Response to Referee #1

This study investigates the SOA formation from -caryophyllene ozonolysis and photooxidation. A series of perturbation experiments were conducted to test the effects of UV, continuous aging with OH, and relative humidity on SOA yield and composition, which are important and relevant. My main concern is that the wall-loss correction method introduced by Pathak et al. (2007) might not be applicable for this multi-generation system. A kinetic model is needed to understand the time scale of gas-phase oxidation steps. Moreover, although the paper is well organized, details about the experimental results are not well explained. Comparisons to previous studies are needed and inconsistencies need to be explored. I think this article requires substantial revision before considering for publishing.

The issue of the wall loss corrections is addressed in our responses to comments 7 and 8 of the referee below. We have provided the necessary evidence to justify our use of the Pathak et al. (2007) correction method for this fast reacting system. We have also performed a number of additional experiments (discussed in comment 8) to quantify the magnitude of vapor losses to the Teflon walls in this system and we have found them to be similar or lower to our experimental variability. We have added the necessary text providing additional experimental details and also improving the comparisons with previous work.

Specific comments

1. Abstract, Line 6-8: The SOA yield highly depends on reaction conditions (residence time, oxidant level, temperature, RH, etc.). Loading is not the only determinant. The information listed here seems a bit misleading.

We have added the rest of the conditions of the experiments (room temperature, very low RH, and excess of oxidants) to the abstract for completeness.

2. P28921, Line 9: BVOC also include some oxygenated compounds (Atkinson and Arey, 2003).

We have rephrased this sentence adding the oxygenated biogenic compounds (methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, etc.) to the list of biogenic VOCs.

3. P28921, Line 15: β-caryophyllene is not always the most abundant sesquiterpene. Many sesquiterpenes remain unidentified. Emissions from different trees/environment are also different.

We have rephrased the sentence. We now just state that β-caryophyllene is often one of the most abundant sesquiterpenes.

4. P28922, Line 2-3: Chen et al. (2012) reported a range of SOA yields depending on the ozone level. Why is there only one value (24.3% at 10 μg/m^3) used when comparing to other studies? Also, how did the authors obtain this value of 24.3%? This value is not reported in Table 2 of Chen et al. (2012).

The value 24.3% at 10 μg/m^3 was calculated by interpolation of the data provided by Chen et al. (2012) to facilitate comparison with other studies. We have replaced this with a sentence explaining better the findings of Chen et al. (2012), discussing the SOA dependence on the ozone level, and then mentioning the measured values for different ozone levels.

5. P28922, Line 3-5 and Line 10-11: Ng et al. (2006) and Lee et al. (2006a, b) reported the results from the same set of experiments, which should not be considered as two independent studies. I also cannot find the value of 53% yield in Ng et al. (2006).
Indeed the studies of Ng et al. (2006) and Lee et al. (2006a, b) used the same experimental data. In the revised manuscript we describe them together as one study.

We have deleted the reference to the Ng et al. (2006) study from this second paragraph.

6. P28922, Line 19-24: The authors should include many other important reasons that explain the different SOA yields observed in different studies. For example, ozone concentration is insufficient for first-generation products to continue oxidation in Winterhalter's study, leading to lower yields. Relative humidity and temperature also affect the yield.
This is a valid point. In the revised manuscript we explain that other differences among the various studies including the relatively low ozone levels used by Winterhalter et al. (2009), temperature, and relative humidity can explain, at least partially, the different yields reported.

7. P28923, Line 10-15: In this study particle wall losses are calculated by Pathak et al (2007)'s method that assumes size-independent loss rate and is developed for monoterpene ozonolysis with seed injection. However, it is known that particle wall losses depend on size (VanReken et al., 2006; Pierce et al., 2008). Are the studied populations (without seed) similar to those in Pathak's study? At least the wall-loss rate for smaller particles formed at the beginning is expected to be greater than that for larger particles. As the size of the studied population changes, especially after perturbations (e.g., temperature change in Fig.1), how would the wall-loss rate change? Moreover, unlike monoterpene, sesquiterpenes have two double-bonds that involve multi-generation reactions in prolonged timescale. The SOA mass concentration is a balance between wall losses and the production. The production may take hours (especially for photooxidation experiments) depending on the conditions. How do the authors pick "no chemical-production periods" (Pathak et al., 2007) to derive the wall loss rate constant? The authors need to clarify the difference and convince the readers that Pathak's method is still applicable here. If not, a new method (maybe a multi-step kinetic model) is needed to derive the wall losses under assumptions.
We agree with the reviewer that the wall loss corrections (probably the Achilles heel of smog chamber experiments) deserve additional discussion and justification.

