

Please find attached our author response to all comments provided by reviewers of Hamilton *et al.*, 2010, “Investigating the use of secondary organic aerosol as seed particles in simulation chamber experiments”, submitted for publication in Atmospheric Chemistry and Physics. We would like to thank the reviewers for their comments. We additionally provide an amended manuscript in accordance with the comments, as detailed below.

Review 1

Detailed Comments

Reviewer 1 suggests that the article might be better suited to the sister journal of ACP, Atmospheric Measurement Techniques. The authors take on board this comment but insist that the article is in line with work previously and currently published in ACP; it does not solely address a measurement technique issue nor does it constitute a technical instrumentation paper. It describes findings from an atmospheric science experiment that are pertinent to studies in atmospheric science. Moreover, the work described within this article was funded as part of the ACES (APPRAISE) programme and as such we would like it to be published alongside its related companion work in the OP3/ACES special issue of ACP.

Anonymous reviewer 1 kindly listed a series of detailed comments and corrections, these have all been considered and addressed accordingly, as detailed below:

25120-9: I suggest writing [one possible explanation]

The red text has been added to the manuscript to provide the requested explanations.

“Recent modelling studies of atmospheric aerosols using explicit chemical mechanisms based on results from simulation chamber experiments have shown a significant under-prediction of secondary organic aerosol formation (SOA) when compared to measurements. **For example, in their respective studies, Volkamer et al. (2006) and Capes et al. (2009), reported under-predictions in modelled SOA by factors of the order 4 – 15, when compared to measurements.**”

25120-14, [it can be considered more reasonable] is awkward

“Whilst organic nucleation is not widely observed in the real atmosphere, it can be considered more reasonable for oxidised VOC products to condense on to pre-existing aerosols.”

Has been altered to:

“**In general, owing to the widespread presence of pre-existing condensation surfaces in the real atmosphere, organic nucleation is not widely observed; the more common phenomenon is the growth of organic aerosol mass via the condensation of oxidized VOC products onto pre-existing aerosols.**”

25120-16, the advantages & disadvantages of using inorganic vs organic seed particles are not well summarised in the paper. Surely the SOA seed has some advantages, but it also introduces additional uncertainties.

- For example the seed may evaporate over long times even if it does not in the short dilution period.
- Also the seed makeup is quite different than the limonene SOA as exemplified by the O:C data presented later.
- Activity coefficients for limonene SOA will be higher than one and distort its composition, favouring partitioning of less polar species and decreasing partitioning of the more polar ones.
- Also partitioning of limonene SOA will increase activity coefficients of less polar seed species, causing some of them to evaporate. Then some chemical changes such as those in figure 6 could arise for this reason, etc.
- The paper should include a prominent table of pros and cons of each approach.

This paper does not constitute a review article for the use of seed species in aerosol simulation chamber work and the authors believe that a substantial enough fraction of the article has been dedicated already to a summary description of other seed types, i.e. see page 25120, line 18 – page 25121, line 21, which essentially constitutes just this.

25120-22, my understanding is that most experiments in the past have used dry ammonium sulphate, rather than aqueous AS. For example see papers by Odum et al.

A reference has been added for the work of Odum et al., and the text has been altered to acknowledge the previous use of dry ammonium sulphate as a seed in aerosol chamber studies. The text now reads:

“Historically, most chamber experiments have used inorganic aqueous solutions of ammonium sulphate or sulphuric acid as seed aerosols to study SOA formation (Hallquist et al., 2009), sometimes dried prior to use, e.g. Odum et al., 1997. Such studies...”

25121-10, use of pure component organic seeds, or of mixtures of a few components, is dismissed without sufficient discussion. Some disadvantages are given, but as discussed earlier the SOA seed also has some disadvantages. It is my impression that use of simpler OA seeds has not been explored all that much in the literature, and deserves further study. This type of seeds should be added to the table suggested above.

We acknowledge that most of the reported literature so far has been on the use of inorganic seed and more work is needed to explore the used of various organic seed. We have focused in this study on smog chamber generated SOA and more work is needed to explore the options suggested by the reviewer. However, it is not the purpose of this work to conduct a full review on the use of and the pro’s and con’s pertaining to the various species of seed used in SOA studies, that work would need an entirely new and dedicated publication.

25122-18, as this paper seems to be the first one about the Manchester chamber, more detail is needed about how the lights were tuned and evaluated.

