

Response to Referee #1

Spiro D. Jorga et al.

Author comment on "Nighttime chemistry of biomass burning emissions in urban areas: A dual mobile chamber study" by Spiro D. Jorga et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-284-AC2>, 2021

(1) *Jorga and coworkers investigate nighttime secondary organic aerosol (SOA) formation in urban ambient air using a dual chamber; one is used for SOA experiments and the other is used as a control reactor. This measurement approach allows for improved understanding of the oxidation chemistry and the secondary pollutant formation in the actual ambient conditions. Specifically, this work is conducted at night during the period when high biomass burning impact is observed. As nighttime oxidation of biomass burning emissions and its impact on secondary organic aerosol formation is relatively less studied compared to the photochemical oxidation, the results in Jorga et al. can potentially help improve our understanding in secondary organic aerosol formation from biomass burning emissions, especially their interaction with urban air during nighttime. One of the major findings in this study is that the ambient chamber experiment reproduced the mass spectra of biomass burning oxygenated organic aerosol (BBOOA) reported in Kodros et al. (2020), where the AMS mass spectra of BBOOA was retrieved from flame chamber experiments and parameterized for simulation application. Further, this study quantified the secondary organic nitrate formation from biomass burning, which is less understood compared to organic nitrate generated from the other sources such as biogenic emissions.*

We would like to thank the reviewer for all the comments and suggestions which have helped us to improve our manuscript. Our responses (in regular font) follow each comment (in italics) below.

(2) *However, there are number of drawbacks in this study that need to be improved. The major comment that the referee would like to make is that the discussion is insufficient. The discussion in the current manuscript solely focuses on comparison of mass spectra with previous studies, providing very limited new scientific insights beyond those reported in previous studies. The role and importance of different oxidants and oxidation pathways (ozone, OH, NO₃) need to be better justified and discussed. While the manuscript is focusing of OA formation from nighttime chemistry of biomass burning emissions, only total OA enhancement is reported. As the ambient air is not pure biomass burning, what are potential contributions from oxidation of non-BB VOCs and/or further non-BB related particle-phase chemistry to the observed OA enhancement? Furthermore, the criteria applied for mass spectra comparison is not consistent throughout the manuscript. Specifically, $\theta = 9-18^\circ$ is considered as "similar" in Line 267 whereas $\theta = 19^\circ$ is considered as "significant difference" in Line 232. This makes it difficult to evaluate if the*

results here are consistent or not with previous studies. Overall, since this manuscript is not submitted as a Measurement Report, major revisions (e.g., to include more in-depth scientific findings and discussions) are needed before the manuscript can be accepted for publication.

We have followed the suggestion of the reviewer and added discussion of the role and importance of different oxidants and the corresponding oxidation pathways, the role of VOCs from sources other than biomass burning, and the role of chemistry not related to biomass burning. We have also improved the presentation of the AMS mass spectra comparisons from different studies.

Our study has been designed so that the experiments start when biomass burning is the major source of both organic aerosol and VOCs. This point was not clear in the original manuscript. We have added information in the paper to illustrate this. As a result, the changes that we are observing are dominated by the biomass burning emissions. We have also added information showing that the reactions of the organic vapors with NO_3 and O_3 are dominant and those with OH secondary.

Concerning the use of the theta angle we have added a description in the text about the use of this metric and how the reader can interpret the results better. We have also corrected any discrepancies concerning the comparison with other spectra. Detailed information about these changes can be found in the corresponding responses below.

Specific comments

(3) *As the manuscript discusses the difference between two experimental conditions (section 3 (typical) and section 4 (others)), there should be a description of the difference in experimental conditions.*

It appears that our separation of the results of our experiments into sections (3 and 4) is causing some confusion. Our intention is to present the results of one typical experiment (Exp. 1) in detail and then summarize the results of the rest (Exp. 2-13) without repeating the same details. There is no difference in the experimental conditions, just on the level of detail of the presentation of the corresponding results. This is why the results of all conducted experiments are grouped together in Table 1. To avoid this problem, we have merged the two sections describing results into one and also explain in the beginning of this section that all experiments were conducted in similar conditions. We also explain that we discuss the details of only one and summarize the major results of the rest.