The first important point is that relatively high oxidant levels are used in this study and therefore the reaction times are short resulting in relatively low losses to the walls during these periods. For example, for all our ozonolysis experiments the time for the first reaction step is of the order of tens of seconds, while the second around 20 minutes. To ensure that these reactions were completed the particle wall loss rate constants were estimated at least one hour after the beginning of the reactions. For example, the corresponding wall loss rate constants estimated for all the ozonolysis experiments were 0.31± 0.11 h^{-1}.

A second issue was the stability of these rate constants with time during each experiment. To test this we estimated them for different sub-periods of each experiment. For example, for Exp. 6 we calculated a wall loss rate constant of 0.29 h^{-1} for the 50-100 min period (with R^2=0.98), also 0.29 h^{-1} for the 100-150 min period (with R^2=0.99), and 0.28 for 150-200 min (with R^2=0.99).

Similar results were obtained for other experiments during periods in which the reactions in the system were assumed to be completed.

To ensure that the rate constants were estimated during periods in which the reactions rate were very low or zero we used three different criteria. The first was the theoretical estimates of the reaction times described above. The second was the use of periods in which the AMS O:C ratio was ratio. The third was the testing of sub-periods to make sure that there was change in the corresponding constant.

The use of a time-independent value for the correction (even if sub-100 nm particles are lost in general faster than larger particles as the reviewer correctly notes) is justified by the fact that particles in our experiments grew to sizes above 100 nm in less than 20 minutes. Therefore the period during which losses may have been different was small and the resulting uncertainty also small. We are estimating for this fast reacting system that the uncertainty in the yields introduced by the particle wall loss correction is of the order of 20%.

Changes in temperature do result in significant changes of the loss rate constants in our chamber. For example, in Exp. 1 when the temperature was increased from 20 to 40 degrees C the particle loss rate constant increased from 0.26 to 0.46 h^{-1}. This increase is due to the increased ventilation outside the chamber which leads to increased turbulence inside the chamber and thus increased losses. We have estimated and used different loss rate constants for periods with different temperatures in the same experiment.

We have added a new paragraph in the revised manuscript summarizing the various issues related to particle wall loss corrections in our experiments and also providing the necessary justification for our use of the relatively simple Pathak et al. (2007) correction method for this fast reacting system.

8. P28923, Line 22-23: The gaseous semi-volatile products, especially second generation products present for much longer lifetime than precursors in the chamber system. I am not convinced that "negligible wall loss of organic vapors" can be assumed. Maybe this sentence is just misplaced because in Table 1 and 3, yield are reported for w=1.

We have corrected for vapor losses to the particles deposited on the chamber walls using the w=1 approach of Hildebrandt et al. (2011). This approach assumes that mass transfer from the chamber to the walls is fast and the particles on the wall behave as if they were suspended in the chamber. However, we have assumed that direct losses of vapors to the Teflon are low in this system and can be neglected.

To test this hypothesis we have performed four additional experiments using ammonium sulfate seeds. The use of the seeds increases the surface area of the aerosol in the chamber and should reduce any artifact related to vapor losses to the Teflon. The yields of these experiments (shown in the revised Figure 2) are not different from the rest of the yields. This suggests that the magnitude of losses of vapors to the walls for this fast reacting system are of the same order as the variability of the yields calculated in the rest of the experiments.

We have added a paragraph discussing the losses of vapors to the walls of our chamber and also the additional experiments performed to investigate the potential magnitude of these losses in this system.

9. P28925, Line 1-2: This procedure confuses me. A figure is helpful to understand exactly how the reactant concentration is achieved. If the injection of β-caryophyllene takes an hour, how could the injection affect your results and wall-loss correction (with dilution and addition of reactant)? Particularly for Exp. 31 (Fig. 7), adding HONO starts before 30 minutes, i.e., before finishing the purge of β-caryophyllene injection line.
Indeed, the 1 hr purge time that was used in a couple of test experiments in which we injected the ozone first and the β-caryophyllene next is confusing this part of the experimental description. We have rewritten this paragraph clarifying that the purging time was 10-20 min for most experiments (with the exception of the test experiments where we kept purging for an hour). We also clarify that the injected air volume was less than 0.3 cubic meters (less than 3% of the chamber volume) so the dilution effect was minimal. The accuracy of the estimated concentration based on the injected β-caryophyllene amount was checked in selected experiments with the PTR-MS.

