

***Interactive comment on “The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of  $\beta$ -caryophyllene secondary organic aerosol” by M. R. Alfarra et al.***

**M. R. Alfarra et al.**

rami.alfarra@manchester.ac.uk

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Please find attached our author response to all comments provided by reviewers of Alfarra et al., 2012, “The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of  $\beta$ -caryophyllene secondary organic aerosol”, submitted for publication in Atmospheric Chemistry and Physics. We would like to thank the reviewers for their comments and suggestions.

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REVIEW 1

GENERAL REMARKS

Comment: O/C and H/C from AMS C-TOF measurements are also reported for condensed phase products. The authors conclude that O/C ratios are dependent on initial precursor concentrations.

Response: We would like to confirm that the O/C and H/C ratios were calculated for the compounds identified in the offline analysis method using the LC-MS/MS technique (as already mentioned in the manuscript). Unlike the HR-ToF-AMS, the cToF-AMS is not capable of providing this type of information due to its limited resolution.

MAJOR CONCERNS

Comment: P2442 L5 states “VOC measurements. . . were only made during two of the higher initial concentration experiments.” How do the authors calculate VOC values in Table 1a for the lower initial concentration experiments? What is meant by Nominal Concentration? is it the estimated/predicted concentration?

Response: All reported VOC values in Table 1a were directly measured by the CIR-TOF-AMS. Description of the measurement principles and calibrations are described in section 2.3. As for the term “nominal concentration”; it refers to experiments where the CIR-TOF-AMS was not available and, therefore, the initial VOC concentration was estimated based on the injected volume of the VOC required to achieve this concentration. This was calculated based on the total volume of the chamber (18 m<sup>3</sup>) and both the molar mass and density of the beta-caryophyllene. A related comment was made by reviewer 2. As a result of the comments from both reviewers, we have made some changes in the revised manuscript to the experimental section text as well as to the footnotes of tables 1a and 1b and table 1a caption to clarify these points. Please see our response to comment # 3 of reviewer 2.

Comment: The discussion on CCN properties of the aerosol is significantly lacking.

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Where are Kappa values in Table 1a (P2455 L11)? It is not clear how kappa values are calculated or where they are presented. How do the authors calculate kappa from their Growth factors? The authors describe different supersaturations were applied (P2443 L 24) in CCN measurements. What were these supersaturations? Are these the calibrated values? Though the description maybe mentioned in another paper, it necessary to describe the protocol in light of the results presented here.

Response: As mentioned in the manuscript, a limited number of CCN measurements were performed during a few of the experiments listed in Table 1a. Given the limited number of measurements and the very narrow range of their derived kappa values, we have chosen to summarise the results of these few experiments in the text by simply stating that the derived kappa values were very low and ranged between 0 and 0.02. We did not collect enough CCN data in this study to enable us to expand our discussion beyond this statement. We consider this limited CCN data as complimentary to the sub-saturated growth factor data measured by the HTDMA, which is the main focus of our water uptake discussion. The HTDMA data is reported in Figure 7 and discussed in detail in section 3.5. We feel that a lengthy description of the CCN setup and calibration is not required in this manuscript given the limited use of the data and our reference to the Good et al. (2010) paper should be adequate. However, we have expanded the technical description of the CCN in section 2.3 to include details of the calculation of k-values as requested by the reviewer. The following text has been added in the revised manuscript:

“Using the instrumental set-up described above CCN and CN number size distributions were measured at delta T’s equivalent to super-saturations between 0.07% and 1.0%. The CCN and CN number size distributions were then inverted to account for charging efficiency and multiple charging (Good et. al. 2010a). The inverted number size distributions were then used to calculate the activated fraction (CCN/CN) as a function of dry size. Sigmoidal functions were then fitted to the activation curved, from which the dry diameter at which 50% of the particles were activated was calculated. Given

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that the aerosol is internally mixed the diameter at which 50% of the particles activate is judged to be the dry diameter at which the particles are activated as CCN at the set-point super-saturation (Good et. al. 2010b). kappa values are then derived from the CCN measurements on the chamber by iteratively finding kappa from the kappa Kohler equation (Petters and Kriedenweis 2007) given that the critical super-saturation and dry diameter are known from the measurements. “

Comment: P2446 L25. “see Sect. 3.5 for further discussion.” Where is the discussion of the pre-treatment of semi-volatiles in relation to DMPS and AMS mass results mentioned? Specifically, section 3.5 describes the semi-volatile effects on hygroscopicity and CCN measurements. Little or no discussion is provided on the discrepancies of the SOA yields. Are the DMPS and AMS sampled at different temperatures? Are the temperatures significantly different to cause such a bias (2 to 3 times larger in the AMS)?