This paper does not constitute a technical description of the chamber facility, it simply reports a series of experiments conducted using the infrastructure. The specific details regarding the chamber itself (and further detail regarding the lights)

will soon be presented in a dedicated publication (McFiggans et al., 2011), which is currently in preparation. A reference to this paper has been added accordingly:

“A comprehensive and detailed description of the University of Manchester Aerosol Chamber will be presented in a future publication (McFiggans et al., in preparation), hence only an introduction and general overview is provided here.

25122-22, some HEPA filters are known to give off large amounts of VOCs that could make SOA. Has this effect been evaluated? The brands and model numbers of the charcoal, purafil, and HEPA filters should also be given, or a previous paper cited if it exists. For the same reason a diagram of the chamber should be given.

This potential effect is regularly evaluated and quantified by conducting chamber background measurements (full simulation without the use of any VOCs). Both aerosol and gas phase measurements are taken during these experiments and there have been no evidence at all of any large amounts of VOCs given off by the HEPA filters.

The charcoal and HEPA filters are provided by Donaldson Filtration (GB) Ltd. The Purafil is (Purafil SP media from Purafil, Inc., USA). The suggested chamber diagram will be presented in the chamber’s full description mentioned above (McFiggans et al., in preparation)

25124-5, need error bars representing the variability of temperature and RH during experiments

We have provided the average and standard deviation of the requested data in the revised manuscript. $T = 25.7 \pm 0.7$ °C and $RH = 71 \pm 1.6$ %.

25124-12, the type of NO_x detector used is known to have artefacts due to NO_y species (see for example Dunlea et al., Atmos Chem Phys 2007). Has this effect been evaluated or corrected for in any way?

The authors recognize that the NO_x detector employed is known to produce data that may be subject to artefacts owing to NO_y interference. This has not been evaluated in this study. However, we believe that this does not have a direct impact on the interpretation of the results provided or the conclusion of the study.

25124-25, what is N6.0?

N6.0 is a reference to the purity of the nitrogen used; it represents an N₂ purity of 99.9999%. The sentence has been changed as follows for clarity:

“In this instance, the hydronium ions were generated from a humidified N₂ carrier gas (purity = 99.9999%).

25125-7, what are the units of 1/4 ? Is that really ID and not OD? (The latter is much more common).

Line 25125-7 contains a typo, the units of “1/4” are inches and it refers to the internal diameter of the tubing. The sentence now, reads:

“Chamber air containing the analyte was delivered in a continuous stream (approximately 230 sccm) to the drift cell via a 0.5 m long, 1/4” (internal diameter) Teflon sample line, heated to 40 (±1) °C.”

25126-18, more detail on Peltier units is needed

As requested further detail regarding the Peltier unit has been added. Such that the sentence now reads:

“The temperature of the DMAs and humidification system is controlled using peltier units (Supercool®, AA-040-12-22, Sweden)....

25128-11, MW should probably be MB

This has been corrected to MB

25129-16, an SMPS & an Aerodyne MS were used here, can the authors derive density from those measurements as others have done?

It is true that this combination can –in principle- yield an effective density measurement. However, in this particular study, the DMPS was running with a dry sheath flow, while the AMS was running without a dryer which made the comparison more difficult to achieve.

25130-9, volatilisation may have occurred over longer time scales and this needs to be acknowledged

The section has been altered accordingly to acknowledge the potential volatilization of some material over longer time scales:

“Our dilution time scale was much shorter and did not lead to any volatilisation of SOA. **It should be noted however, that volatilisation of some of the SOA material may occur over longer time scales; this was not explored here.**”

25132-14, particle losses should be discussed more clearly here

It is unclear what the reviewer wants here. There are likely to be a number particle loss mechanisms but as yet we have not quantified these. Thus we cannot give wall corrected yields and this is clearly stated in the text.

25132-17, my understanding of the Ziemann results is that species of intermediate volatility may be most affected. Species of very low volatility will partition to particles very quickly and not have time to get to walls. Species of intermediate volatility will stay longer in the gas-phase -going in and out of particles- and will have more of a chance to reach walls. This effect will depend on the particle surface area concentration.

The section has been altered accordingly to express the reviewer's comments:

“Recent work has shown that wall losses of SVOCs may be significant in chamber studies (Matsunaga and Ziemann, 2010), which could lead to an additional factor of uncertainty in the yield values quoted here. However, high molecular weight and low volatility oxidation products (such as those derived from β -caryophyllene and limonene) are believed to partition quickly to the aerosol phase and hence their gas phase concentrations will be less influenced by the presence of chamber walls. As the measured SOA mass loading of the chamber does not account for loss of particle mass to the chamber walls, the yields presented here are expected to constitute a lower limit for these experiments.”