10. P28926, Line 6: See my comment above (#9), should "at time zero" be "at time zero to 1h"?
The injection of the reactants was completed in approximately fifteen minutes in this experiment with the ozone injection first. Time zero corresponds to the completion of the injection of both reactants. This is now explained in the revised manuscript.

11. P28926, Line 13-21: The reported density and O:C are much lower than the values reported in Chen et al. (2012). Chen et al. (2012) also showed that the SOA density and O:C ratios vary with SOA concentration, which seems not shown in this study (values are rather constant for a wide range of SOA concentration). Why? For the derived density, how big is the uncertainty? Also, H:C should be reported. The AMS O:C and H:C ratios are biased low (Chen et al., 2011; Canagaratna et al., 2014). Are the reported ratios corrected? Has the elemental analysis considered organonitrates (Farmer et al., 2010), especially for high NOx experiments?

The difference in O:C between this study and Chen et al. (2012) is partially due to the use of the Aitken et al. (2008) fragmentation table in this study while the Chen et al. (2011) approach was used in the latter. This is now explained in the revised manuscript and the effect of the fragmentation table choices is discussed.

The densities that we estimated for the ozonolysis experiments are lower than the Chen et al. (2012) values and their uncertainty was approximately 0.1 g m^{-3} so it can only explain part of the discrepance. The approaches that were used for the density estimation are different (we matched the full distributions while Chen et al. (2012) relied on the mass mode diameters). The variation of composition with size (seeds were used and there could be more organics condensing on the smaller and less on the larger particles) could introduce some additional uncertainty in the Chen et al. (2012) approach. We do mention in the revised manuscript these differences in the findings of the two studies.

We have added in the paper the H:C values for the different SOA types. They were all close to 1.5. Their values for the aging experiments are now included in Table 3. We also mention that the organonitrates were not included in the elemental analysis.

12. P28926, Line 22, Fig. 2, and Table 2: Chen et al. (2012) reported three sets of yield, which differ in the fraction of first- to second-generation conversion. Only data at 200 ppb ozone are considered as close to "ultimate" yield. It seems inappropriate to use all of them together. While comparing to Chen et al. (2012), what are the estimated mean conversions of first- to second-generation for each of your experiments? The data in Fig. 2 are quite scattered. Can the reaction timescale explain some of the scattering? Does temperature and RH lead substantial difference (25 ^{o}C, 40% RH in Chen et al. (2012) vs 20 ^{o}C, dry in this study)? If temperature does, the authors should convert data based on the measured enthalpy.
We have followed the reviewer's suggestion and excluded from Figure 2 and the analysis leading to Table 2 the Chen et al. (2012) which may not correspond to the "ultimate" yield. The excluded data points are those with SOA concentrations above 10 μg m^{-3} and ozone concentrations less than 200 ppb. The results of the analysis do not change substantially (a few percent).

For the conditions used in our experiments (ozone equal to 300 ppb or more and 293 K) the lifetime of β-caryophyllene is less than 15 seconds while the lifetime of its first generation products should be less than 20 minutes. Given that all our experiments covered periods much longer than these timescales, the incomplete reactions cannot explain the observed scatter in the yields. We performed a few experiments at higher RH and the yields did not appear to be substantially different from the low RH experiments. Finally the small temperature difference can explain only a few percent of the difference. Uncertainties in losses of vapors and particles and the reacted VOC are probably responsible for most of the scatter in Figure 2.

We have updated Figure 2 and Table 2 in the revised paper and we have also added a brief discussion of the uncertainty of the results and the corresponding scatter.

13. P28927, Line 17 and 26 (also P28926, Line 15): The reported CE values are low. Chen et al. (2012) reported a CE of 1. Can you explain why? What are the CE values for high relative humidity experiments?
We estimated a CE=0.58±0.12 for the ozonolysis experiments under low RH conditions. Docherty et al. (2013) reported an even lower AMS CE of 0.36 ±0.01 for β-caryophyllene ozonolysis SOA under dry conditions. The CE in our higher RH experiments (Exp. 30 and Exp. 31) was around 0.5 similar to the experiments under dry conditions. We believe that the difference between our study and Chen et al. (2012) is probably due to AMS instrument differences.

14. P28927, Line 26: Has ozone concentration been measured during those experiments? Would the combination of ozone (generated) and OH pathways contribute to the difference as well?
The ozone formed in these experiments was a few ppb so its contribution to the SOA formed was small. This is consistent with the differences in the AMS spectra of the SOA formed during the ozonolysis and the OH experiments.