(4) *PMF results are used for the discussion in the manuscript (Line 189-196, Line 263), but there is no description about the application, or the literature from which this study adopted the results from.*

This is a valid point. The dual chamber experiments took place together with a traditional month long field campaign, in the city of Patras Greece. The PMF results of the ambient OA measurements are described in a companion paper that is ready for submission. We have added a paragraph summarizing the details of the PMF application and the major results of this second paper together with a reference to a presentation of these results.

(5) *Line 243: does this mean that the wall-loss is aerosol composition dependent? How*

about particle size or other parameters?

The size-dependent particle wall loss rate constants were measured in the end of each experiment. The corresponding constants were higher for the smaller particles, but they were practically size independent in the size range of 170-800 nm. We used the average wall loss rate constant in this size range for the correction of our measurements for wall corrections. We have added a section in the Supplementary Information describing the details of this correction approach and added there a figure with a typical wall loss rate constant as a function of particle diameter.

(6) *Line 243-261: What did the authors achieve from the comparison? Does the similarity mean that the authors observe BBOA from this experiment? Please elaborate. Although the initial OA is mostly BBOA, it would have been better if the authors not just report the OA enhancement during the experiments but also quantify the possible BBOA formation. Separating BBOA from the OOA would be more informative.*

We now stress in the revised paper that our experiments were designed so that at the time of the filling of the chamber most of the ambient OA was bbOA. We have added a column in Table 1 in which we show the fraction of the initial OA that was bbOA during this period based on the PMF analysis. This percentage was approximately 70% or above for most of our experiments. Separating the bbSOA formed in our experiments from the SOA from other sources is quite challenging. We used a zeroth order approach using a couple of simplifying assumptions. In the first approach we assume that the formed bbSOA is proportional to the fraction of the bbOA in the initial OA. This is probably closer to lower limit given that the more aged OOA is probably accompanied by low concentrations of VOCs and IVOCs from the same sources (they have already reacted) so little additional SOA can be contributed. In the second approach we assume that the bbSOA formed is proportional to the fraction of the bbOA in the initial primary OA. This is probably closer to the truth, but it is still based on the implicit assumption that the VOCs/IVOCs from all sources have the same SOA formation potential under the conditions of our experiments. Despite the uncertainty of these approaches, they both agree that most of the SOA formed in our experiments was due to the biomass burning emissions. We also tried a third approach of analyzing the chamber data with PMF but the results were inconclusive. This was due to the small duration of the experiments and the fact that all took place during periods in which biomass burning was the dominant source.

The comparison of our results with the work of Kodros et al. (2020) can also be viewed as an independent test of the validity of our assumption that most of the SOA formed in our experiments was indeed due to biomass burning. This latter study used only biomass burning emissions therefore there is no doubt that their results represent bbSOA. The good comparison of the produced SOA spectra in the two studies both strengthens our argument that we mainly observe bbSOA formation and also strengthens the argument of Kodros et al. (2020) that their laboratory results are a reasonable representation of realistic atmospheric processing of biomass burning emissions.

We have followed the suggestion of the reviewer and added a discussion of the above issues in the revised manuscript.

(7) *Line 249-250: what do the authors want to address from Figure 4 and Figure 5? Neither the description nor discussion of these figures can be found in the manuscript. Also, this sentence would be better as in: "Figure 4 and Figure 5 show the estimated produced OA and corresponding AMS mass spectrum in Exp. 1, respectively."*

Figure 4 is used to illustrate the concentrations of the OA components (primary and produced) during the corresponding experiment. This is now mentioned in the revised text. Figure 5 shows the resulting spectra for the produced SOA both for Exp. 1 and the average SOA spectra for all experiments. We have followed the suggestion of the referee, rephrased the corresponding sentence and added a better discussion of the two figures.