25133-17, the work of Li et al. was not mentioned before. The contrast needs to be expanded upon at this point.

The difference between this work and that of Li et al., has been expanded upon; the key differences between the major components of the SOA in each study has been quoted.

“Compositional analysis indicated that the main β -caryophyllene oxidation species in the seed were β -caryophyllonic acid and β -caryophyllinic acid, which are first generation products. This finding is in agreement with the work of Jaoui et al. (2003, 2007), who reported the first measurements of β -caryophyllinic acid in SOA generated from the photo-oxidation of β -caryophyllene, but is in slight contrast to the recent work of Li et al. (2010), who reported the presence of several other compounds amongst the most abundant species in their β -caryophyllene SOA, formed from the dark ozonolysis of β -caryophyllene. Besides β -caryophyllinic acid (and its structural isomers), the most abundant species observed by Li et al. included: 3-(4-acetyl-7,7-dimethyl-3-oxabicyclo[4.2.0]oct-4-en-2-yl) propanoic acid, 2,3-dihydroxy-4-[2-(4-hydroxy-3-oxobutyl)-3,3-dimethylcyclobutyl]-4-oxobutanoic acid and 4-[3,3-dimethyl-2-(3-oxobutyl) cyclobutyl]-3-hydroxy-4-oxobutanoic acid (and structural isomers). Furthermore, Li et al. state that these latter three compounds, amongst the most abundant components of their SOA, constitute second-generation species.”

25133-26, it is confusing to talk about the [detailed composition] here, when only rough patterns are discussed for the most part

The authors feel that this sentence is not at all confusing. The SOA composition was investigated in detail, using comprehensive 2D GC-MS, LC-MS and FTICR techniques, to state otherwise would simply be incorrect. Furthermore, a very detailed and comprehensive table is given (Table 2), detailing numerous limonene oxidation compounds found within the condense phase seed. In addition, Figures 5, 6 and 7 give detailed insight into the composition of the SOA. Further detail is not given regarding the composition of the β -caryophyllene seed, as this is the subject of a further paper (currently in preparation) and its inclusion here would make the manuscript to large and shift the focus of the paper.

25134-16, change [correlates] to [qualitatively correlates]

The text has been altered accordingly. The sentence now reads:

“This **qualitatively** correlates well with the increase in f44 seen in the AMS spectra.”

25134-20, no evidence is given about 350C being insufficient to volatilise some of the b-c SOA. How is this known?

This is based on an estimate of the vapour pressure of some of the higher molecular weight products found in the FTICR-MS and potential oligomers but it has not been studied experimentally. The wording has been changed to reflect this.

25135-1, is it really proper to shift all the peaks by 23 Da? Electrospray still makes other adducts such as those formed by protonation. This may then

introduce a large error.

Using this type of system, we find that sodium attaches itself to nearly every oxygenated molecule. This is true for standard mixtures and previous SOA samples. For these samples, this is confirmed by the FTICR-MS, where the >95 % of molecular formulae identified in positive mode contain a Na ion. Therefore, shifting the mass spectrum by 23 Da is an appropriate method of data analysis. Explanatory text has been added to the manuscript.

25135-3, the evidence for the statement in the sentence starting by [using] is not given and needs to be.

The compounds in question were identified using LC-MSⁿ. This technique allows isolation of specific ions followed by controlled fragmentation. The resultant fragmentation patterns are compared to library spectra to confer identity. The identified products were then compared to those that are known to form from the reaction of β -caryophyllene with OH and ozone, following basic gas phase chemical reaction theory. The sentence has been altered accordingly:

“Using LC-MSⁿ these species were isolated and subjected to fragmentation, to give distinct, compound specific mass spectra, from which it was possible to assign respective identities using library spectra obtained from previous β -caryophyllene SOA experiments. The distinct fragmentation patterns produced indicate that these species are known primarily first and second-generation products of OH and O₃ chemistry.”

25135-24, what about N being present in the SOA? There are high levels of NO_x in the chamber so some organic nitrates will be formed. This seems too rough and simplified.

In order to check the presence of N in the aerosol, we have reanalyzed the data, allowing the presence of up to 3 N atoms per molecule. The software identified very few additional species, and most of these proved to be impossible based on composition, unsaturation and starting materials. This led to no change in the O:C ratio.

25136-5, the word [exactly] should not be there. The electrospray signal does not scale with concentration at all in many cases. Some species may not be ionised at all, while species that are easy to ionise will have intense signals despite low concentrations.