15. Figure 4: It is difficult to look at the ion markers through the dotted spectra. I suggest plotting the mass spectra separately. The fact that SOA produced by ozonolysis has lower peak at m/z 43

and greater peak at m/z 44 is consistent with the observed greater O:C. However, the O:C ratio for high-NOx SOA is greater than the ratio for low- NOx SOA when the spectra look similar. Why? I think it is better to show high-resolution spectra which may provide more information about various ions.
We have redrawn Figure 4 so that now the ion markers can be seen clearly. The apparent discrepancy was due to the selection of spectra from specific experiments. In the revised paper we include the average spectra and now the differences in O:C can be seen.

16. P28928, Line 25-28 and P28929, Line 4: Is first paragraph misplaced? I am confused about which experiments have used OH scavenger. Several in Table 1? Or Just Table 3. Please clarify (maybe add OH scavenger information in the tables.)
The OH scavenger was used only in experiments 1-14 summarized in Table 1. We refer to these as simple ozonolysis experiments. The order of the paragraphs is probably creating the confusion. We have changed their order in the revised manuscript and also stated clearly in the Tables using the appropriate footnotes the use of OH scavenger.

17. P28929, Line 1: Higher by what percent? Please be specific.

We now clarify that this yield can be as much as a factor of two higher depending on the conditions.

18. P28929, Line 8-11: What is the definition of "no change"? What does this result mean?
We have rephrased this sentence. We now state the angle between the two mass spectra was less than 2 degrees indicating that they were practically the same.

19. P28930, Line 1-10: What reaction leads the increase of SOA mass concentration? Gas-phase oxidation of semi-volatile products (first- or second- generation) or heterogeneous oxidation? The discussion of Exp. 29 ended hastily. Do you conclude that the increase of SOA mass concentration in Exp. 29 support the wall loss of organic vapors (i.e., the negative artifacts)? Please be specific about the reasoning.
Gas-phase oxidation and transfer of the corresponding later generation products to the particulate phase can probably explain the increase in SOA mass concentration and the change in O:C. However, we cannot eliminate the possibility of existence of heterogeneous processes that also contribute to this increase. We have added a sentence making this point in the revised manuscript.

The results of Experiment 29 do support the wall loss of organic vapors to the walls (an artifact of around 30%). We have tried to address this point further performing several additional experiments with different amounts of seeds. The results do suggest such artifacts of the order of 20-30%. These are similar to the uncertainty of our experiments but they do appear to be present. We describe the additional experiments and analyze these artifacts in the revised paper.

20. P28930, Line 14-16: Is this result consistent with other's finding? Winterhalter et al. (2009) showed elevated yield when RH increased. How would you compare the scavenging of reactive

Criegee intermediates in your system to other studies? Why the maximum reached so earlier in Exp. 31 compared to other experiments in Fig. 1 and Fig. 5?
Our results are not consistent with those of Winterhalter et al. (2009) regarding the effect of RH as we did not see a significant effect on either the SOA yield or the O:C for the ozonolysis experiments. However, there are numerous experimental differences in the two studies so it is difficult to draw any firm conclusions about what is causing this discrepancy. We do mention the difference in the conclusions in the revised paper.

The earlier maximum in experiment 31 is mainly due to a much higher wall loss rate constant for this experiment compared to the others. It was 0.42 h^{-1} compared to 0.28 h^{-1} for Exp. 1. These faster losses led to an earlier decline of the concentrations by 15 min or so compared to other experiments.

Technical corrections:
21. P28294, Line 25: What is "organic volume"? Liquid volume? Please clarify. IP28923,
We have clarified this by stating that it is the organic mass injected.

22. P28925, Line 22: Brief descriptions about AMS data analysis (e.g., RIE) and elemental analysis are needed.
We have added the recommended brief description of AMS data and elemental analysis.

23. P28926, Line 1: Add "Table 3".
Done.

24. Figure 2: "solid line" instead of "dashed line"?
Corrected.

25. P28928, Line 5: NO3 should be the nitrate ion form. Add one sentence about why organonitrates being detected as nitrate signal by the AMS and reference Farmer et al. (2010).
We added the explanation and the reference.

26. P28928, Line 20-21: "lower m/z 43" should be "lower relative intensity of m/z 43 (i.e., f43)". What is θ angle? Please explain.
We have made the suggested correction and added the definition of the angle theta at this point together with a reference.