Response: We have clarified the statement in the revised manuscript to refer to the discussion of the presence of semi-volatile material in the sampled aerosol as inferred from the HTDMA measurements discussed in section 3.5. We have also clarified the different pre-treatment of aerosol samples prior to the AMS and DMPS measurements (this was also requested by reviewer # 2). The revised text reads as follow:

“A possible explanation for the discrepancies between the DMPS and AMS mass measurements is the difference in pre-treatment of the semivolatile-containing particles prior to the instrumentation. The DMPS sample was subjected to a dry sheath air (RH < 10%), while the AMS sample was not dried. Section 3.5 provides further discussion of the possible presence of semi-volatile material in these samples.”

Both of the AMS and DMPS were sampling from the same line at the same temperature, therefore differences in temperature should not be responsible for the measured differences in mass. The size distribution of the aerosol was well within the measurement range of both instruments and therefore, differences in instrument transmissions

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are not expected to contribute to these discrepancies.

Comment: P2452 L 27. The authors compare LC data from one high and one lower initial concentration experiment. The results are interesting and unique. However, are the ratios for these select experiments replicated in other combinations of high to low experiments? What is the standard deviation in these ratios? How much deviation exists between the experiments. It is mentioned that the authors check for consistency in daily variation but there is little or no discussion in the consistency between experiments. Which experiments were selected for the comparison presented?

Response: The experiments picked for comparison are the 16/04/2008 and 24/04/2008. An additional comparison of 12/03/2008 and 13/03/2008 gave slightly different values but the compounds followed same general trend and could be grouped in the same way as in table 3. There is insufficient data to be able to determine a meaningful error for these ratios. See Review 2, comment 9 for a discussion of consistency between experiments.

#### MINOR CONCERNS

Comment: P2442 L1. Insert the word "after"? i.e., "in this case after 2 and 6h"

Response: This has been done in the revised manuscript.

Comment: P2445 L23. Change "min" to "minutes"?

Response: This has been done in the revised manuscript.

Comment:P2442 L15/ "subsequent experiments have achieved: : ." Which experiments are the authors referring to if not in this study? It is not clear to the reader why this statement is relevant to the current discussion.

Response: The statement is just to clarify that this was the NO background level in the Manchester chamber during the time the work reported in this manuscript was carried out. We have modified and improved the scrubbing system since this work was

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performed and the current background of NO is around 1ppb. It is true the statement is not related to this discussion; however, it is relevant to readers who are interested in the current state and conditions of the Manchester chamber.

Comment: Table 1. What is SD? Standard Deviation?

Response: Yes, it is. We have clarified this in the revised manuscript.

Comment: Fig. 6. It seems that the inset figure is a repeat of the larger figure. Is it possible to just zoom in on the pertinent data and have one figure? Does the entire "triangle" need to be seen?

Response: The entire "triangle" needs to be seen, in order to understand the relationship of the current beta-caryophyllene SOA data with previously published ambient data from a wide range of locations. This also provides a "reference" space for comparison with data from other precursors in other chambers.

Comment: Table 3. The authors should provide m/z or names of compounds listed in Table 3 to guide readers.

Response: This has been done in the revised manuscript.

#### REVIEW 2

##### MAJOR COMMENTS

Comment # 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.

Response: We would like to thank the reviewer for this comment and have inserted the structure of the beta-caryophyllene in figure 1 as suggested.

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Comment # 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.