(8) *Line 249: Δ OA enhancement is estimated here. Does the Δ OA enhancement corresponds to the expected SOA amount (based on the yield of individual VOCs)? Also, how do the authors evaluate the loss of OA between evaporation loss vs. wall loss in the chamber? Were there any changes in specific compounds from either gas-phase or particle-phase composition before the oxidation began (other than O/C mentioned in the manuscript)? Since there is a recent study that proposed the evaporated gases from BBPOA can be the major source of BBSOA, it would be better to discuss thoroughly about other possible effect that can affect the Δ OA enhancement.*

The produced SOA is based on the mass balance approach and not the yields of the individual VOCs. Given the uncertainties in the concentrations and the yields of the various VOCs and IVOCs in the system this is a more accurate estimate. We assume the main process responsible for the reduction of the initial OA is loss of particles to the walls and that the loss of particle mass by evaporation and then loss of the vapors to the walls is negligible. The accuracy of this assumption can be confirmed by the change of the OA in the reference chamber (Figure 1a). The small change of the particle wall loss-corrected OA concentration (less than 7%) supports our assumption. If evaporation and vapor wall loss were important processes the corresponding concentration would be decreasing significantly. This is one of the advantages of our approach. The evaporation of the bbOA after its emission has already taken place in the atmosphere. Therefore, the SOA production that we measure does account for the SVOCs that have moved to the gas-phase as the bbOA gets diluted in the atmosphere. The changes in the reference chamber illustrate well the changes that continue to happen in the system without our acceleration of the chemistry. A more detailed description of the mass balance method and the above discussion has been added to the manuscript.

(9) *Line 263-270: When compared with previous studies, it is difficult to tell from the manuscript how the results here are different or similar to the others. The authors should have provided more background (e.g., citing relevant literature) specifically how these cities are affected by biomass burning. Further, if available either as in literature or experiment results, it would be interesting if the mass spectra of this study are compared and discussed with the mass spectra evolution of daytime oxidation of biomass burning emissions.*

We have added some information about the bbOA contribution to the OA in the field studies that are mentioned in the paper and are used for comparison with our results. For example, in the study of Ge et al. (2012) for Fresno, California biomass burning accounted on average for 16 % of OA, while in the Florou et al. (2017) study the bbOA contributed 40-60% of the OA. The corresponding references can be found in our paper.

We have followed the suggestion of the reviewer and added a brief discussion of the comparison of the AMS spectrum of the SOA produced in this study with the spectra of the SOA produced during daytime oxidation. There are notable differences, with theta angles approaching 30 degrees. This has also been noted by Kodros et al. (2020).

(10) *In line 295, OH is reported to be 20-40% of the daytime ambient level when O₃ is injected in perturbation chamber. The authors comment that this is not significant and conclude that NO₃ or O₃ is responsible for SOA formation based on the chamber experiment results. However, wouldn't some VOCs be susceptible to OH oxidation in addition to NO₃ and O₃ oxidation? Since additional ozone is making unintended OH as a byproduct of ozonolysis, the authors need to justify how the perturbation experiments in this study are representative of nighttime chemistry. Further, since the "4.2 NO₃ and OH radical levels" is in the "4 Results of other experiments" section, does this mean that the authors did not observe any OH formation in "3 Results of a Typical Perturbation Experiment"? Lastly, please add a brief comment why OH is observed when O₃ was injected in perturbation chamber, but not in control chamber.*

This is due to a misunderstanding of our notation. The concentration mentioned is absolute and it is not 20-40% of the ambient levels. Given the sunlight in Greece even during the winter, it is less than 10% of the daytime levels in this area during that period. We have corrected this in the revised manuscript. We also provide some estimates of the characteristic reaction times with OH at these levels for some of the VOCs (toluene, xylenes, isoprene, monoterpenes, phenol) emitted during residential biomass burning. We also mention in the revised paper that some OH is produced during nighttime chemistry as the O₃ is mixed with biomass burning emissions. We also clarify now that the OH levels could be measured only when the PTR-MS was available. This was not the case unfortunately in Exp. 1. However, the OH results were pretty consistent in all the experiments for which the PTR-MS was used. We now explain that the very low OH levels in the perturbation chamber are below the detection limit of the d9-butanol approach. This information has been also added to the paper.