27. Figure 4: Add label for y axis.
We added the missing label.

28. P28929, Line 23: Add "at" before "m/z 43".
Done.

29. P28930, Line 11: Revise "SOA corrected mass" (wall-loss corrected SOA mass concentration?). Similarly, P28930, Line 26.
Done.

References

Aiken, A. C.; DeCarlo, P. F.; Kroll, J. H.; Worsnop, D. R., Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C; Kimmel, J. R.; Sueper, D.; Sun, Y; Zhang, Q; Trimborn, A; Northway, M.; Ziemann, P.J.; Canagaratna, M. R.; B. Onasch, T. B.; Alfarra,M. R.; Prevot, A. S. H.; Dommen, J.; Duplissy, J; Metzger, A; Baltensperger, U; Jimenez, J. L. ; O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478-4485, 2008.

Alfarra, M. R. ; Hamilton, J. F.; Wyche, K. P.; Good, N.; Ward , M. W.; Carr, T.; Barley, M. H.; Monks, P. S.; Jenkin, M. E.; Lewis, A. C.; McFiggans, G. B.; The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of β-caryophyllene secondary organic aerosol, Atmos. Chem. Phys., 12, 6417–6436, 2012.

Atkinson, R. and Arey, J.; Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, 197-219, 2003.

Canagaratna, M. R.; Jimenez, J. L.; Kroll, J. H.; Chen, Q.; Kessler, S. H.; Massoli, P.; Hildebrandt Ruiz, L.; Fortner, E.; Williams, L. R.; Wilson, K. R.; Surratt, J. D.; Donahue, N. M.; Jayne, J. T.; Worsnop, D. R.; Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications; Atmos. Chem. Phys., 15, 253-272, 2015.

Chen, Q.; Liu, Y.; Donahue, N. M.; Shilling, J. E.; 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, 2011.

Chen, Q.; Li, Y. J.; McKinney, K. A.; Kuwata, M. Martin, S. T.; Particle mass yield from caryophyllene ozonolysis, Atmos. Chem. Phys. 12, 3165–3179, 2012.
Docherty, K. S.; Jaoui, M.; Corse, E.; Jimenez, J. L.; Offenberg, J. H.; Lewandowski, M.; Kleindienst, T.E.; Collection Efficiency of the Aerosol Mass Spectrometer for Chamber-Generated Secondary Organic Aerosols, Aerosol Sci. Tech,47, 294-309, 2013
Farmer, D.K.; Matsunaga, A.; Docherty, K. S.; Surratt, J. D. ; Seinfeld, J. H.; Ziemann, P. J.; Jimenez, J. L.; Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry P. Natl. Acad. Sci. USA, 107, 6670-6675, 2010.

Helmig, D.; Bocquet, F.; Pollmann, J.; Revermann, T.; Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, Atmos. Environ., 38, 557-572, 2004.
Helmig, D.; Ortega, J.; Duhl, T.; Tanner, D.; Guenther, A.; Harley, P.; Wiedinmyer, C.; Milford, J.; Sakulyanontvittaya, T.; Sesquiterpene emissions from pine trees − identifications, emission rates and flux estimates for the contiguous United States, Environ. Sci. Technol., 41, 1545–1553, 2007.

Henry, K. M.; Donahue, N. M.; Photochemical aging of α-pinene secondary organic aerosol: effects of OH radical sources and Photolysis, J. Phys. Chem. A, 116, 5932−5940, 2012.

Hildebrandt, L.; Henry, K. M.; Kroll, J. H.; Worsnop, D. R.; Pandis, S. N.; Donahue, N. M.; Evaluating the mixing of organic aerosol components using High-Resolution Aerosol Mass Spectrometry, Environ. Sci. Technol., 45, 6329–6335, 2011.

Hoffmann, T; Odum, J. R.; Bowman, F; Collins, D; Klockow, D.; Flagan, R. C.; Seinfeld J. H.; Formation of organic aerosol from oxidation of biogenic hydrocarbons, J. Atmos. Chem., 26, 189–222, 1997.

Jaoui, M.; Kleindienst, T. E., Docherty K. S.; Lewandowski, M.; Offenberg J; H; Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: a-cedrene, b-caryophyllene, a-humulene and a-farnesene with O_3, OH and NO_3 radicals, Environ. Chem., 10, 178–193, 2013.

Kostenidou, E; Lee B. H.; Engelhart,G .J.; Pierce, J. R.; Pandis,S. N.;Mass Spectra Deconvolution of Low, Medium, and High Volatility Biogenic Secondary Organic Aerosol; Environ. Sci. Technol., 43, 4884–4889, 2009.