Response: We have added the following short description of the DMPS along with references in the revised manuscript, as requested by the reviewer:

“A Differential Mobility Particle Sizer (DMPS) was used to measure the aerosol number size distribution between 20 nm and 500 nm (Williams et al., 2007). The DMPS performed a complete mobility scan every 10 min, which allowed adequate sampling time for each mobility size. The DMPS was composed of a Vienna-design differential mobility analyser (DMA) (Winklmayr et al., 1991), and a condensation particle counter (3010 CPC, TSI Inc., USA).”

Comment # 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

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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.

Response: The reviewer is correct; values in column 2 are “measured VOC concentrations” except the ones marked with an asterisk (\*), which are “estimated” based on the amount of VOC injected without taking into account any losses. We have modified the text highlighted by the reviewer as well as the caption of table 1a and footnotes of both tables 1a and 1b in the revised manuscript to confirm and clarify these points.

Comment # 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?

Response: As mentioned in our response to a similar comment by reviewer 1, the statement is just to clarify that this was the NO background level in the Manchester chamber during the time the work reported in this manuscript was carried out. We have modified and improved the scrubbing system since this work was performed and the current background of NO is around 1ppb. The NO background was about 10ppbV for all of the experiments reported in this study. The lower background of around 1 ppbV is an additional piece of information which might be relevant to readers who are interested in the current state and conditions of the Manchester chamber.

Comment # 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

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by the authors. Once again, some information on how does the DMPS works would be very useful.

Response: Please see our response to a similar comment made by reviewer # 1. The pre-treatment of SOA refers to the drying of aerosols prior to DMPS measurements, while there was no drying performed before AMS measurements were performed. The link to section 3.5 is meant to highlight the discussion suggesting the possibility of the loss of semi-volatile material due to aerosol drying before the HTDMA. Therefore, the possible explanation we suggested for the discrepancy between the DMPS and AMS measurements is the difference in pre-treatment of the semi-volatile containing particles prior to the instrumentation. We have followed the reviewers request and provided a brief description of the DMPS (see response to comment # 2).

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

Response: Yes it is [M-H]<sup>-</sup>. We have changed this in the table. We have also inserted the suggested comment by the reviewer about negative mode in the caption.

Comment # 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.

Response: This is a good idea and we have now included this figure, along with the actual product ion mass spectra in a supplementary file in the revised manuscript.

Comment # 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

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functional groups as a justification of their observations.

Response: We would like to thank the reviewer for this suggestion and have included this reference in the revised manuscript.

Comment # 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)?

Response: The reviewer may have misunderstood this statement as our analysis does use a LC column. We have analysed the samples by both LC-MS and direct ESI-MS using a syringe pump. The sentence: "the mean day-to-day LC peak area ratio was 1.17 for 8 compounds" has been misinterpreted and so has been changed in the revised manuscript for clarity. Actually, we have carried out two chamber experiments on different days but under the same conditions and collected filters at the same point in the experiment. We have then analysed these two filters and found that the peak areas obtained by the LC-MS were very similar, with an average ratio of peak areas for 8 compounds (including pinonic acid and MBTCA) between the two experiments of 1.17. Thus we are sure that any differences between the two b-caryophyllene experiments are real and not a result of inconsistencies in the chamber method.

In the revised manuscript we have changed: "the mean day-to-day LC peak area ratio was 1.17 for 8 compounds" to: "Filter samples were collected at the same point in each experiment and the samples were analysed using LC-MS. Eight  $\alpha$ -pinene SOA peaks were chosen (including cis-pinonic acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)) and the peak area determined. The ratio of peak areas between the two samples was calculated and gave an average value of 1.17".

Comment # 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

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the SOA is transformed into more oxidized material for the “lower” experiment, but the “higher” experiment isn’t.

Response: We thank the reviewer for this suggestion. We have now addressed this request in the revised manuscript. We have labelled the peaks both in Figure 3 and Figure 4 and modified the figure captions to refer to structures in Table 2.

Comment # 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-octenyltrichlorosilane 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.

Response: We thank the reviewer for this suggestion. We agree with the basic concept of this idea in a system similar to that studied in the recommended paper. However, we feel that it is less likely to be applicable to a dynamic gas/particle system generated from the oxidation of atmospheric VOCs.