(11) *Line 311-316: how did the difference in the speciation of initial VOCs affected the results?*

We could not find a strong link between the small variations in the speciation of the initial VOCs and the SOA formed. This is probably due to the fact that we only quantified a small fraction of the VOCs and IVOCs that serve as SOA precursors in the system. This is now mentioned in the paper.

(12) *Line 317: why would low level of initial NO have the lowest SOA production? Low NO corresponds to low VOCs in Figure S2. Please add this information in the discussion.*

This is indeed a point that deserves some additional discussion. This is due to the low NO_x availability in the atmosphere during these experiments. These low NO_x levels result in low NO₃ levels in the perturbed chamber and therefore together with relatively low VOC levels, during the same days, lead to low SOA production. This is consistent with our NO₃ measurements. This information has been added to the discussion.

(13) *Line 324: NO₃ concentration is not available for more than half of the experiments. Most of the experiments with high VOCs are missing this information. Further, the Exp. 8 not only shows higher NO₃, but also reports higher VOCs than the rest of experiments which NO₃ data is available (except Exp. 6, and this is the outlier in Figure 8). It is not reasonable to make a comment with limited data, with missing information from the most important experiments.*

Please note that NO₃ measurements were not available for only 4 out of the 11 experiments discussed in the paper. These are challenging measurements so there were some unavoidable instrument problems. In the two experiments (Exps 3 and 10) NO₃ radicals were not detected probably because their concentration was below the detection limit of the instrument. To the best of our knowledge it is the first time that NO₃ measurements are available in ambient chamber experiments of this nature. Although, the available data are limited the good correlation with the organic nitrate concentration formed is encouraging and can help strengthen the point of NO₃ reactions in the perturbed chamber. We do believe that the information provided by the NO₃ measurements (despite the gaps) is a major strength of the present work.

(14) *Conclusions. The main takeaway message is unclear. Please provide the novelty of this study and emphasize the main findings. Moving the main discussion sentence to the beginning of each paragraph will help readers to understand the main points that this paper addresses.*

We have revised the conclusions placing a greater emphasis on the novelty of this work as well as emphasizing the main points of the work.

(15) *Line 345: does this mean than the OOA (biomass burning affected) in this study does not show any differences with the urban OOA that are not impacted by biomass burning, but only seasonal change matters?*

We now clarify that we compare the SOA formed in our experiments with the OOA measured in wintertime studies in areas in which the fresh bbOA contributed 15-70% of the OA. We also stress that OOA as viewed by the AMS and PMF formed by a variety of sources has certain similarities, so any efforts to derive even stronger conclusions from this similarity in spectra regarding the importance of biomass SOA in urban areas in the winter could be problematic.

Technical comments

(16) *Firstly, please edit the manuscript for language and proofread the manuscript thoroughly. Some of comments below pointed out phrases written in an inappropriate manner, but not all grammatical problems have been noted in this review. Many of sentences are written in a colloquial style and need to be modified.*

We thank the reviewer for the suggested improvements. We have edited and proofread the manuscript.

(17) *Line 33: OA increase in the abstract is reported as percentage, but organic nitrate is reported as concentration. What is the fraction of organic nitrate formed among total OA?*

The organic nitrate represented on average 10% of the total SOA formed. We have added this information to the abstract.

(18) Line 56-57: please complete the sentence: "..., but reactions of emitted monoterpenes with ozone can also contribute."