Lambe, A. T.; Miracolo, M. A.; Hennigan, C. J.; Robinson, A. L.; Donahue, N. M.; Effective Rate Constants and Uptake Coefficients for the Reactions of Organic Molecular Markers (n-alkanes, Hopanes and Steranes) in Motor Oil and Diesel Primary Organic Aerosols with Hydroxyl Radicals, Environ. Sci. Technol., 43, 8794–8800, 2009.

Lee, A; Goldstein, A. H.; Keywood, M. D.; Gao, S.; Varutbangkul, V; Bahreini, R.; Ng, N. L.; Flagan, R. C.; Seinfeld , J. H.; Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res., 111, D07302, 2006a.

Lee, A; Goldstein, A. H.;Kroll, J., H.; Ng, N. L.; Varutbangkul, V.; Flagan, R. C.; Seinfeld , J. H.; Gas-phase products and secondary aerosol yields from the photoxidation of 16 different terpenes, J. Geophys. Res., 111, D17305, 2006b.

Matsunaga, A. and Ziemann, P. J.; Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements, Aerosol Sci. Tech., 44, 881-892, 2010.

Ng, N. L.; Kroll, H. J.; Keywood, D. M.; Bahreini, R.; Varutbangkul V.; Flagan R. C.; Seinfeld J. H.; Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, Environ. Sci. Technol., 40, 2283–2297, 2006.

Pathak, R. K.; Stanier, C. O.; Donahue, N. M.; Pandis S. N.; Ozonolysis of a-pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), J. Geophys. Res., 112, D03201, 2007.

Pierce, J. R.; Engelhart, G. J.; Hildebrandt, L.; Weitkamp, E. A.; Pathak, R. K.; Donahue, N. M.; Robinson, A. L.; Adams, P. J.; Pandis, S. N.; Constraining particle evolution from wall losses, coagulation, and condensation-evaporation in smog-chamber experiments: Optimal estimation based on size distribution measurements, Aerosol Sci. Technol., 42, 1001-1015, 2008.

Shu, Y. H. and Atkinson, R.; Atmospheric lifetimes and fates of a series of sesquiterpenes, J. Geophys. Res., 100, 7275–7281, 1995.
VanReken, T. M.; Greenberg, J. P.; Harley, P. C.; Guenther, A. B.; Smith, J. N.; Direct measurement of particle formation and growth from the oxidation of biogenic Emissions; Atmos. Chem. Phys., 6, 4403-4413, 2006.

Winterhalter, R.; Herrmann, F.; Kanawati, B.; Nguyen, T. L.; Peeters, J.; Vereeckenb L.; Moortgata G. K.; The gas-phase ozonolysis of b-caryophyllene ($C_{15}H_{24}$). Part I: an experimental study, Phys. Chem. Chem. Phys., 11, 4152–4172, 2009.

Zhang, X; Cappa, D. C.; Jathar, S. H.; McVay, R. C.; Ensberg, J. J.; Kleeman, M. J.; Seinfeld, J. H.; Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, P. Natl. Acad. Sci. USA, 111, 5802-5807, 2014.

Response to Referee #2

This manuscript by Tasoglou and Pandis presents detailed aerosol physical and chemical results obtained from smog chamber experiments examining the formation and chemical aging of secondary organic aerosol (SOA) during the beta-caryophyllene oxidation. Specifically, this study generated SOA from the ozonolysis of beta- caryophyllene and the OH-initiated oxidation of beta-caryophyllene under low-NOx (no NOx added where H2O2 photolysis was employed to generated OH) and high-NOx (where HONO photolysis was employed to generated OH) conditions. In this study, the authors ambitiously set out to measure the SOA yields (and thus derive fitting parameters using the VBS approach that could be used in chemical transport models), examine the effect of UV light and temperature on these SOA types, examine the volatility and the effective vaporization enthalpy of these SOA types, and then conduct chemical aging of the SOA as it continues to react with OH radicals.

1. In the abstract and even in the main text, it wasn't always clear how exactly the chemical aging was performed. From carefully looking through all the details, it appears that only the SOA generated from beta-caryophyllene ozonolysis was aged with OH radicals. This is fine, but I think this should be more clearly written in the abstract.

We have clarified in the revised abstract that we study the aging of the beta-caryophyllene ozonolysis products with OH radicals.