Comment # 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  $[M+H-H_2O]^+$  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

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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.

Response: The authors believe that they have discussed the linkages between the phases quite clearly in the current text, but to increase clarity the text has been amended slightly with the inclusion of the ion  $m/z$  for LC-MS and CIR-TOF-MS measurement in parentheses after each specific molar mass discussed:

“...these included compounds of molar masses 200 (199/201), 238 (237/239), 252 (251/253), 254 (253/255), 268 (267/269) and 288 (287/271) (each mass corrected for ionisation method and in the case of the latter, potential parent ion dehydration in the CIR-TOF-MS. LC-MS ion/CIR-TOF-MS ion  $m/z$  given in parentheses after each molar mass. See Table 2 for further information).” As for the second part of the comment, we thank the reviewer of his good suggestion, which we did consider during the writing process, however, we decided to proceed with the current section order, as proof reading proved it to make more logical sense and allowed to the paper to flow much better. In this order we discuss, gas phase composition and how it potentially links to the aerosol phase composition and then we look at how the system ages and how the different starting conditions might or might not influence that aging.

#### TECHNICAL CORRECTIONS

Comment #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.

Response: This has been done in the revised manuscript.

Comment # 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

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reactive and abundant sesquiterpenes: : :”).

Response: This has been done in the revised manuscript.

Comment # 3: On page 2442, line 17, “secondary organic aerosol” can be abbreviated to “SOA”.

Response: This has been done in the revised manuscript.

Comment # 4: On page 2446, line 7: “c-ToFAMS” is misspelled. It should read “cToFAMS”.

Response: This has been done in the revised manuscript.

Comment # 5: On page 2451, line 10: “semi volatile” should be hyphenated.

Response: This has been done in the revised manuscript.

Comment # 6: 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 partitioning, : : :”. On page 2464, line 28: “Goldstein et al., Known and unexplored: : :”. On page 2465, line 17: “Ng et al., Contribution of first-versus second-generation products: : :”. On page 2466, line 4: “Topping et al., The sensitivity of secondary organic aerosol component partitioning: : :”. On page 2466, line 14: “Winklmayr et al., A new electromobility spectrometer: : :”.

Response: This has been done in the revised manuscript.

ADDITIONAL COMMENT FROM THE AUTHORS:

Prof. A. C. Lewis has been added to the list of authors.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2435, 2012.

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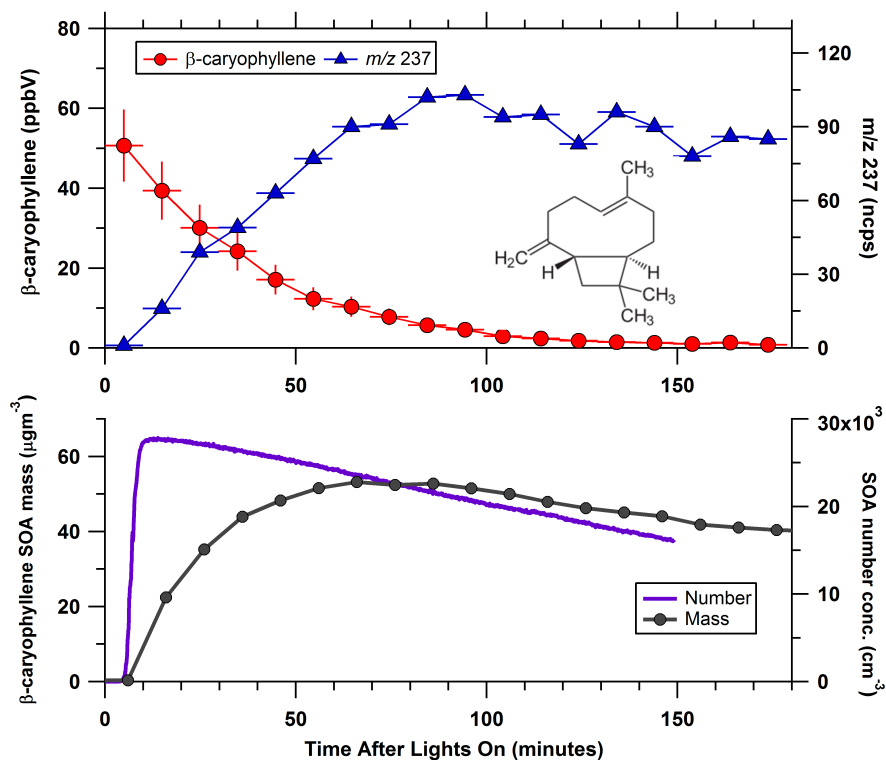


