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Response to Referee #2

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-AC1>, 2021

(1) *The manuscript by Jorga et al. reported the night-time SOA production from the urban ambient air influenced by biomass burning using a mobile dual smog chamber. By injecting ozone into one reactor while leaving another one unchanged as a reference, the authors found significant SOA production, which was attributed to NO₃ oxidation. The authors compared the AMS mass spectra in this study to the OOA formed from the NO₃ oxidation of fresh biomass burning emissions and found high similarities. Organic nitrate production was also investigated and the results are helpful to better understand the organic nitrate formation from urban air influenced by biomass burning. However, there are quite a few issues throughout the manuscript, which need to be addressed before it can be considered for publication.*

We appreciate the comments and suggestions of the reviewer. We provide point-by-point responses (in regular font) to the comments of the reviewer (in italics) below.

(2) *L86-89: These lines should not be here. The advantages of using a mobile dual chamber compared to traditional chambers need to be introduced before Line 81.*

We have added a brief description of the advantages of using a mobile dual chamber system in the Introduction.

(3) *L100: It is recommended to provide a map of the site, probably in SI.*

Following the suggestion of the referee, we have added a map of the site in the Supplementary Information (Figure S1).

(4) *L102: A general description of RH and temperature of all experiments is needed here.*

The RH in the chambers was in the range of 35-45% while the temperature in the room was ranging from 12-20 °C, while the outdoor temperature was a few degrees lower. We

have now added this information in the text.

(5) L160: *PIKA version is not right.*

We have corrected the typo and now the correct PIKA version is cited.

(6) L168-169: *The theta (θ) angle is quite an important parameter in this paper. The authors should provide more details about it, rather than only citing references here. Otherwise, the readers won't know how it is calculated, and why it can be used as a parameter for similarities.*

The theta angle is a useful metric for the comparison of OA mass spectra, similar to the often used R^2 (Kostenidou et al., 2009). A theta angle for the AMS spectra ranging from 0-5° indicates an excellent match between the compared spectra which should be considered identical for all practical purposes (R^2 ranging from 1-0.99). For a θ angle of 6-10° there is a good match (R^2 approximately 0.98-0.96) but there are some small differences. A θ of 11-15° shows that the spectra are quite similar but they are not the same (R^2 : 0.95-0.92), while for a θ in the 16-30° the spectra as coming from different sources, but there are some similarities (R^2 : 0.91-0.73). A theta angle higher than 30° suggests clearly different AMS spectra. We use the theta angle due to its ability to better represent smaller differences than the coefficient of determination. The above explanation of the theta angle was added to the revised manuscript.

(7) L180: *Just curious when was the sunset? The experiments were supposed to start only after the sunset.*

During the campaign the sunset was from 17:10 – 18:00 LT. Approximately 30 min later we initiated the flushing of the chambers. After 1-2 hours of flushing, the experiments started with the ozone injection. This information has been added to the paper.

(8) L191-192: *Should provide a reference or more details about the PMF analysis.*

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 figure showing the time series of the resulting factors during the campaign.

(9) L209-211: *The authors need to be careful when stating this. The OA formation rate of $25 \mu\text{g m}^{-3} \text{h}^{-1}$ is only true with the extremely high ozone concentration here (240 ppb). These lines need to be revised.*

This is a valid point. This high rate is the result of the high ozone levels used in these experiments to accelerate the corresponding chemistry and reduce the problems caused by losses of both particles and vapors to the walls of the chamber. We have added a

qualifying statement explaining the above to avoid misleading the readers about the rates expected in ambient conditions with lower ozone levels.

(10) L219-221: *The calculation details of organic nitrate need to be provided in SI.*

We now provide the details of the organic nitrate calculation in the SI.

(11) L223: *Why the ammonium concentration increased? Need some discussion here.*

The increase of the ammonium concentration is due to the formation of ammonium nitrate. The total nitrate formed as measured by the AMS at the end of the experiment was $6 \mu\text{g m}^{-3}$. Approximately $2.5 \mu\text{g m}^{-3}$ of this was inorganic nitrate which require around $0.8 \mu\text{g m}^{-3}$ of ammonium for its neutralization. This corresponds well to the observed increase of ammonium. We have added the above explanation for the increase in the ammonium levels to the revised paper.

(12) L225: *This sentence needs to be moved to somewhere around L189-196.*

We have deleted this sentence from this point in the paper. Now we report the RH at the beginning of the section where we describe the initial conditions in the perturbed chamber.

(13) L232-233: *What is the threshold of similarity for θ ? The authors mentioned θ several times in this paper but never said anything about the threshold. Without this, one cannot tell if the mass spectra are similar or different from each other.*

A detailed explanation of the angle theta and its application in the AMS data analysis has been added to the paper. Please see also our response to Comment 6.

(14) L234: *Move this line to the beginning of this paragraph.*

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

(15) L247: *"particle loss rate constant".*

Corrected.

(16) L276-282: *The authors should summarize the produced OA concentration, the OA enhancement ratio, and the O:C after oxidation in a table, probably in Table 1. Besides, it's better to use numbers rather than percentages when describing O:C.*

We have added a table in the SI that summarizes the OA enhancement ratio

($OA_{\text{final}}/OA_{\text{initial}}$) as well as the changes of the O:C in the perturbed chamber.

(17) L290-291: *Not only this, the authors should also consider the non-BB emissions in urban ambient air.*

We agree with this point of the referee and we added this as another potential reason for the difference between the two studies.

(18) 4.2: *The OH concentration is 15%-30% of the atmospheric average concentration, and the ozone concentration is extremely high. Therefore, the authors need to estimate the fractions that react with OH, ozone, and NO_3 , rather than simply stating that NO_3 oxidation dominates the overall reaction. It should be done for the major VOCs at least.*

To address this issue we now 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 O_3 is mixed with biomass burning emissions. We do state now these characteristic reaction times in our experiments.

(19) L302-303: *The NO_3 concentration did not increase immediately. As shown in Fig. S1, the NO_3 concentration is still 0 at 0.3 h. Need some discussion here.*

We appreciate this comment. We have redrawn this figure as the actual ozone injection was performed at $t=0.4$ h according to the time in the original Figure S1. We have changed the time axis so that time zero now corresponds to the injection time of ozone.

(20) L318-319: *Why low initial NO leads to lower SOA production? Because of lower NO_3 ? If so, should say that here.*

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 NO_3 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 NO_3 measurements. This information has been added to the discussion.

(21) L320-321: *How is the relationship between NO_3 and formed OA? Better show it in Fig. 8 as well.*

We estimated an $R^2=0.66$ between the formed SOA and the levels of NO_3 in the perturbed chamber. A figure showing these results has been added to the SI and the corresponding discussion has been added to the paper.

(22) Table 1: *Ozone and total VOC concentration should be included.*

We have included the initial VOC levels in Table 1 in the revised manuscript. The injected ozone levels are reported in a separate table (Table S1) to avoid confusion between the ambient ozone levels and the injected ones.

(23) *The theta (θ) angle needs to be included in Figs. 2 and 5.*

We have updated the two figures with the theta angles.

(24) *SI: Merge Table S1 and Table S3. If possible, put them in Table 1.*

We have followed the referee's suggestion and we have merged Tables S1 and S3. We have kept this in the SI because there is too much information for one table.

(25) *SI: It is better to show the VOC species in Figure S2.*

The initial values of the VOCs are now shown in Table 1. Figure S2 has been deleted to avoid repetition.