The word “exactly” has been removed, so that the sentence now reads:

“Although peak intensity does not necessarily scale with concentration, a comparison of the relative intensity patterns is still informative.”

25136-9, can the authors compare these results with those from the AMS? Many people are presenting O:C ratios based on the AMS based on a 44 correlation. It is very important to compare both methods.

The O:C obtained from the f44 is not based on actual experimental data obtained during this experiment but rather a factorial analysis of previous AMS data. We feel that we do not have enough data to allow this type of comparison here. In future

experiments using a high resolution AMS, we would of course attempt this type of analysis.

25136-17, it is not clear here whether the O:C / GF relationship is qualitatively or quantitatively the same as in Jimenez et al. A graph would be best. Otherwise the statement needs to be labelled as qualitative

Added “qualitative”

25148, the size of the particles in the upper graph needs to be given in the caption
This is based on the entire range of 50-500 nm. This has been clarified in the text.

25149, figure 5 is very difficult to read. A white background should be used instead of a blue one. Axes are needed. Zooming in the region of interest would help

A white background has been tested with this figure and the data is more difficult to visualize. A blue background provides the best image. Axes have been added.

25150, all the labels in figure 6 are tiny and difficult to read

New labels done

25151, labels of figure 7 are too small, and a different colour contrast is needed (white for no signal instead of dark blue)

A white background has been tested with this figure and the data is more difficult to visualize. A blue background provides the best image. The authors feel that the labels are the correct size for the image.

Review 2

Specific Comments

1. There appear to be some slightly unusual aspects regarding the use of NO_x in these experiments and clarification is required on a number of issues.

(i) The source of NO_x should be stated in section 2.2, where only details for NO₂ addition are provided. In classical photo-oxidation experiments, NO_x is typically added as NO, which becomes partially oxidized to NO₂, with the result that the NO mixing ratio is several factors larger than that of NO₂. However, as shown in figure 1, the initial NO₂ levels are higher than those of NO. Was this deliberate or was it due to the method for introducing NO_x? Some comment is required here.

For our experiments, NO_x was introduced into the chamber in the form of NO₂ only, directly from cylinder. The text has been altered accordingly to state this.

For such studies NO_x is often added to chamber experiments either as NO, NO₂ or a mixture of the two (NO + NO₂); in this instance NO₂ alone was employed. The text now states this in a clear manner.

Owing to limitations in the NO scrubbing mechanism of the Manchester Chamber at the time the experiments were conducted, it was not possible to remove all of the NO from the zero air gas used to fill the chamber. As such a small chamber

background of around 10 – 15 ppbV NO was present during the experiments, therefore no additional NO introduction was required and NO₂ alone was employed. The scrubbing mechanism of the Manchester Chamber has subsequently been modified to achieve a background of 1-2 ppbV levels of NO. The text has been modified to make this clearer.

When chamber experiments are initiated with NO only, wall reactions are required to initiate the chamber chemistry, i.e. under illumination of the chamber lamps, HONO and NO₂ are liberated from the chamber walls (e.g. Stroud et al., 2004; Metzger et al., 2008), before undergoing photolysis to produce OH and atomic oxygen, and hence subsequently, oxidized VOC, RO, RO₂ and O₃ and ultimately SOA. If NO₂ is introduced in appreciable abundance before the start of the experiment, direct photolysis and radical and O₃ production will occur rapidly, resulting in a quicker “start up” phase. Previous studies have shown small difference in experiments that have been initiated with NO vs. NO + NO₂.

All modification to the text to address reviewer comment 2 are given below:

“Section 2.2 Experiment Methodology

The secondary organic aerosol seed was generated from β -caryophyllene in the presence of NO_x (Initial VOC:NO_x ~1–2) using a conventional nucleation and growth experiment. The experimental details are summarised in Table 1. Approximately 98–99% of the precursor β -caryophyllene had reacted after about 3 h. This was verified using the CIR-TOF-MS. After this time, chamber lights were turned off, and a fraction of the chamber content was flushed out and replaced by clean air. This resulted in dilution of the seed concentration down to approximately 4 to 13 $\mu\text{g m}^{-3}$, depending on the experiment, and also the dilution of the gas phase reactants. During the dilution phase, limonene was injected into the chamber and, if required, the NO_x level was adjusted **by the injection of an additional quantity of NO₂ gas**, to keep the VOC:NO_x ratio at around 2 (a fixed ratio was **chosen to reduce system variables pertaining to the presence of NO_x and hence to enable comparisons to be made** between experiments). Following this flush/refill phase, chamber lights were turned back on again to allow for the photooxidation of limonene.