Fig. 1. Revised version of Figure 1

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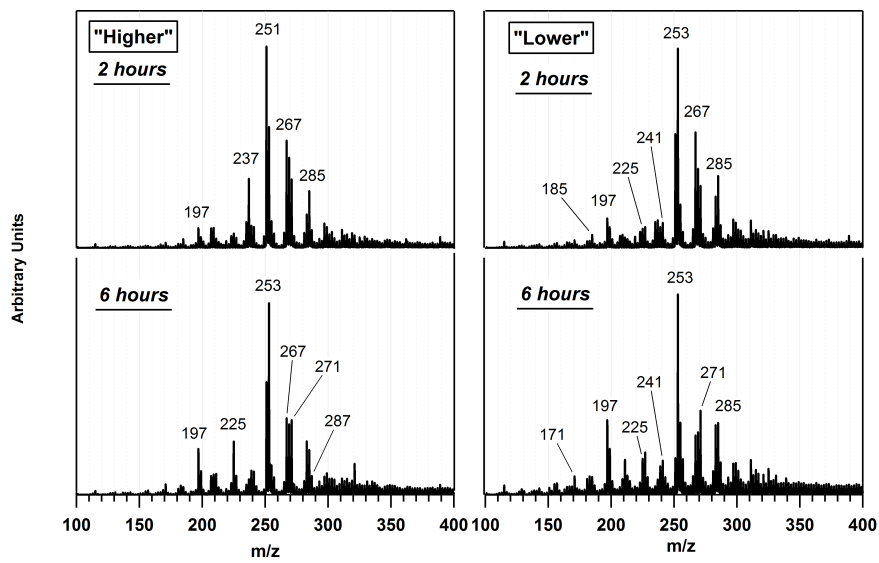


Fig. 2. Revised version of Figure 3

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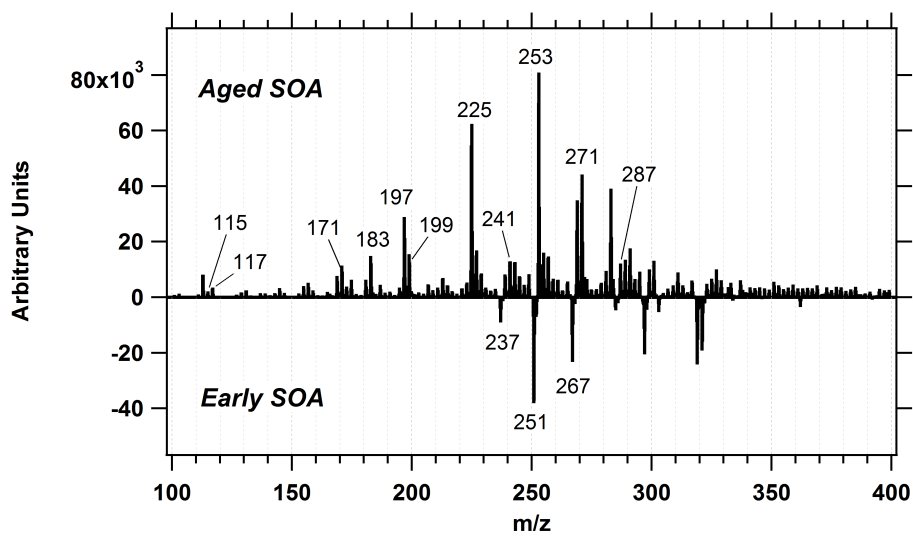


Fig. 3. Revised version of Figure 4

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