for the reader.

Details

Abstract: I feel the abstract is very broad, hence should become more specific and highlight the most important quantitative findings. Especially, more substance-specific results should be given.
The abstract was rewritten. However, as most of the results from the isotope analysis are not substance-specific, it was not possible to be more specific in that sense.

Experimental: The S/V of the new chamber should be given close to where the volume is mentioned.
Of course, thank you for pointing that out. We added the following text:
"(the volume/surface ratio is 0.275 m)"

Page 7, line 18: This is not a particularly high mass resolution. I would just state '...the PTR-MS had a mass resolution () allowing....
Thank you for your comment. We changed the sentence in question to:
"The PTR-MS had a mass resolution of $m/\Delta m \approx 4000$ allowing detection of ions with differences in m/z larger than 30mDa."