Filters were collected in a specially constructed holder, positioned in the chamber vent line. Aerosol samples were collected onto 47 mm quartz fibre filters (Whatman) at a flow rate of 3 $\text{m}^3 \text{min}^{-1}$.

Filters were collected during the dilution stage to obtain a β -caryophyllene seed sample, which was used as a background for the limonene SOA. Limonene SOA+seed samples were collected at the end of the experiment. After sampling, filters were immediately placed in pre-cleaned glass vials and stored below $-20\text{ }^\circ\text{C}$ until analysis.

Experiments were carried out at 25 $^\circ\text{C}$ and nominal relative humidity of 70%. Chamber humidity was controlled using vapour from heated ultra pure water (Purelab Ultra System, Elga). Known amounts of β -caryophyllene (C₁₅H₂₄, Sigma Aldrich) and limonene (C₁₀H₁₆, Fluka $\geq 99.0\%$) were evaporated from a heated glass bulb and continuously flushed into the chamber using a flow of nitrogen. **During each experiment the initial chamber NO_x concentration was controlled by introducing NO₂ gas** into the chamber from a cylinder containing 10% NO₂ in nitrogen .

“3. Results and Discussion

The evolution of certain key parameters is shown in Fig. 1 for a typical example of the organic seed experiments (25 June 2008). In Fig. 1, the beginning of Phase 1 occurs at time=0 and the vertical red dotted lines show the beginning and end of phase 2. In this experiment 49 (± 9) ppbV of β -caryophyllene was introduced into the chamber along with sufficient NO_2 gas to give an initial NO_x (i.e. the sum of NO and NO_2) concentration of 34 (± 1) ppbV. This VOC and NO_x combination thus gave an initial VOC/ NO_x ratio of approximately 1.4. It should be noted that no additional NO gas was added to the chamber matrix at any time and the initial quantity of NO observed in Fig. 1 at the beginning of each experiment phase, results from incomplete scrubbing of the charge gas for NO.”

(ii) For the photo-oxidation of limonene, only NO_2 was added. This resulted in an even larger ratio for NO_2 to NO. Why was NO_2 added instead of NO_x ?

As detailed above for point (i), it was not possible to completely remove NO from the chamber “fill” gas, as such a background of approximately 10 ppbV was present in the chamber at the start of the limonene oxidation phase of the experiments. In the particular experiment shown in Figure 1, a larger injection of limonene was tested (see text), thus to keep the VOC: NO_x ratio at around 2 (to allow for comparison between the experiments, see (iv)), a larger injection of NO_x was required. It was decided that this would be in the form of NO_2 as this was the methodology used during the β -caryophyllene phase and to allow for rapid start up in the gas phase chemistry. The aim here was not to set the NO: NO_2 such that the limonene phase would be directly comparable to the β -caryophyllene phase, but rather for the different β -caryophyllene and limonene phases be comparable between experiments.

(iii) Figure 1 indicates that the NO mixing ratio appears to increase as the chamber is being flushed, while both NO_2 and O_3 decrease considerably at this time. Is there an explanation for this?

The explanation for this is essentially that provided above for (i), i.e. at the time that the experiments were conducted, limitations in the chamber air scrubbing mechanism meant that not all of the NO present in the chamber “fill air” could be removed, hence as the chamber was refilled following the dilution “flush” phase, the concentration of NO increased. After the fill phase had ended, the NO concentration was checked and NO_2 gas was added accordingly to achieve the required VOC: NO_x ratio for the limonene oxidation phase of the experiment. As described above, the text has been altered in Section 3 to clarify that no NO was added and that the residual NO observed is due to carry over from imperfect scrubbing of the fill gas at the time the experiments were conducted. This has been addressed since and the chamber now has a much cleaner NO background (~ 1 -2 ppbv).

(iv) Why did the authors want to achieve a VOC: NO_x value of 2?

A VOC: NO_x ratio of 2 is common for such chamber studies; from previous experimental experience, a VOC: NO_x of 2 appears to lie in the optimal range for this kind of experiment. Moreover, a set VOC: NO_x ratio across the experiments was required to eliminate one particular variable in the system and also such that different experiments could be easily be intercompared. Furthermore, a harmonized VOC: NO_x ratio was employed across a wider VOC precursor range which comprised a larger experiment suite for the ACES project, this allowed intercomparison and analysis of multiple VOC/SOA systems to be performed, this will be the subject of a

future publication. The authors did state this previously, by have now strengthened the statement in the text (see above: “a fixed ratio was chosen to reduce system variables pertaining to the presence of NO_x and hence to enable comparisons to be made between experiments”).

