

Reviewer 2

We thank the reviewer for reading our revised manuscript and providing additional insightful suggestions. We hope that the following responses and additions to the manuscript address these comments.

- 2.1 Response to comment 2.3: *Figure 2 only shows the composition of the repeated aging experiment. Please clarify whether the compositions of the fresh emission for the flaming experiments (FL-AGED-1, FL-AGED-2 and FL-FRESH) are comparable or not and how the similarity was examined. This is because when the authors were comparing fresh and aged samples, these samples were obtained from two different burning experiments (e.g. FL-AGED-1 on 21/04/2022 vs. FL-FRESH on 30/08/2022). Therefore, it is vital to ensure that the chemical composition of the fresh emission in FL-AGED-1 is similar to FL-FRESH. I believe that without this crucial information, the data quality would not fit into the very high standards of the Journal of Atmospheric Chemistry and Physics. Moreover, the observed good repeatability in Figure 2, claimed by the author, is somewhat subjective. I found observable differences between aged samples from the two flaming experiments. For example, the second most dominating species are C11 compounds with DBE = 0 in FL-AGED-1, while the second most dominating species in FL-AGED-2 are C10 compounds. Please clarify how the similarity between repeated aging experiments was examined in the main text. In addition, the difficulty of collecting the diluted fresh samples from the chamber, which was mentioned in the response, must be acknowledged in the main text.*

The authors previously mentioned in the original manuscript on line 167 that the aerosol was exclusively sampled from the chamber in the first campaign, therefore, there are no direct comparisons with the flue. The emissions from the FL-FRESH sample on 30/08/2022 were aged in the chamber, however, the sampling of the fresh emissions occurred separately to the filling of the chamber and proceeded after the emissions were injected. Furthermore, this aging experiment had a lack of several key gas phase measurements which meant we chose not to include it in the paper. Despite this, we do see the same overarching trends as in Figure 2 with a peak at C₈, fragmentation and loss of aromaticity including significant reductions of the polyaromatic CHO content. The authors do acknowledge that in burning experiments it can be difficult to achieve the exact chemical composition each time due to the complexity of lignin breakdown in a fire and the naturally existing small differences between different pieces of wood even from the same source. However, we disagree with the repeatability of our results as we show that the overall trends are replicated in the repeats. In Figure 2, we show that the general overarching trend in fragmentation to C₇-C₁₀ compounds with a peak at C₈ and loss of aromaticity upon aging is consistent across the flaming aged repeats despite small differences such as those mentioned by the reviewer. We also refer the reviewer to Figure 1 showing the f₄₄ vs f₆₀ space measured by AMS, where it is clear the flaming burns are similar in their initial values and temporal evolution upon aging as these points occupy the same area of space. Furthermore in Figures 4 and 5 the flaming aged burns have very similar O:C probability density functions and occupy the same H:C and O:C space in the Van Krevelen diagram. Therefore, we believe our experiments to be repeatable across the entire bulk chemical composition despite some small differences in individual compounds and therefore the comparisons made between the fresh and aged emissions to be acceptable. We will include that we could not sample from the chamber directly due to mass constraints as we mention in our previous responses. We have also added a sentence to the conclusions to indicate that the experiment methodology could be improved by sampling the fresh emissions at the start of the experiment from the chamber but that this remains challenging due to the low mass present and the need to sample large volumes for offline approaches (See comment 2.4).

“Page 6 line 150: Due to the relatively low particle concentration of 200 $\mu\text{g m}^{-3}$ inside the chamber the fresh aerosol was sampled directly from the flue of the wood burner to yield sufficient mass for offline chemical compositional analysis rather than from the chamber itself. POA was sampled from the flue at 2 L min⁻¹ for 5 minutes.”

- 2.2 Generation of OH: *The author gave explicit details about how OH was produced in the chamber in response to comment 2.1. The same levels of detail need to be included in the main text to clarify OH production and the estimated OH concentrations.*

The authors will add this explanation to the existing description of the chamber lighting for the aging experiments on page 5 line 126.

“The chamber was illuminated using two 6 kw xenon arc lamps with quartz fibre glass filters and 4 rows of halogen lamps (64 bulbs) to simulate atmospheric solar wavelengths, which enables the photolysis of NO₂ to produce O₃. O₃ is then subsequently photolysed in the presence of water molecules to produce OH [1–3]. Heterogeneous wall chemistry will also produce HONO, which is photolysed to yield OH and NO. The OH concentration inside the MAC has been previously calculated as ca. 1×10^6 molecules cm⁻³ [1, 4] at similar NO_x concentrations to these experiments.”

- 2.3 Lines 265 – 266: *Thanks for the revision. Given that oxidised POA (oPOA) and SOA are indistinguishable using f44 and f60, we cannot rule out the possibility that the oxidation of POA from fresh domestic BB emissions only forms oPOA. If so, please revise the sentence.*

The authors disagree with this statement, it is highly unlikely that SOA is not formed during the oxidation and it is well known that SOA is formed upon OH exposure of biomass burning emissions in chamber studies. We refer the reviewer to a previous study of SOA formation from the oxidation of biomass burning emissions where an increase in SOA mass measured by AMS was observed in all 20 aging experiments during the FIREX chamber study [5].

- 2.4 Response to Comment 2.18: *Thanks for your explanation. I recommend that the authors include similar levels of detail in the abstract and/or conclusion to highlight the importance and novelty of the current study*

We have adapted some of our statements in the abstract and conclusion as shown below.

“**Abstract line 19:** This study presents the first reported quantitative non-target compositional analysis of domestic BBOA using retention window scaling and demonstrates compositional changes between burn phase and after aging may have important consequences for exposure to such emissions in residential settings. **Conclusion line 503:** The chemical composition of domestic biomass burning organic aerosol (BBOA), from a series of controlled burn chamber experiments, was investigated using a newly developed semi-quantitative non-target analysis (NTA) methodology and is the first study to account for ionisation effects in an NTA of BBOA using retention window scaling [6]. The NTA approach enabled the detection of up to 2357 features in a single sample [6] which is simply impossible from a targeted approach with a limited number of standards. Significant compositional differences between the organic aerosol (OA) derived from emission under different burn phases (i.e. flaming dominated and smouldering dominated phases) and after aging were observed. However, the experimental methodology used here could be improved by sampling directly from the chamber at the start of the experiment but this remains challenging for offline approaches due to the higher sample volume required and the low particle mass used in this study. Overall, the composition of domestic BBOA was dominated by oxygenated compounds (CHO). On average CHO compounds constituted 90% of the total detected mass with a smaller contribution ($\leq 10\%$) of organonitrogen species (CHON), which suggests the wide usage of nitroaromatic compounds as tracers of biomass burning may not be ideal as these compounds typically have high ionisation efficiencies and therefore appear more abundant when using peak area metrics.”

- 2.5 Response to Comment 2.19: *The additional analysis of organic nitrates (ON) from AMS is straightforward. Comparing ON between AMS and Orbitrap measurements is potentially interesting to the community. If the editor feels this will be too much work, the author can leave this one out.*

As stated in our previous response this work is being carried out by one of our co-authors and will appear in a separate companion publication. The main findings of this work is the non-target analysis of the high resolution Orbitrap mass spectra and we believe it is beyond the scope of the current manuscript to include the additional AMS analysis.

Bibliography

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