2. In the opinion of this reviewer, there is a lot of territory the authors are trying to cover and not much time is spent on each item to carefully discuss the details of how some of the data were interpreted exactly. For example, deriving SOA fitting parameterizations from these experiments using VBS could be its own paper, especially if the authors more carefully address how the SOA yields are corrected for vapor wall losses. Since their stated objective for this paper "is to measure the amount of aerosol produced by reaction of beta-caryophyllene with ozone and hydroxyl radicals and suggest aerosol yield parameterizations for atmospheric chemical transport models" then I think the authors have to seriously consider the potentially important wall losses of vapors, especially since there is not seed aerosol used in these experiments. How can the authors be justified that vapor wall losses from large beta-caryophyllene oxidation products are negligible when determining SOA yields? Have the authors tried measuring select vapors by PTR-MS or CIMS to see how large these can be? I can imagine if you used substantial seed aerosol to compete with the wall of your chamber, you would find that aerosol yields would even be higher, as observed by Kroll et al. (2007) for aromatic VOCs. I don't think this effect can be neglected, especially for potentially large and sticky oxidation products produced from beta-caryophyllene oxidation. This issue is one of the main reasons I suggest major revision for this paper.

This is a fair point. We have provided additional information in the revised paper about the calculation of particle and vapor wall losses. Please also see our responses to comments 7 and 8 of the previous reviewer. More specifically we have performed additional experiments with various amounts of seeds to estimate the magnitude of the vapor wall losses to the Teflon walls.

We have also tried different reaction timescales (the longer the timescale the higher the corresponding losses). Our conclusion is that there are such losses in the beta-caryophyllene system, but they are modest (less than 30 percent in most cases) due to the fast kinetics of the system. These additional results and the corresponding analysis are included in the revised paper.

3. In addition, I have several specific comments below that need to be considered in a revision below. Overall, I do find these experiments very interesting and important to have published in the literature, and certainly Atmospheric Chemistry and Physics would be an appropriate venue for such information once these issues are carefully considered by the authors.

We do appreciate the constructive criticism of our work.

Specific Comments:

4. Acronym usage: Be consistent with acronyms or chemical formulas. If you define it earlier in the text, then why not use it instead of spelling it out again? I noticed this for several acronyms and formulas used. For example, VOCs and ozone.

We have improved the use of acronyms throughout the revised text.

5. Introduction:

Why not reference work by Chan et al. (2011, ACP) and Offenberg et al. (2009, ES&T), that showed that beta-caryophyllene SOA can be enhanced due to aerosol acidity? Since aerosol pH is now known to be lower than pH 2 in southeastern U.S. (Guo et al., 2014, ACPD, and other recent work from the GA Tech groups), the effect of aerosol acidity on beta-caryophyllene SOA formation is worthy of mention in the introduction since this effect is explained in part due to the increased formation of organosulfates and other hydrolysis reaction products. It now appears that particle-phase reactions cannot be neglected.

We do mention in the revised introduction that aerosol acidity can enhance the SOA formation in this system together with the corresponding references. This effect was not investigated in the current work.

6. Experimental Section:

Were any experiments done to confirm that OH + 2-butanol doesn't contribute to any measurable SOA, especially in the presence of some sort of low-volatility seed (like sulfate aerosol)?

We have tested the possibility of formation of aerosol from the reaction of OH and 2-butanol in the presence of ammonium sulfate seeds. There was no detectable organic aerosol formation for the conditions used in our experiments. This information has been added in the experimental methods section.

7. Should the authors explain more how the HONO was collected and stored from the combination of the H_2SO_4 solution and sodium nitrite solution? How was it then handled upon injection into the chamber?

We have added the corresponding information. A fresh solution of HONO was produced and used in each experiment so there was no need for storage.

8. I'm curious why the authors didn't consider the effect of seed aerosol on the SOA yields, and thus, the potential importance of vapor wall losses that could affect the yields. Work by Ehn et al. (2014, Nature Letters) recently showed that extremely low-volatility organic compounds (ELVOCs) were produced from alpha-pinene + O3 and OH and found that seed aerosols could help prove their existence. I think a careful treatment like this could help to better constrain the SOA yields.

We have followed the reviewer's suggestion and performed four additional ozonolysis experiments in the presence of high concentrations of ammonium sulfate seeds. The results of these experiments were added in Table 1 and Figures 2 and 3. The corresponding yields were consistent with the yields of the non-seeded experiments but at the high range of the corresponding variability. The SOA O:C in the seeded experiments was the same as in the non-seeded ones. We are using these results together with those of experiments where we tried to expose the ozonolysis products to OH as fast as possible to estimate the magnitude of these vapor losses. These losses appear to be modest (less than 30 percent) possibly because of the rapid reaction rates leading to fast nucleation and growth of particles as soon as the reactants are both in the chamber.

