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Interactive comment on "The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of <i>β</i>-caryophyllene secondary organic aerosol" *by* M. R. Alfarra et al.

Anonymous Referee #2

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Interactive comments on "The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of b-caryophyllene secondary organic aerosol" by M. R. Alfarra et al.

General. This paper investigates the photo-oxidation reaction of b-caryophyllene in presence of NOx from Teflon reaction chamber experiments. The work seeks to investigate the influence of the precursor concentration on the SOA properties and composi-

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tion. To answer that question, gas phase products were measured and speciated using Chemical Ionization Reaction Time- of-Flight Mass Spectroscopy (CIR-TOF-MS) while the condensed phase products were measured and speciated using aerosol mass spectrometry (AMS) and filter-based measurements (followed by off-line analysis by liquid chromatography followed by mass spectrometry [LC-MS/MS]). Hygroscopicity of the aerosols was also studied using hygroscopicity tandem differential mobility analyzer (HTDMA). The paper report new and interesting results, and I support the publication of this manuscript in ACP; however, there are few areas, discussed below, where further clarification and/or revisions would enhance the quality of the paper.

Major comments. #1. In the introduction, on line 15, the sentence “[b-caryophyllene] has two double bonds (one endocyclic and one exocyclic) and has high reactivity towards ozone...” attempts to describe the structure of b-caryophyllene. It may be useful to show the structure of the molecule as the authors pointed out, this molecule isn’t very commonly studied. The structure could be added, for example, as an insert to figure 1 where the decrease of its concentrations shown or in a separate figure.

#2. Experimental methods: Results from the differential mobility particle sizer (DMPS) are mentioned in the abstract and many times throughout the paper, however there is no description of this technique anywhere in the experimental section. It would be beneficial to add a short description or reference to a previous publication in the experimental methods section.

#3. Experimental methods: The way the concentrations of the precursor are presented in the text is quite confusing for the reader. Specifically, the sentences on page 2442, lines 3-8: “Experiments were carried out at two nominal initial precursor mixing ratios of 50 and 250 ppbV in order to study the effect of initial precursor on SOA properties and composition. VOC measurements (described in Sect. 2.3) were only made during two of the higher initial concentration experiments and showed that approximately 140 ppbV were present in the chamber at the start of each experiment.” lead to confusion. For which experiments the gas phase concentration of b-caryophyllene were actually measured (from Table 1 one can interpret the values in column 2 as “measured VOC concentration” except the ones marked with a star (*), but the text only refers to the measurements made at the highest concentration)? It would also be beneficial to define “nominal concentration” (i.e. estimation based on the amount introduced without taking into account any losses), as well as labeled the VOC concentrations in Table 1 as “measured” versus “estimated”. In all cases, it seems that the estimated concentrations (either 50ppbV and 250ppbV) are an upper limit due to the potential losses described by the authors. Revision of the text as well as a footnote on Table 1 would help clarify which VOC concentrations were measured and which were only estimated.

#4. Experimental methods - Page 2442, lines 14-15: The sentence “A background level of around 10 ppbV of NO was present in this study (subsequent experiments have achieved an NO background of around 1ppbV)” needs clarification. For which experiments the background of NO was 10 ppbV, and for which it was 1 ppbV?

#5. Results and Discussion: The discrepancy between the measurements obtained from the DMPS and the AMS is NOT presented in Sect. 3.5 of the Results and Discussion section of the paper as mentioned by the author on page 2446-2447. What is the pre-treatment of the SOA that the author continuously refer to? Are the particles modified (e.g. dried) prior entering the DMPS, which might result in a lower mass loading for this measurement compared to the AMS measurement, as observed by the authors. Once again, some information on how does the DMPS works would be very useful.

#6. Table2 could be improved. What does the column labeled “m/z” refers to? Is it the [M-H]- molecular specie that was observed for each identified species in the LC-MS/MS analysis? If so, the caption should specify “LC-MS/MS negative mode” and the header should state that clearly.