2. Page 25133, line 19: The composition of beta-caryophyllene SOA is only briefly discussed, as it will be reported in more detail in another publication. Nevertheless, the authors should at least refer to the work of Jaoui et al. (2007), which first identified beta-caryophyllinic acid as a photo-oxidation product of beta-caryophyllene. It should also be noted that Li et al. (2010) generated SOA form the ozonolysis of beta-caryophyllene, rather than photo-oxidation.

In accordance with the comments of both reviewers, this section has been altered accordingly, see reviewer 1 reply:

Page 25135, line 20 and Table 2: The species in limonene SOA are identified from LC-MS data. The results should be compared to those of Jaoui et al. (2006), who determined many compounds in limonene SOA.

A section has been added comparing the major compositional results of Jaoui et al. (2006) with those of this study:

“In a previous study investigating SOA formation from the photo-oxidation of limonene, Jaoui et al. (2006) were able to identify twenty-eight different compounds in limonene SOA formed under laboratory conditions. The majority of these compounds (in the molecular weight range 86 – 204 g mol⁻¹) were products of ring cleavage, the most abundant of which included, maleic acid (116), ketonorlimonic acid (174), ketolimonic acid (186), 5-hydroxyketolimonic acid (202), 3-carboxyheptanedioic acid (204) and 7-hydroxylimononic acid (200) (molecular weight given in parentheses). Also identified in significant abundance in the aerosol phase was the ring retaining compound 4-isopropenyl-1-methyl-1-hydroxy-2-oxocyclohexane (168). Of these compounds, only ketolimonic acid and 7-hydroxylimononic acid were identified in the present study, with the latter compound being the most abundant in this study. A further six particle phase compounds were found to be common between this study and that of Jaoui et al., these include, limonaldehyde (168), ketolimononaldehyde (170), limonic acid (170), limononic acid (184), 7-hydroxylimononaldehyde (184) and limonic acid (186). No ring retained compounds were identified in the SOA of the current study.”

Minor Comments

1. Page 25119, line 7: Sulfate is the spelling recommended by IUPAC.

The text has been corrected accordingly.

2. Page 25120, line 7: Chamber instead of chambers

The text has been corrected accordingly.

3. Page 25123, line 14: ...was generated from the photo-oxidation of beta-caryophyllene. . .

The text has been corrected accordingly.

4. Page 25124, line 11: Maybe change title to Gas Phase Measurements?

The text has been corrected accordingly.

5. Page 25127, line 8: How did the authors know that 10-20 mg of a filter was being cut?

The filter was weighed. Text has been added`

6. Page 25129, line 16: . . .the mass concentration. . .

The text has been corrected accordingly.

7. Page 25131, line 14: . . .a series of experiments was carried out. . .

The text has been corrected accordingly.

8. Page 25131, line 22: increases instead of increase

The text has been corrected accordingly.

9. Page 25132, line 22: ppbV instead of ppb

The text has been corrected accordingly.

References

The references have been added accordingly.

Jaoui, M., S. Leungsakul, and R. M. Kamens, Gas and particle products distribution from the reaction of β -caryophyllene with ozone, *J. Atmos. Chem.*, 45, 261–287, 2003.

Jaoui, M, Corse, E., Kleindienst, T. E., Offenberg, J. H., Lewandowski, M., Edney, E. O.: Analysis of secondary organic aerosol compounds from the photooxidation of d-limonene in the presence of NO_x and their detection in ambient PM_{2.5}, *Environ. Sci. Technol.*, 40, 3819-3828, 2006.

Jaoui, M, Lewandowski, M., Kleindienst, T. E., Offenberg, J. H., Edney, E. O.: β -caryophyllenic acid: An atmospheric tracer for β -caryophyllene secondary organic aerosol, *Geophys. Res. Lett.*, 34, L05816, doi:10.1029/2006GL028827.

Li, Y. J., Chen, Q., Guzman, M. I., Chan, C. K., and Martin, S. T.: Second-generation products of β -caryophyllene ozonolysis are the dominant contributors to particle mass concentration, *Atmos. Chem. Phys. Discuss.*, 10, 17699–17726, doi:10.5194/acpd-10-17699-2010, 2010.

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