9. Results and Discussion - Oxidation by OH: The authors should note that Chan et al. (2011, ACP) did observe nitrated products, such as nitrated organosulfates in beta-caryophyllene SOA providing evidence of the NOx effect.

In the revised document we have added a sentence about the formation of nitrated organosulfates and their effect on the SOA yield together with a reference to Chan et al. (2011).

10. Results and Discussion - Chemical Aging of beta-caryophyllene SOA:
The test of RH seems weak if you are only considering 2 RH conditions and only conducting 1 experiment at each condition. Shouldn't this be repeated to confirm re-producibility of this result? How does the DMA/SMPS system behave at high RHs like 90%? Is the sheath air from the chamber or is it dried sheath air and can this affect the sizing measurement? How will the latter affect your SOA yield measurements?
For the high-RH experiments, I wonder if the authors used ammonium sulfate seed aerosol if they would contain higher liquid water contents (LWCs) than the pure SOA they generated via nucleation? That is, would you have LWCs with sulfate seed aerosol that would more directly mimic conditions like that commonly found in the S.E. USA? How would this aerosol water affect chemical aging?

We agree that the small number of experiments at high RH limits the generality of their results. We have qualified the corresponding conclusions in the abstract and the conclusions sections stating that these were based on a limited number of high yield experiments.

The SMPS sheath air flow was not dried and therefore the SMPS measurements were at a RH similar and a little lower of that in the chamber chamber. The hygroscopic growth of β-caryophyllene SOA has been investigated by Alfarra et al. (2012). The corresponding water uptake even at 90 percent RH was low (diameter growth factor of 1.03 on average) and therefore any increase in the volume of the particles should be less than 10 percent. This is no mentioned in the revised paper in the discussion of the corresponding experiments.
Our experiments with ammonium sulfate seeds were all at low RH. The interactions of aerosol water and the SOA compounds in this system requires an additional detailed study.

11. Even if the SOA mass didn't change, how confident are the authors from just AMS data that nothing in terms of functionality changed in the SOA upon exposure to UV light and OH under low NOx conditions? For example, how stable are the potential organic peroxides produced in this system? I always worry when conclusions are only being made with AMS data, which typically is used for measuring bulk chemical properties of SOA and not detailed changes in SOA composition. For the latter, techniques like GC/MS, LC/MS or even FTIR might be useful to consider.

This is a fair point. In the revised manuscript we state clearly that there was no change in the AMS spectra of the corresponding SOA. This stability of the spectra does not necessarily prove that there were no chemical changes in the particles. Unfortunately, we did not use other analytical techniques in the specific experiments.

12. Finally, one thing I think needs to be stressed here more clearly is are the authors trying to examine heterogeneous oxidation of SOA by OH or both aging of particles and gases? This needs to be made more clear and if the former was the goal is the current setup the best approach for that? I wonder if flow tube studies would be warranted if the goal was to examine chemical aging due to heterogeneous oxidation by OH radicals?

Oxidation of gas-phase compounds are contributing to the changes in SOA mass concentration and O:C ratios. However, we cannot eliminate the possibility of OH oxidation taking place at the same time and contributing to the changes. Studies in which the gas-phase organic compounds were not present (or were present at much lower levels) are needed to separate the effects of homogeneous and heterogeneous reactions in this system. We now make this point explicitly in the revised manuscript.

13. Results and Discussion - Vaporization Enthalpy of beta-caryophyllene SOA:
If the authors are hoping that the vaporization enthalpies measured could be used by modelers, why not provide error bars on these estimates?

We have added in the manuscript the estimated uncertainties of the effective enthalpies of vaporization for each system.

14. In general, can the authors make sure to provide error bars for their reported data?

We have added a discussion of the uncertainties of the estimated yields. The major source of uncertainty appears to be the correction due to wall losses of vapors for the fresh SOA and vapors and particles for the aging experiments and not the uncertainty of the various instruments and measurements. We prefer not to add explicitly the error bars in the diagrams to avoid misleading the reader about our understanding of these uncertainties. We believe that published yield uncertainties of less than 10 percent in past smog chamber experiments have proven to be unrealistic. The variability of our experimental results (e.g., Figure 2) does suggest uncertainties of the order of 30 percent.