The sentence was changed to "..., but reactions of emitted monoterpenes with ozone can also contribute to the SOA formation during the chemical aging of biomass burning emissions."

(19) Line 152: "BC" appears the first time here, so this should be "black carbon (BC)" (and not in Line 162.).

We have added the definition of the acronym here.

(20) Line 164-168: Was the RH of particles controlled using a dryer before the instrument?

We did not use a dryer before the instruments and the RH of the sample was recorded. We added that information in the manuscript.

(21) Line 177: Was the neutralizer attached to the atomizer during the wall-loss characterization of the chamber?

The ammonium sulfate seeds after the atomizer passed through a diffusion dryer and then were injected in the chambers. We did not use a neutralizer after the atomizer. In past experiments we have seen little difference in the measured deposition rate constants with or without the use of a neutralizer. This information has been added to the paper.

(22) Line 207: The authors use "Fig" for some figures and "Figure" for others. Please keep it consistent.

We now use "Figure" throughout the text.

(23) Line 221: "organics" to "organic nitrate" for the clarification.

We have made the recommended change.

(24) Line 223-224: What percentage change does the 1 mg/m³ increase in ammonium correspond to? What was the 8% change in mass concentration from control experiment? Please keep it consistent. It would be useful to report both concentration change and relative change.

The ammonium concentration increased 90% relative to the value before the injection of ozone. We have now added this information in the text.

(25) *Line 228-232: Please check the grammar of this sentence.*

We have rewritten this sentence.

(26) *Line 234: the sentence "Figure 2 represents....end of Exp. 1." should be moved to the first part of paragraph. The change in each mass is better to be described afterwards.*

We have moved the sentence to the beginning of the paragraph.

(27) *Line 236: O : C change from 0.4 to 0.41 is difficult to justify "low but non-zero chemical "activity" since the change is too small, should be within the uncertainties of the instrument. Also, it is very difficult to see this difference from Figure 3.*

We have removed that sentence from the manuscript.

(28) *Line 239: not only O₃, but NO₃ should be also existing in the control chamber, although it would react away faster.*

We have rephrased that sentence adding this information.

(29) *Line 248: should be "pre-existing".*

Corrected.

(30) *Line 251-262: rearrange the sentences in this paragraph for better readability. Also, no need to describe the conditions in Kodros et al. (2020) repeatedly.*

We have changed the order of the sentences in this paragraph.

(31) *Line 258: add a comma after "Here".*

Done.

(32) *Line 263: OOA appears in Line 193. Please change the previous one to "oxygenated OA (OOA)".*

We have added the abbreviation in the text the first time it appears.

(33) *Line 277: be consistent with either organic nitrate or organonitrate.*

We changed the organonitrates to organic nitrate.

(34) *Line 280: add a comma before "ranging from..."*.

Comma added.

(35) *Line 282: add a comma after "At the same time"*.

Added.

(36) *Line 312: what are the authors trying to say in "therefore took place during polluted conditions"?*

We have deleted the second part of this sentence to avoid confusion.

(37) *Line 312: it is recommended to include initial VOC concentration in Table 1.*

We have added the initial VOC levels in Table 1.

(38) *Line 314-316: it would be better to make a statement after the evaluation of both VOCs and NO₃ level. Then propose which factor is affected the most and is recommended as an indicator for SOA formation.*

Due to the limitation from the available instrumentation to measure the SOA precursors, by summing the measured VOCs we can have an estimate on which experiments higher SOA formation is expected. In this sentence we are referring to the potential of the VOC levels to produce SOA. We discuss the influence of the NO₃ levels later in that section.

(39) *Line 335: "organics" to "organic nitrate" for the clarification.*

Changed.

(40) *Line 338: it would be better to remove "injected" when describing control experiments. It may confuse the readers.*

We have removed the word "injected" from the sentence.

(41) *Figure 4: Dot plots are difficult to see. Please change the figure into line plot (or line with markers).*

We have changed Figure 4 into line with markers following the suggestion of the reviewer.