

## ***Interactive comment on “Formation and chemical aging of secondary organic aerosol during the $\beta$ -caryophyllene oxidation” by A. Tasoglou and S. N. Pandis***

**Anonymous Referee #1**

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This study investigates the SOA formation from  $\beta$ -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

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substantial revision before considering for publishing.

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.
2. P28921, Line 9: BVOC also include some oxygenated compounds (Atkinson and Arey, 2003).
3. P28921, Line 15:  $\beta$ -caryophyllene is not always the most abundant sesquiterpene. Many sesquiterpenes remain unidentified. Emissions from different trees/environment are also different.
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  $\mu\text{g}/\text{m}^3$ ) 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).
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).
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.
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

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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.

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  $w=1$ .

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  $\beta$ -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  $\beta$ -caryophyllene injection line.

10. P28926, Line 6: See my comment above (#9), should "at time zero" be "at time zero to 1h"?

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

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(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 NO<sub>x</sub> experiments?

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 °C, 40% RH in Chen et al. (2012) vs 20 °C, dry in this study)? If temperature does, the authors should convert data based on the measured enthalpy.

I suggest specifying those details and only select the data that represent similar chemical conditions to derive parameterization. As described in comment #7, unless the authors show further evidence that support negligible wall loss of organic vapors, the reported yield needs to reflect the uncertainty from  $w=0$  to  $w=1$  (also for Fig.3). Uncertainties (error bars) for the VBS fitting are needed.

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?

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?

15. Figure 4: It is difficult to look at the ion markers through the dotted spectra. I sug-

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gest 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-NO<sub>x</sub> SOA is greater than the ratio for low-NO<sub>x</sub> 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.

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).

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

18. P28929, Line 8-11: What is the definition of “no change”? What does this result mean?

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.

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?

Technical corrections: 1. P28294, Line 25: What is “organic volume”? Liquid volume? Please clarify. 2. P28925, Line 22: Brief descriptions about AMS data analysis (e.g., RIE) and elemental analysis are needed. 3. P28926, Line 1: Add “Table 3”. 4. Figure 2: “solid line” instead of “dashed line”? 5. P28928, Line 5: NO<sub>3</sub> should be the nitrate ion form. Add one sentence about why organonitrates being detected as nitrate signal

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by the AMS and reference Farmer et al. (2010). 6. P28928, Line 20-21: “lower  $m/z$  43” should be “lower relative intensity of  $m/z$  43 (i.e.,  $f_{43}$ )”. What is  $\theta$  angle? Please explain. 7. Figure 4: Add label for y axis. 8. P28929, Line 23: Add “at” before “ $m/z$  43”. 9. P28930, Line 11: Revise “SOA corrected mass” (wall-loss corrected SOA mass concentration?). Similarly, P28930, Line 26.

References Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos. Environ.*, 37, S197-S219, 10.1016/s1352-2310(03)00391-1, 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., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys. Discuss.*, 14, 19791-19835, 10.5194/acpd-14-19791-2014, 2014.

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

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, *Proc. Natl. Acad. Sci. U. S. A.*, 107, 6670-6675, 10.1073/pnas.0912340107, 2010.

Pierce, J. R., Engelhart, G. J., Hildebrandt, L., Weitkamp, E. A., Pathak, R. K., Donahue, N. M., Robinson, A. L., Adams, P. J., and 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, 10.1080/02786820802389251, 2008.

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VanReken, T. M., Greenberg, J. P., Harley, P. C., Guenther, A. B., and Smith, J. N.:  
Direct measurement of particle formation and growth from the oxidation of biogenic  
emissions, *Atmos. Chem. Phys.*, 6, 4403-4413, 10.5194/acp-6-4403-2006, 2006.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 28919, 2014.

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