#7. On page 2447-2448: The authors might consider adding a Supplementary Information to the paper which would include additional figures showing the total ions and extracted ions chromatograms (m/z 251 and 253) mentioned in the text for better clarity.

#8. On page 2449, line 17-18: The authors might consider citing the previous work of Glasius et al. (Environ. Sci. Technol., 2000) that shows that electrospray mass spectrometry is indeed very sensitive to carboxylic acids, compared to other functional groups as a justification of their observations.

#9. On page 2450, line 18: The following sentence: “the mean day-to-day LC peak area ratio was 1.17 for 8 compounds” needs clarification. The analysis does not include a LC column, thus there is no separation occurring. Does the authors mean that the area of a given m/z peak for a given compound doesn’t vary much on a day-to-day basis (data analysis made for 8 individual compounds)?

#10. Labeling the highest peaks observed in Figure 3 (which the reader can then relates to the compounds identified in Table 2) would help to see that upon ageing the SOA is transformed into more oxidized material for the “lower” experiment, but the “higher” experiment isn’t.

#11. Results and discussion, section 3.5: The authors might consider discussing the work of McIntire et al. (Atmos. Environ., 2010) who showed that the formation of particles in the ozonolysis of a 7-octenyltriclorosilane self-assembled monolayer did not lead to increased water uptake at it was initially anticipated by the authors due to the formation of more oxidized oxygenated groups. Nano-secondary ion mass spectrometry (nano-SIMS) analysis provided evidence that the polar product groups were actually buried inside a hydrophobic shell. Such phenomenon might explain the authors’ absence of temporal growth factor upon ageing.

#12. Results and discussion, section 3.6: The author attempt to link the masses observed in the gas phase (CIR-TOF-MS measurements) with the masses observed in the condensed phase (LC-MS analysis). It is however relatively hard to follow the authors’ interpretation here. How does the list of the most abundant masses observed in the CIR-TOF-MS (which should correspond mainly to [M+H]+ or [M+H-H2O]+ fragments according to the experimental section description) relate to the compounds listed in Table 2 and the molar masses listed on line 18 of page 2457 (m/z 200, 238, 252, 254, 268, 288)? Maybe more details could be added to Table 2 (additional column or footnote) for better clarity.

The authors might want to consider switching section 3.7 (link between gas phase and condensed phase) and 3.6 (gas phase results). I think it would improve greatly the quality of the paper if section 3.6 related to the gas phase distribution of the oxidation products (supported by Figure 8) first, and then have a discussion related to the partitioning of the different species between the gas phase and the condensed phase.

Technical corrections. #1. In the abstract, line 8: “DMPS” should be spelled out as “differential mobility particle sizer (DMPS)”. The “AMS” should be spelled out as “Aerosol mass spectrometer” on line 8 as well, and not on line 22 as it is now.

#2. Throughout the paper, b-caryophellene could be capitalized when it starts a new sentence (e.g., page 2438, line 13: ”b-Caryophellene is one of the most reactive and abundant sesquiterpenes. . .”).

#2. On page 2442, line 17, “secondary organic aerosol” can be abbreviated to “SOA”.

#3. On page 2446, line 7: “c-ToFAMS” is misspelled. It should read “cToF-AMS”.

#4. On page 2451, line 10: “semi volatile” should be hyphenated.

#5 References: The following references should have the first word capitalized only. On page 2463, line 17: “Arey et al., Terpenes emitted from. . .”. On page 2464, line 21: “Donahue et al., Coupled partitionining, . . .”. On page 2464, line 28: “Goldstein et al., Known and unexplored. . .”. On page 2465, line17: “Ng et al., Contribution of first-versus second-generation products. . .”. On page 2466, line4: “Topping et al., The sensitivity of secondary organic aerosol component partitioning. . .”. On page 2466, line 14: “Winklmayr et al., A new electromobility spectrometer. . .”.

Glasius et al., Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone, Environ. Sci. Technol., 2000, 34, 1001-1010

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McIntire et al., Why ozonolysis may not increase the hydrophilicity of particles, Atmos. Environ., 2010, 44, 939-944

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